

Anodic Stripping Voltammetry at Mercury “Films” Deposited on Conducting Poly(3-Methylthiophene) Electrodes

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ABSTRACT

The incorporation of mercury into a conducting poly(3-methylthiophene) [P3MT] film results in an effective electrode for the analysis of lead in aqueous media. Mercury “films” were deposited electrochemically following the electropolymerization step. The resulting surfaces were characterized by cyclic voltammetry, scanning electron microscopy, and X-ray analysis techniques. The analytical performance of the electrode was examined for the determination of lead(II) ions in aqueous media. The differential pulse peak current, at -0.59 V, is ca. 10-fold larger than the corresponding peak at the plain platinum electrode. Linear calibration curves are obtained for lead concentrations ranging from 0.1 to 0.8 ppm. The detection limit is 0.05 ppm. The relative standard deviation (at the 0.3 ppm level) is 2%. Interference effects were also studied. The new polymer modified electrode showed great promise toward resistance to surfactant fouling.

KEY WORDS: Modified electrodes, trace metal analysis, conducting polymers, stripping analysis, mercury film electrodes.

INTRODUCTION

Since their inception in the early seventies investigations on organic conducting polymers have continued to attract a high level of interest and active research. These materials have been proposed for a wide variety of technical applications such as solid state batteries and energy storage, electrochromic displays, rectification, microelectronics, photovoltaic devices, etc. [1]. Recently, intensive research has been devoted to the modification of electrode surfaces with thin films of polymeric materials [2]. Film-coated electrodes have been used to immobilize redox-mediators in order to facilitate the electron transfer with the analytes in the solution [3], for measurements in liquid chromatography [4], and to preconcentrate the analytes prior to subsequent electrochemical determinations [5].

The most common methods used for preconcentration are solution evaporation, solvent extraction, precipitation, ion exchange, and electrochemical methods. Electrochemical and ion-exchange methods are less susceptible to contamination or modification of the species of interest in a matrix where interference is likely to cause complications for the analysis. The determination of trace metals using voltammetric techniques, such as anodic stripping voltammetry (ASV), with detection limits down to 10^{-10} M, is one of the few analytical methods sensitive enough for direct analysis at these concentration levels. The use of mercury or mercury thin films, as the working electrode, has prevailed in anodic stripping techniques [6]. Chemically modified electrodes, on the other hand, have been employed to enhance selectivity and to prevent electrode fouling in analytical measurements of many substances [7]. Several studies showed that the chemically modified carbon paste electrode could be used successfully for the determination of some metal cations in solution. For example, Baldwin and co-workers proposed the use of a carbon paste electrode containing dimethylglyoxime for the determination of nickel(II) [8a] and 2,9-dimethyl-1,10-phenanthroline for the determina-

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*This work is dedicated to the memory of a wonderful friend, colleague, and eminent scientist: Professor Gaston Patriarche.

tion of copper(I) [8b]. Wang and co-workers reported that a montmorillonite clay-modified carbon paste electrode could be used for the preconcentration of iron(II) followed by electrochemical determination [9a], a zeolite-containing carbon paste electrode for the determination of silver [9b], and a tropolone-modified carbon paste electrode for the trace analysis of tin [9c].

The static mercury drop electrode (SMDE) was used as a polarographic detector with flowing solutions [10]. However, mercury drop electrodes are limited in their use in flowing solutions because of their mechanical instability [11]. The use of the thin-film mercury-electrode (TFME), on the other hand, seemed to have overcome this problem [12]. Nevertheless, other problems associated with the lack of inherent selectivity, adsorption of unwanted species from solution, and the discrimination against other interfering Faradaic processes, such as oxygen reduction, proved that the TFME is inadequate to function as a detector for metal ions in many cases.

Recently attention has been paid to the possibility of using the polymer-coated mercury "film" electrode for anodic stripping voltammetry [13]. These electrodes have been successfully applied to the direct analysis of biological samples and polluted waters and have overcome the interference effects caused by organic constituents of the sample matrix. However, the use of Nafion as the coating polymer [13b] was limited by the thickness of the film, which in turn affects the electrode response.

The work presented here describes the preparation of a conducting polymer-based mercury "film" electrode (CPMFE) and its use for the analysis and determination of trace metals. The analytical potential of conducting polymer electrodes was shown by different research groups [14]. Recently we demonstrated that the conducting poly-3-methylthiophene- (P3MT) based electrodes can be used for the determination of certain anions and a number of organic and biologically important species [15]. While these studies have proved the potential use of the P3MT electrode in these areas, voltammetric studies and trace metal analysis at conducting polymer electrodes coated with mercury "films" have not been reported. The results obtained in this research proved that the CPMFE could be used for the (ASV) analysis of trace amounts of lead(II) with improved response in the presence of surfactants. Moreover, the electrode response was found to be mass-transport-independent. The effects of the electrode preparation conditions on the electrode response were studied. With the optimum conditions of preparation, as described below, the CPMFE showed long term stability and high sensitivity. Scanning electron microscopy studies reveals the drop-shape morphology of the mercury, which is uniformly distributed over the conducting polymer surface.

