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Voltammetric Determination of Lead (II) in Medical Lotion and Biological Samples Using Chitosan-Carbon Paste Electrode

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A simple method for anodic stripping voltammetric determination of lead using carbon paste electrode modified with biomolecular chitosan, is described. In this method, the electrode is activated electrochemically by 5 replicated scanning over the potential range –1000 to –400 mV in 0.5 M HCl solution. Following this step, the lead sample containing 0.1 M KCl solution as supporting electrolyte is purged by nitrogen gas for 2 min, pre-concentrated on the activated electrode at –1000 mV for 30 s. The deposited metal is then oxidized by different modes of sweep in the oxidation direction. Chemical and electrical parameters affecting the voltammetric measurements are optimized. The peak current is proportional to the Pb(II) concentration in a range 10-110 ng/ml, with detection limit 2 ng/m using differential pulse mode. The relative standard deviation is 1.96% for 10 ng/ml (five replicates). The proposed method is applied to the determination of Pb(II) in acidified samples of tap water, pharmaceutical preparations, human blood and urine with satisfactory results. No interference due to 10 fold excess of Cd, Tl, Sn and Cu is observed. The result obtained by the modified electrode is more accurate and selective than the unmodified electrode.

Keywords: Chitosan; Carbon paste electrode; Lead; Anodic stripping voltammetry; Tap water, Biological samples.

1. INTRODUCTION

Chitosan is natural product extracted from the shell of shrimps, crabs and insects. [1] Because of its ability to bind strongly with many metals [2] chitosan and its derivatives have been applied for electrochemical determination of silver [3,4], platinum [4], palladium[4], gold [4,5], lead [6,7], and iron [8]. All the methods mentioned are based on formation of thin coat of chitosan salt of acetate or formate on the pretreated glassy carbon electrode, GCE. However, the salt is normally readily to leak and to dissolve in water and therefore the durability of the electrode is small ranging between 10 days

to one month [6,7] and the sensitivity is down to 0.5 μg/ml Pb. Furthermore, the procedures for preparing the thin coated electrode needs various instruments for ultrasonation, infra red drying, polishing as well as purchasing the GCE itself. Carbon paste electrode, CPE, on the other hand, has been recognized as one desirable alternative. It is characterized by ease and simple fabrication, low cost, easy renew ability, high selective and sensitive towards analyte. [9] This electrode could be modified by many chemical modifiers applicable for determining lead such as, cetyltrimethylammonium bromide [10], thiol self-assembled monolayer on mesoporous silica [11], diacetyldioxime [12], morin [13], quercetin [14], 1,4-bis(prop-2'-enyloxy)-9,10- anthraquinone [15], Acid Chrome Blue K [16], complexing polymers of thiourea with poly(ethylenimine) (PEI) or poly(1-vinyl-2-pyrrolidone) [17], N-p-chlorophenylcinnamohydroxamic acid [18], tributyl phosphate [19], diphenylthio carbazone [20], aluminium phosphate [21], bismuth alloy electrodes [29], humic acid [22], Sphagnum moss [23] and polymeric calixarene. [24] The present work is aimed to develop new CPE modified by chitosan in favor of more durability, sensitivity and selectivity.

2. EXPERIMENTAL PART

2.1. Apparatus

A Metrohm model 693 VA processor and 694 VA stand equipped with a Ag/AgCl-3 M KCl and a platinum counter electrode are employed. The modified carbon paste described below is used as the working electrode for electrochemical measurements.

The concentration of lead in solution is measured with a Perkin-Elmer Model 372 atomic absorption spectrophotometer. A Metrohm model 654 pH meter is also used.

2.2. Preparation of the modified electrode

The carbon paste is prepared by mixing 0.2 ml paraffin oil (Fluka), 250 mg synthetic carbon powder 1-2 micron (Aldrich) and 10 mg low-viscous Chitosan (Fluka) in agate mortar. The electrode is consisted of stainless steel tube with i.d. 2.5 mm and 30 mm deep, moving through it an inner screwed stainless steel connector. The tube is coated externally with Teflon. The tube is packed with the modified carbon paste, compressed with inner screw and smoothed on a wetted Whatman filter paper.

2.3. Procedure

The fresh surface electrode is first electrically activated by five replicated direct current sweeping from –1000 to –400 mV with scan rate 40 mV/s, immersing in 0.5M HCl solution. The solution is then exchanged by a sample solution containing 0.1 M KCl, purged by pure nitrogen gas for 2 min and pre-concentrated for 30 s at –1000 mV with stirring at 2000 rpm. After resting for 10 s, one of electrical modes (direct current tast DC, differential pulse DP, square wave SW or first-harmonic

alternating current AC1) is ramped from –1000 to –400 mV with scan rate 40 mV/s, pulse amplitude 50 mV, pulse duration 20 ms, measurement time 10 ms, frequency 30 Hz for SW and AC1. The experiment is triplicated without electrode regeneration and two standard solutions of lead are added sequentially. Average of current peaks due to the sample and standard solutions are taken. For new sample, the experiment is repeated with electrode regeneration as described before.

2.4. For analysis blood samples: [25]

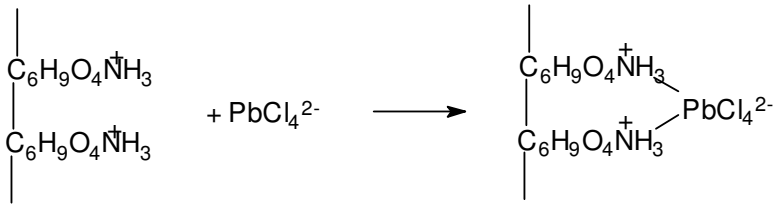
Approximately 2 ml blood sample is digested with 5 ml nitric acid (69%) and 2ml perchloric acid (60%), then add few drops hydrogen peroxide (30 %), heating to dryness and then transferred into 25 ml-measuring flask using distilled water. Portion of the prepared sample containing 10-110 ng/ml Pb is then transferred to 10 ml flask and the procedure for voltammetric measurement is completed as described above.

2.5. For analysis urine samples: [26]

The sample (10 ml) was placed in a conical flask containing 10 ml nitric acid (69%) and 5 ml hydrogen peroxide (60 %) and heated to transparent solution. If necessary, further few drops of hydrogen peroxide is added and continued boiling to dryness, then transferred to 50 ml measuring flask with water washing. Portion of the sample containing 10-110 ng/ml Pb is then transferred to 10 ml flask and the procedure is completed as described above

3. RESULTS AND DISCUSSION

In order to evaluate the performance of the new modifier, the working electrode containing 0, 5, 10 and 15% chitosan are prepared and examined under identical conditions, i.e. immersing in 0.5 M HCl prior accumulation and differential pulse stripping voltammetric measurements of lead in 0.1 M KCl solution. It is obvious from figure 1, the 10% chitosan accumulates lead ions from the solution onto the electrode surface and gives highest stripping peak at potential of -600 mV. Thus, the modifier enhances the sensitivity of the electrode 5 times more than using bare CPE. This enhancement could be explained by the fact that the $–NH_2$ group is converted into $–NH_3^+$ which makes it easy to increase the electrostatic attraction of negatively charged tetra-chloro lead complex, forming ion pair on its surface.



This mechanism is in accordance with that proposed by Ye et al [4] for determining palladium and platinum chloride complexes and is totally in contrast to that stated by Jinrue et at [7] who mentioned that the protonating chitosan will increase the electrostatic repulsion of Pb^{2+} ions leading to lower the peak height. The present mechanism is more favorable because of existence lead ions as tetrachloro complex soluble only in excess of chloride ions, otherwise, the positively charged divalent ion itself will be precipitated. [27] This ion pair complex, however, is unstable as proved by small peak current formed by accumulation in open circuit compared with that obtained in closed circuit.