EXPERIMENTAL

Apparatus

A PAR 173 Potentiostat/Galvanostat equipped with a plug-in PAR Model 176 current-to-voltage converter and a PAR

Model 379 Digital Coulometer (Princeton Applied Research, Princeton, NJ) were used for the electropolymerization of 3-methylthiophene and the electroplating of the mercury "film." Cyclic voltammetry experiments were performed using a Model CV-1B cyclic voltammetry unit (BAS, Inc., West Lafayette, IN) with a Hewlett Packard Model 700413 x-y recorder and a Fluke 8000A Digital Multimeter. A BAS- 100 Electrochemical Analyzer (BAS, Inc.) was used in the differential pulse stripping voltammetry (DPSV) studies and in the Osteryoung square wave voltammetry (OSWV) experiments. A standard (one compartment) three-electrode cell consisting of a platinum working electrode (MF2013, BAS, Inc.), a platinum sheet ($2 \times 2 \text{ cm}^2$) auxiliary electrode, and an Ag/AgCl reference electrode (Model RE-1, BAS, Inc.) was used in all experiments.

Reagents and Procedure

The conducting polymer-based mercury "film" electrode CPMFE was prepared in the following manner. The conducting poly(3-methylthiophene) film was first electrochemically formed as described earlier [16]. The polymer film thickness was estimated by measuring the charge passing during the electropolymerization step. A typical electropolymerization solution consisted of 0.05 M tetrabutyl-ammonium tetrafluoroborate and 0.05 M 3-methylthiophene in dry acetonitrile. Following the electropolymerization step, the electrode was thoroughly rinsed with acetonitrile and water. The mercury "film" was electrochemically deposited from 20 mL, 10^{-3} M mercuric nitrate solution containing 0.0025 M HNO_3 , 0.1 M KNO_3 , and acetate buffer (acetic acid ($= 0.068 \text{ M}$) / potassium acetate ($= 0.05 \text{ M}$)). In the case of mercury deposition, a potential of -0.2 to -0.5 V vs. Ag/AgCl was applied for 5–30 minutes to the polymer electrode. The electrode was then rinsed with water and stored in 0.1 M KNO_3 solution for future use.

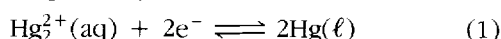
The stripping voltammetry experiments were performed in the following manner. The preconcentration step for lead(II) ions was carried out by applying a potential of -0.9 V (vs. Ag/AgCl) for 10 min at the CPMFE from a solution containing 0.1–0.8 ppm Pb(II) ions in 0.1 M KNO_3 . The stripping step was accomplished using differential pulse anodic stripping voltammetry (DPASV). The differential pulse signal was applied between -0.9 and -0.2 V (vs. Ag/AgCl) as the initial and the final potential limits, respectively. Typically, the pulse's amplitude, width, and period were 50 mV, 50 msec, and 1 sec, respectively. The catalytic effect of the CPMFE surface on the hydrogen evolution process was also studied. The OSWV technique was used for the latter studies. All solutions were deaerated by bubbling argon gas through the electrolytic cell for at least 10 min prior to each experiment run.

The scanning electron microscopy studies were performed with a Cambridge Stereoscan 600 instrument. All chemicals and reagents were analytical grades and were used as received without further purification.

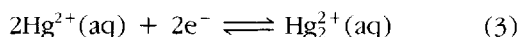
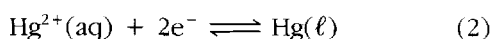
RESULTS AND DISCUSSION

Electrochemical Behavior of Mercury(II) Ions at the Poly(3-methylthiophene) Surface

Figure 1A shows the cyclic voltammogram of 50 mV/s for poly(3-methylthiophene)-coated platinum electrode (2000 Å) in 0.1 M potassium nitrate solution containing 40 mg/l mercury. Two distinct anodic peaks are observed; the first at 450 mV is probably the result of the redox reaction:



while the second peak at 670 mV is probably associated with the following two mercury redox reactions:



and the simultaneous oxidation of the polymer as a result of the nitrate anion "doping" process [17]. The cathodic peaks corresponding to the mercury reactions could not be observed because of the large envelope displayed during the reverse "undoping" process (polymer reduction) by the nitrate ions. On the other hand, Figure 1B depicts the cyclic voltammogram of the same electrode in a mercury-free electrolyte. This result confirms the conclusion drawn for "the doping-undoping" behavior of the nitrate ion from the polymer film. Moreover, one further experiment was performed in order to confirm the redox behavior of the mercury on the polymer surface. Figure 2 shows the data obtained upon cycling the CPME in 0.1 M KNO₃. Two distinct anodic peaks appear at 480 mV and 670 mV respectively, which are similar to those given in Figure 1A. In contrast to the cyclic voltammogram shown in Figure 1A, a well-defined cathodic peak is observed at 400 mV. However, it is not conclusive at this stage as to whether the mercury redox reactions occur on the surface and if the bulk of the polymer takes part in the redox reaction.

Differential Pulse Stripping Voltammetry at the CPMFE

Differential pulse voltammetry was used to evaluate and optimize the analytical performance of the CPMFE. The ability to use a single CPMFE surface in multiple determinations of lead-containing samples was examined. The differential pulse voltammograms obtained upon sequential analysis of Pb²⁺ solutions of differing concentrations are given in Figure 3. Reproducible peaks were observed following 3 deposition times and after switching between the 0.3- and 0.1-ppm lead solutions. It is important to note that no memory effects were observed during the sample switching process. Moreover, no post- or preconditioning procedures have to be applied for the regeneration of the CPMFE surface after each cycle. The latter is an essential criterion for any practical chemically modified electrode (CME) [18]. A series of ten repetitions with a 0.3-ppm lead-containing solution yielded a mean peak current of 1.87 μA (a range of 1.85–1.92 μA) and a relative standard deviation of 2%. Such relatively high precision compares favorably as required by various other preconcentrating CMEs [9].

The differential-pulse voltammograms for a 0.4-ppm lead solution after different preconcentration (deposition) times are reported in Figure 4A. The height of the peak, at –0.59 V, increases with increasing the preconcentration time, which indicates the increase in the lead concentration in the CPMFE. For the 0.4-ppm lead solution, a 10-min preconcentration time resulted in a 4-fold enhancement of the peak current height when compared to that achieved after 1 min preconcentration. A plot of peak current vs. preconcentration