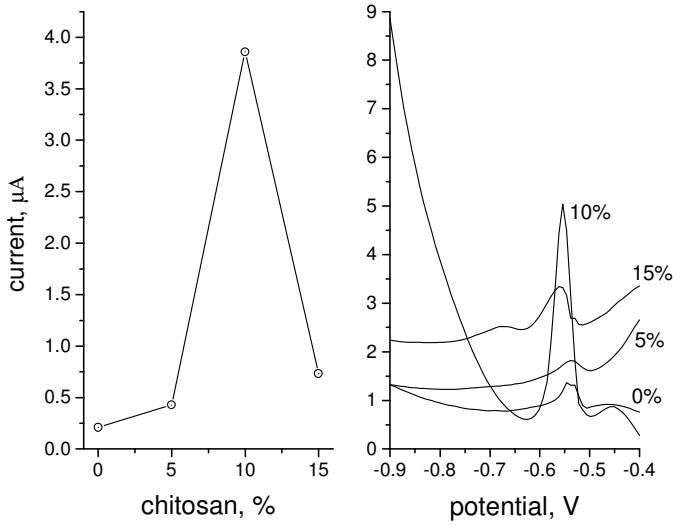


Figure 1. Differential pulse voltammograms of 21 ng/ml Pb using different percentages of chitosan plus 25% paraffin oil in CPE, 0.5M HCl in protonating step and 0.1M KCl in accumulation step. The accumulation time t_a is 60 s at potential E_a: -1000mV, scan rate ν: 40 mV/s and pulse amplitude ΔE: 30 mV.

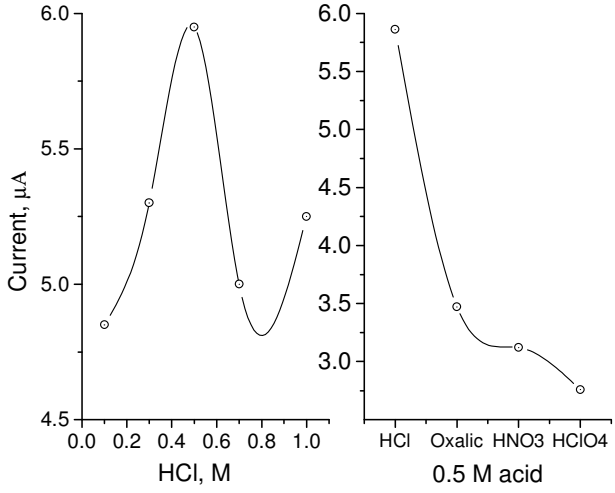


Figure 2. Dependence of peak height on type and concentration of acid using 10% chitosan CPE. Other conditions are the same as in Fig.1.

On the other hand, mixing solutions of HCl-KCl as supporting electrolyte gave weak peak, compared with that obtained by separating two solutions on two sequential steps, HCl for the protonation of chitosan and KCl for the chelation of lead. Accordingly, two studies are done, type and strength of acids and ligands. Various types of acids such as HCl, nitric, perchloric, oxalic acids are examined. The hydrochloric acid is selected as indicated by Figure 2, where the stripping current gave the highest at concentration 0.5 M HCl. Similarly, the peak is optimized by 0.1 M KCl compared with other supporting electrolytes such as KBr, KI, KF, NH_4Cl, NCl as shown in Figure 3.