time for 0.4-ppm lead ion solution is illustrated in Figure 4B. As expected, the peak current generally increases with increasing deposition time. However, the peak current increases rapidly at first, as the preconcentration time increases, and then shows a slower rate of increase. This indicates a faster accumulation rate of lead for short preconcentration times, and then a slower rate as the lead concentration increases in the CPMFE. Similar concentration-dependent rates of metal ions uptake have been reported earlier [9b]. Moreover, the change in the analyte solution pH (in the range of pH = 1–9) had no effect on the peak potential or the peak height.

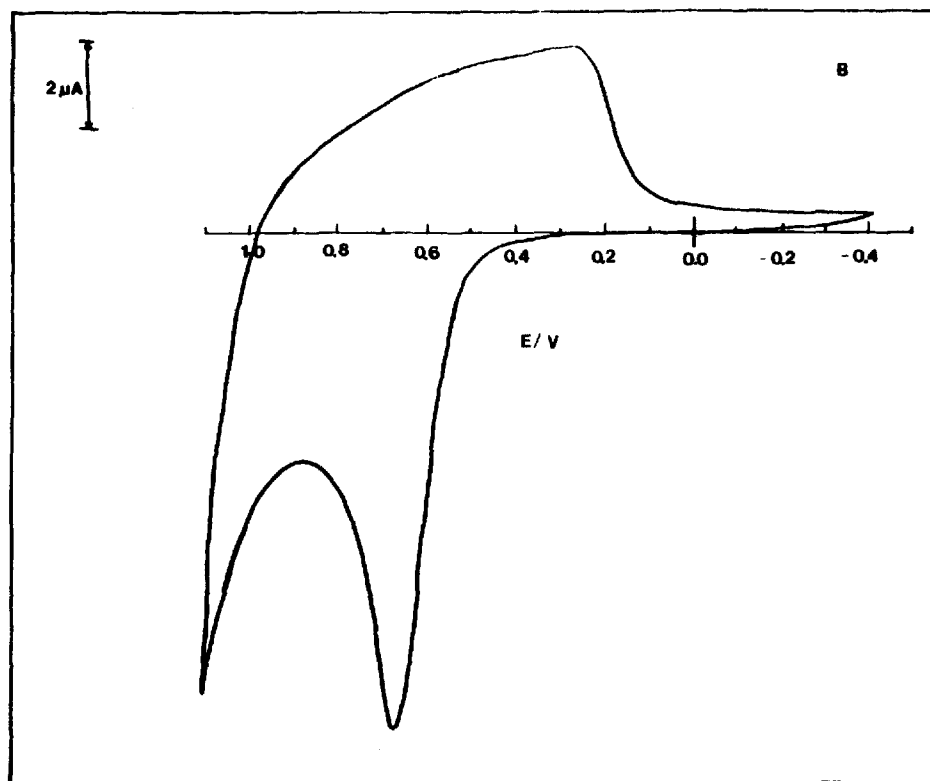
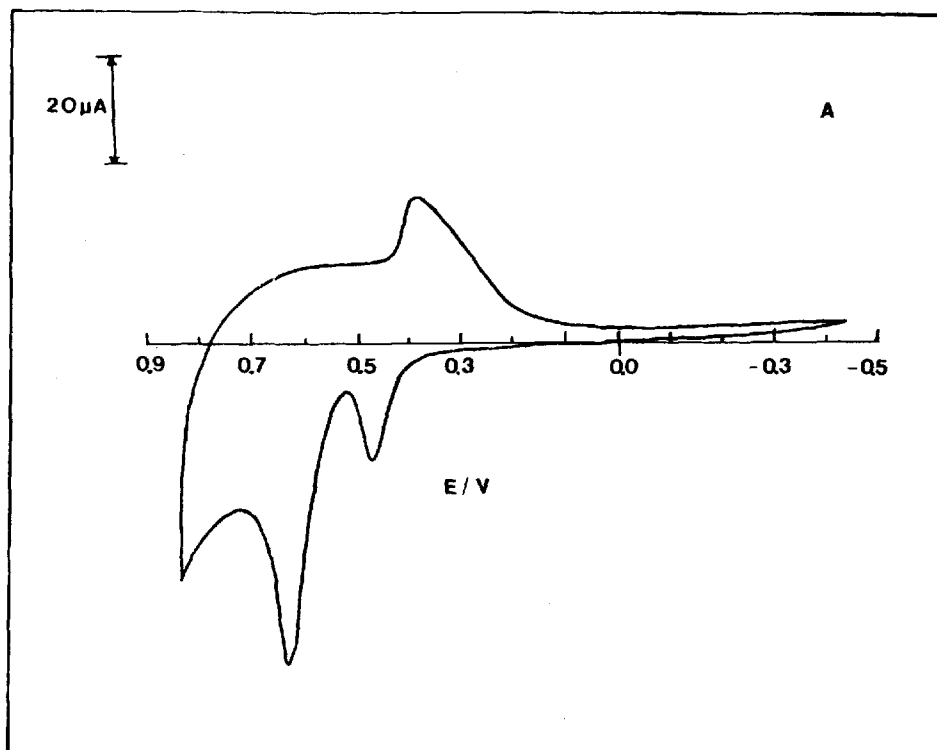
The dependence of the differential pulse voltammetry peak height on the lead concentration is given in Figure 5A. The calibration data were obtained for 0.1 M KNO₃ solutions containing increasing levels of lead (0.1–0.8 ppm) following a 300-s electrochemical deposition and are shown in Figure 5B. Fresh sample solutions were used for each individual concentration at the same electrode. The calibration plot showed a linear behavior. Furthermore, the correlation coefficient was calculated to 0.998 whereas the slope of this regression line was 6.66 in arbitrary units. We noticed an increase in the slope of the calibration curve as the preconcentration time was extended. This indicates a relative increase in the analytical sensitivity of the CPMFE. A similar experiment for lead analysis using a thin layer mercury film coated platinum electrode yielded much smaller (ca. 10-fold) peak than that obtained at the CPMFE.