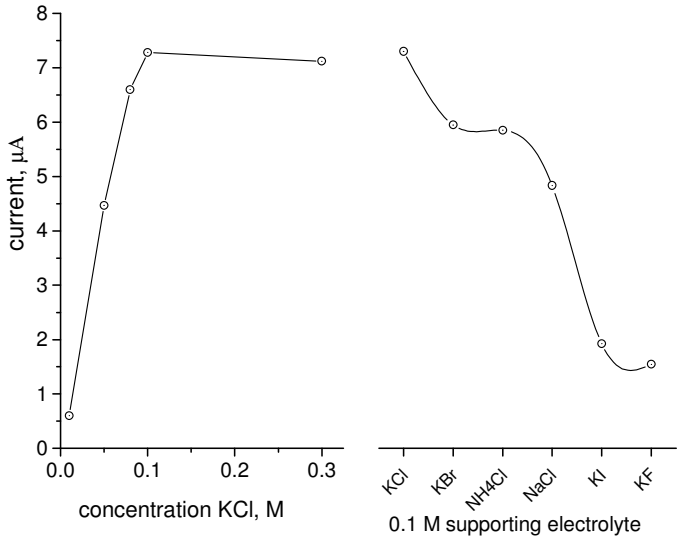


Figure 3. Dependence of peak height on type and concentration of supporting electrolyte using 10% chitosan CPE. Other conditions are the same as in Fig.1.

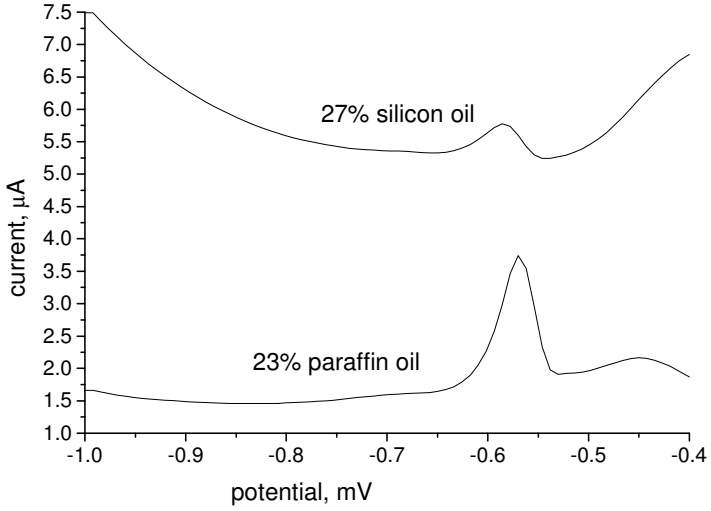


Figure 4. Dependence of peak height on type of binder using 10% chitosan CPE. Other conditions are the same as in Fig.1.

Based on these results, the fresh surface electrode is first activated by immersing in 0.5M HCl solution and sweeping from –1000 to –400 mV six replicates with scan rate 40 mV/s,. The solution is then exchanged by a Pb sample solution containing 0.1 M KCl, purged by pure nitrogen gas for 2 min and pre-concentrated for 30 s at –1000 mV with stirring at 2000 rpm. After resting for 10 s, differential pulse stripping oxidation sweep is achieved from –1000 to –400 mV with scan rate 40 mV/s, pulse amplitude 50 mV, pulse duration 20 ms, measurement time 10 ms.

The effect of type and percentage of binding materials are tested, and found that paraffin oil gave well defined peak than silicon oil (Figure 4) and that the percentage of 38% paraffin oil gave best calibration over the concentration range 10-42 ng/ml Pb (Figure 5).

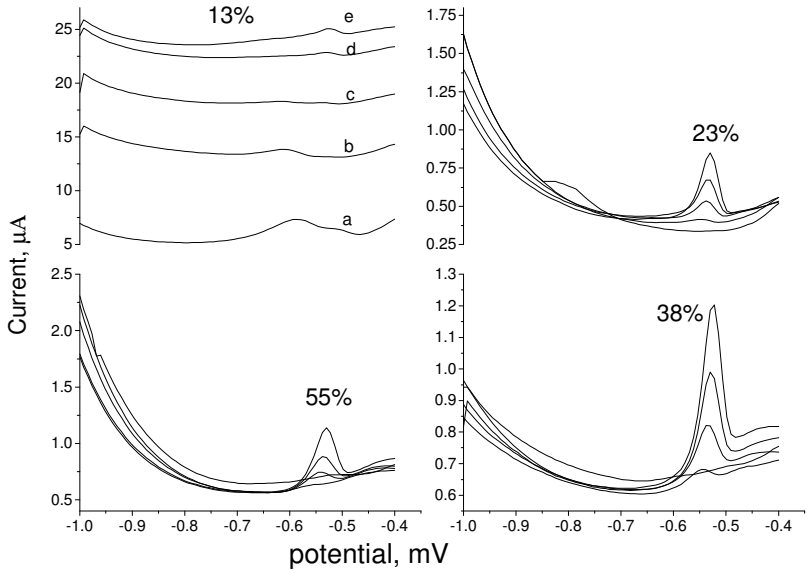


Figure 5. Dependence of stripping current on the percentage of paraffin oil, a=blank, b=10.5 ng/ml, c=21 ng/ml, d=31.5 ng/ml and e=42 ng/ml Pb

The variation of scan rate from 10 to 120 mV/s revealed that the diffusion current is related linearly with square root of scan rate, but the oxidation reaction proceeded irreversibly as the peak potential shifted linearly to less negative potential with increasing the scan rate up to 60 mV/s as shown in Figure 6. The value 60 mV/s is selected for following studies. This irreversibility is also confirmed on studying the effect of pulse amplitude as shown in Figure 7, where the peak potential is shifted to more negative values on increasing the pulse amplitude up to 100 mV. The value of 50 mV amplitude is chosen.

The effect of the preconcentration time on the peak height for four solutions containing 10.5, 21, 42, and 105 ng/ml Pb are shown in Figure 8. The peak height increases on increasing the preconcentration period and starts to level off at 90 s for concentration 105 ng/ml Pb. This evidence confirms the adsorption behavior of the accumulation process between chitosan and lead chloride complex. The time of 30 s is selected in this experiment.