Limit of Detection and Interferences

A detection limit of 0.05 ppm (ca. 2.7×10^{-7} M) was estimated from analyzing 0.1-ppm Pb²⁺ solution (assuming a signal to noise ratio of 3). Therefore, the CPMFE at this preliminary stage shows inferior sensitivity as relatively compared to the mercury film electrodes using glassy carbon as a substrate [6a, d]. However, as mentioned in the above section, the dependence of the CPMFE response on the Pb(II) concentration was, of course, dictated to a great extent by the time period used for the deposition step. Co-existing metal ions (such as copper, chromium, and nickel ions) did not cause interference with the determination of lead or any overlapping response.

The direct determination of heavy metals in some samples might be complicated by the presence of organic compounds, particularly surface-active substances. Figures 6a, b, c illustrate the effects of albumin, gelatin, and Triton X-100, respectively, on the analysis of a 0.3-ppm Pb²⁺ solution. In contrast to the plated mercury-film elec-

FIGURE 1. Cyclic voltammogram of poly(3-methylthiophene)-coated platinum electrode in 0.1 M KNO_3 , (A) in the presence and (B) in the absence of Hg(II) ions. Scan rate 50 mV/s.



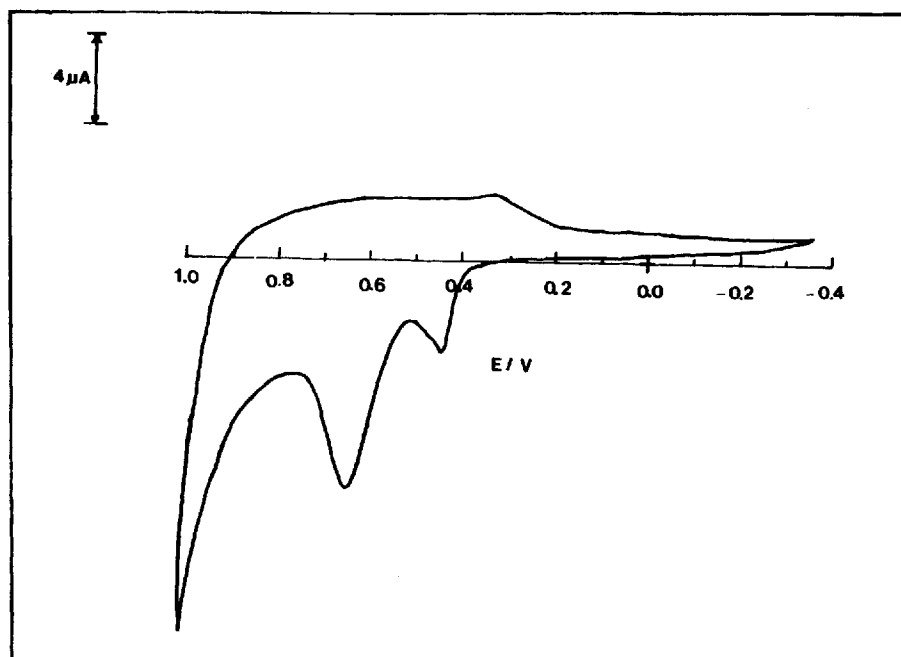


FIGURE 2. Cyclic voltammogram of poly(3-methylthiophene)-based mercury "film" electrode in 0.1 M KNO_3 . Scan rate 50 mV/s.

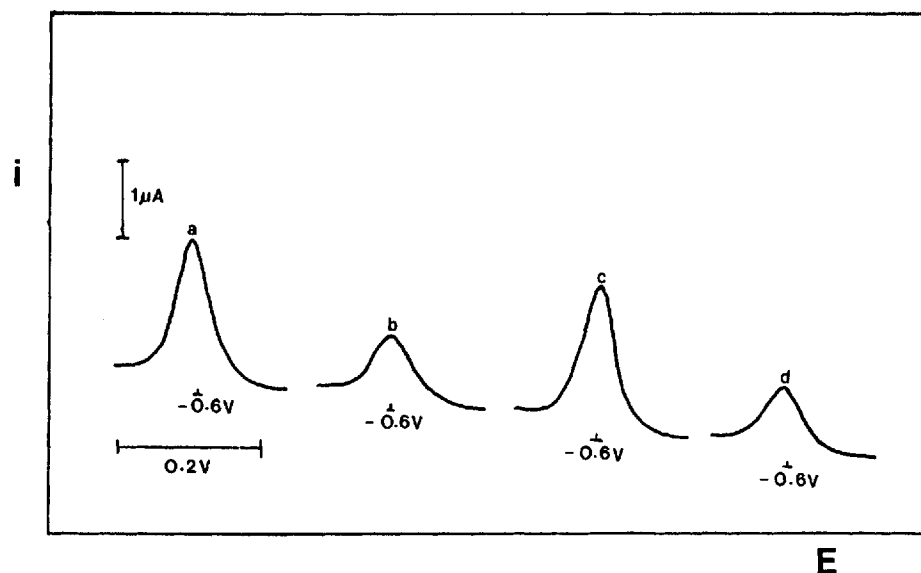


FIGURE 3. Differential pulse stripping voltammetry at the CPMFE in 0.1 M KNO_3 upon sequential analysis of Pb(II) ions containing solutions. (a) and (c) 0.3-ppm, (b) and (d) 0.1-ppm Pb(II) ions concentration.

trode [19], no peak height depression, peak shape change, or peak shifts were observed when using the CPMFE in the presence of up to 100 ppm of the albumin or the gelatin for the analysis of lead. The presence of 100 ppm of Triton X-100, on the other hand, resulted in an 81.9% peak current attenuation. Mercury plated wax-impregnated graphite electrode (WIGE) was developed by Maston *et al.* [20]. This electrode suffered from problems associated with incomplete mercury coverage of the graphite substrate. This resulted in lowering of the hydrogen overvoltage and broadening of the stripping peaks. The WIGE exhibits a

hydrogen overvoltage of 500–600 mV and can be used up to about -0.8 volt vs. S.C.E. [20]. Moreover, this electrode showed poor stability in acidic solutions ($\text{pH} < 2$) [21]. In acidic solutions ($\text{pH} 1$ to 2), a WIGE will fail within a few days to a few hours of use depending upon the age of the electrode. Also, the longevity of a WIGE in any aqueous solution is dependent upon the type of wax employed [21b]. Further, neither wax nor polystyrene impregnation was helpful in halting the detrimental effect of mineral acids to the electrode. The CPMFE has the capability of overcoming many of the aforementioned problems,

FIGURE 4. (A) Differential pulse voltammogram for 0.4-ppm lead solutions containing 0.1 M KNO_3 at the CPMFE after different preconcentration times: (a) 60, (b) 120, (c) 180, and (d) 240 s. (B) Peak current i_p vs. preconcentration time.