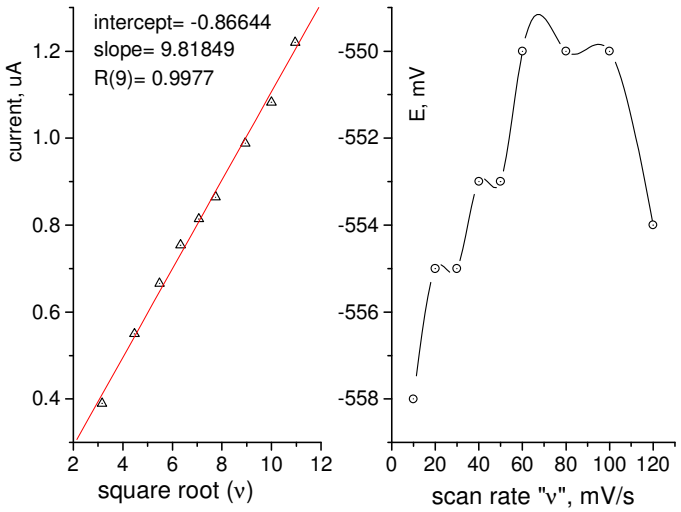


Figure 6. Effect of scan rate on stripping potential and current

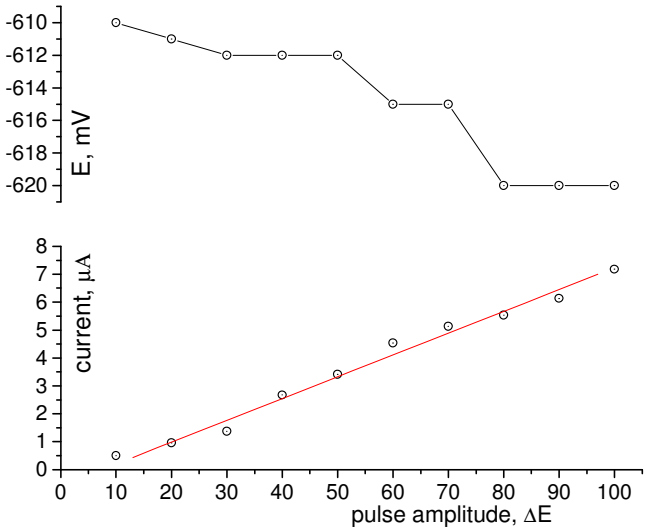


Figure 7. Effect of pulse amplitude on the stripping potential and current

Modulating the direct current tast ramp DC with various wave forms also studied to minimize the large capacitive current component enabling the accurate recording of the smaller Faradaic current. This can be achieved by using superimposed differential pulse DP, square-wave SW or first harmonic a.c. modulation AC, with the result of a further increase in sensitivity over conventional DCT mode, as shown in Figure 9.

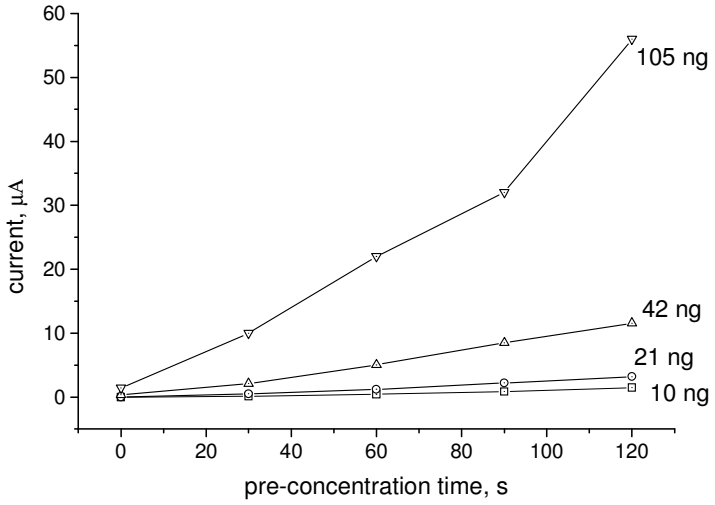


Figure 8. Effect of preconcentration time on stripping current for different concentration of Pb

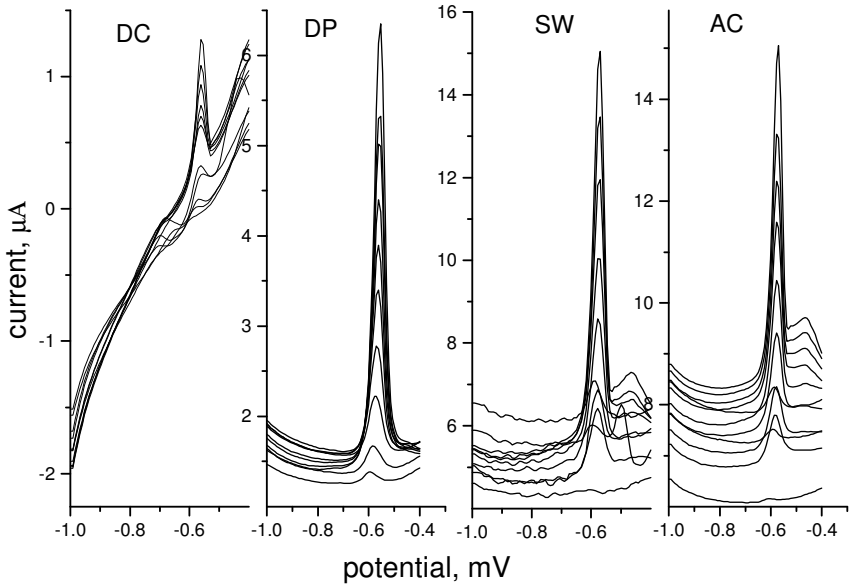


Figure 9. Effect of pulse mode on the stripping current for different concetrations of Pb