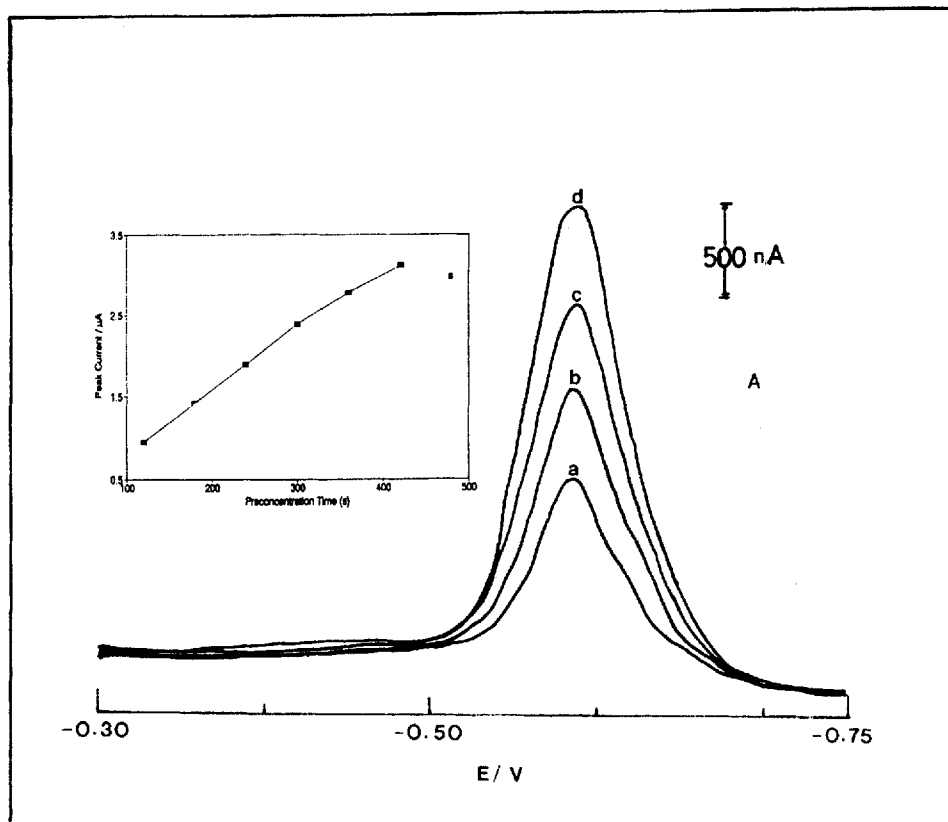
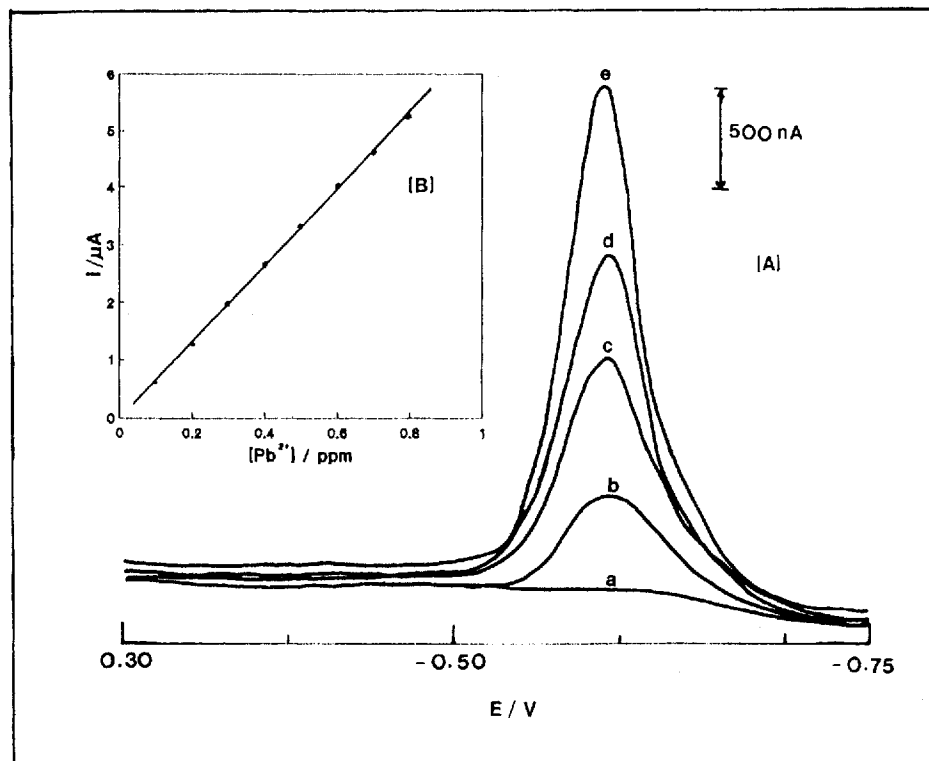


FIGURE 5. (A) The dependence of the differential pulse voltammetry peak current value on the lead(II) ions concentration in 0.1 M KNO_3 : (a) 0.0, (b) 0.1, (c) 0.2, (d) 0.3, and (e) 0.4-ppm lead(II) ions concentration. (B) Calibration curve obtained for 0.1 M KNO_3 solutions containing 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 ppm lead(II) ions, respectively, from the DPSV data at the CPMFE.



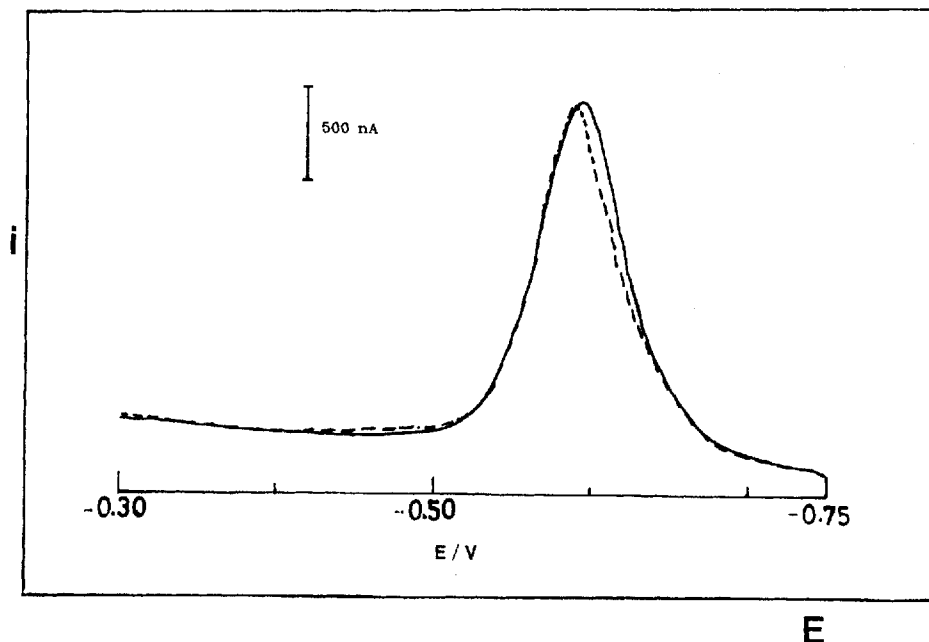


FIGURE 6. Differential pulse voltammogram for 0.1 M KNO_3 solution containing 0.3 ppm Pb(II) ions: (A) in the absence (-) and in the presence (---) of 100 ppm albumin. (B) in the absence (-) and in the presence (---) of 100 ppm gelatin. (C) in the absence (I) and in the presence of 5 (II) and 10 (III) ppm Triton X-100.

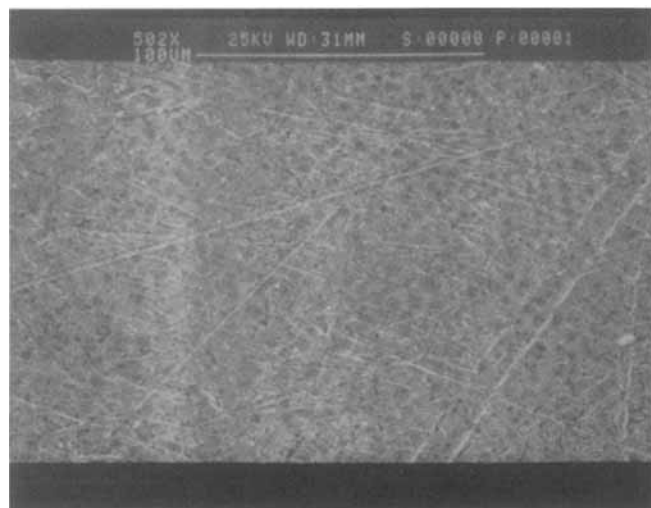
namely those resulting of solution diffusion into channels that existed along the wax-graphite interface. On the other hand, restrictions imposed by the high background current at epoxy-bounded graphite [21a], which precludes the analysis of some elements such as Zn and Cd, were not observed when using the CPMFE. For example, the CPMFE have been used to analyze a sample containing Pb(II) , Bi(III) , and Cu(II) ions in acetate buffer ($\text{pH} = 1$) without any complication [24].

Scanning Electron Microscopy (SEM) of the CPMFE

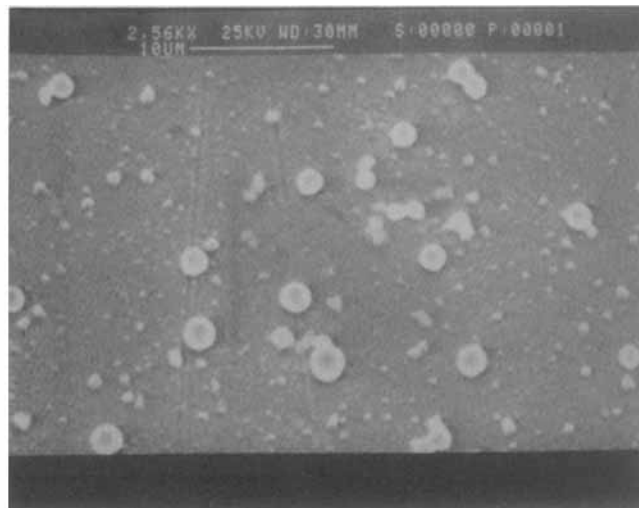
SEM experiments were performed on the CPMFE in order to examine the morphology of the electrode surface. As we

mentioned earlier in the experimental section, the mercury "film" was formed on the conducting poly(3-methylthiophene) layer immediately after its deposition on the platinum substrate. Other methods [22] such as the simultaneous deposition of the mercury and the analyte metals have also been introduced. However, we were not able to obtain reproducible results when following the latter method for mercury film formation. This could be attributed to the simultaneous incorporation of the analysis metal with the mercury into the polymer film. The data reported in Figure 7B show that the mercury on the polymer surface forms as finely divided droplets, similar to the observation by Štulíková [23] at the glassy carbon surface. The non-uniform morphology of the resulting

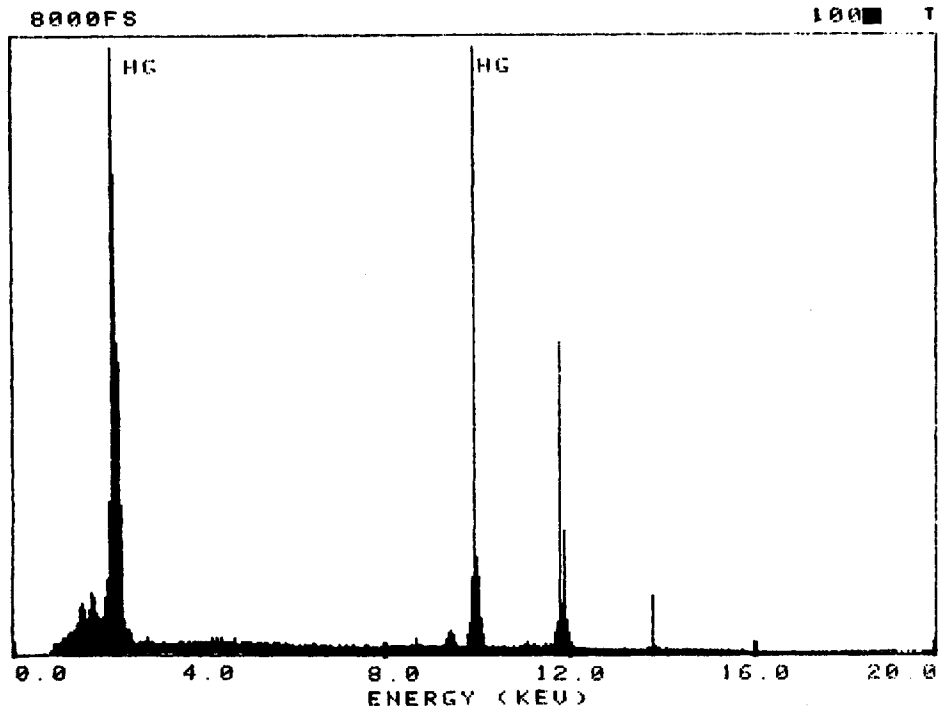
FIGURE 7. (A) SEM of poly(3-methylthiophene) film (2000 Å) deposited on platinum potentiostatically at 1.7 volts vs. Ag/AgCl . (B) SEM of mercury deposited at the poly(3-methylthiophene) film. $[E]_{\text{app}}: 0.2 \text{ V vs. Ag/AgCl}$ for $t = 15 \text{ min}$.



(A)



(B)

FIGURE 8. X-ray analysis of the CPMFE.

mercury "film" probably results from the fact that the polymer surface consisted of sites of varying activity for the mercury plating or nucleation. Moreover, the mercury deposition potential employed determines the size and distribution of the mercury droplets obtained. Thus, at relatively low deposition potentials (such as -1.0 V, vs. Ag/AgCl), a rather continuous and uniform mercury "film" was obtained. The SEM of a poly(3-methylthiophene) film in the absence of a mercury coating is represented in Figure 7A. The presence of mercury in the polymer film was also confirmed by X-ray analysis (EDAX) as illustrated in Figure 8. The chemical shifts for the mercury are indicated in Figure 8.

Conclusions

In conclusion, this work indicates that conducting polymer electrodes modified with mercury are suitable CMEs for use in a preconcentration/voltammetric technique. The conducting poly(3-methylthiophene) polymer proved to meet the requirements of uniform high electrical conductivity, electrochemical inertness over the potential region of interest, and chemical inertness to the mercury and the sample solutions as an ideal substrate. The CPMFE is very simple to prepare and offers high sensitivity, rapid response, and high degree of reproducibility. While the principle of the application of the CPMFE is illustrated here with lead ion it could be extended to the determination of other metal ions [24]. The new electrode showed a relatively high resistance to surfactants fouling. For instance, while the presence of up to 100 ppm of either albumin or gelatin showed no appreciable effects on both the potential and the current signals, the presence of Triton X-100, on the other hand, caused a slight decrease in the current signal obtained. Furthermore, the possible use of the

CPMFE in flow injection preconcentration is currently under investigation in our laboratory.

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