Thus, under the optimum conditions, variation of current with concentration of Pb(II) ions (Figure 10) showed a linear behavior between 10 and 110 ng/ml of Pb with correlation coefficients 0.99, 0.98, 0.993, 0.97 and 0.94 for different modes of current DC, DP, SW and AC1, respectively. The detection limit based on "three standard deviations of the blank $3s_B$ method"[28] is found to be in

turn, 12, 1.3, 0.3, 0.7 and 1.2 ng/ml Pb. Repeatability "RSD" using DP mode is found to be 3.45% for six successive determination of 42 ng/ml Pb. For the same modified electrode, reproducibility, without and with successive cut off/ polishing eight times, is found to be 2.9% and 12.4%, respectively, for 42 ng/ml Pb.

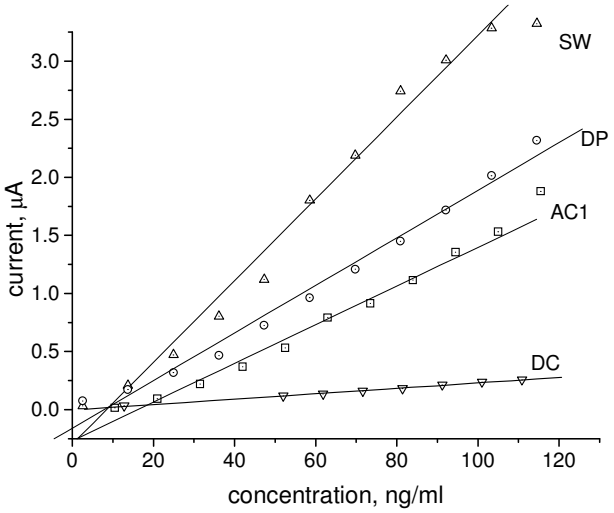


Figure 10. Variation current with concentration of Pb under the optimum conditions

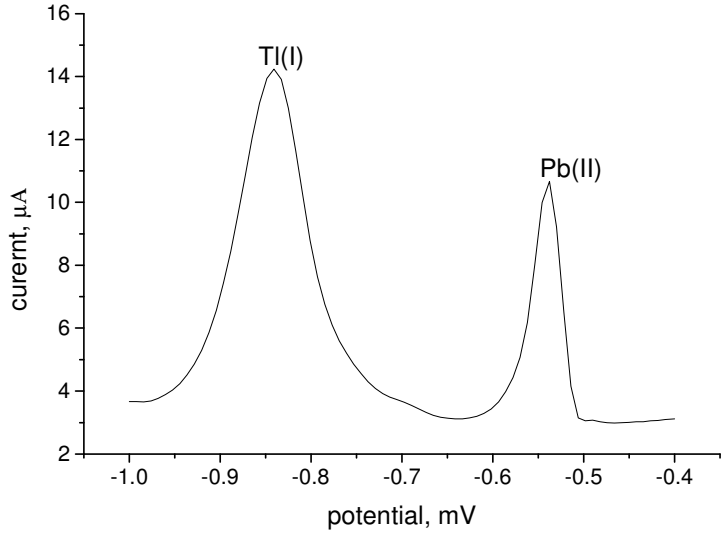


Figure 11. Simultaneous determination of Tl(III) and Pb(II)

4. EFFECT OF INTERFERENCE

No peak is observed other than that of 21 ng/ml Pb in the presence of 10 fold amounts of Hg, Cu, Cd, Sn, while Tl ion appeared at -850 mV (Figure11) which can be determined simultaneously with lead.

The proposed method is applied for the determination of lead in tap water, pharmaceutical lotion (DERMA-C), both are acidified with a few drops of nitric acid. Derma-C is Egyptian-made lotion containing 2% lead acetate and is used for treating sunburn, simple burn, wet rashes, small pox, insect bites, jelly fish secretion, napkin rashes. Other samples included human biological samples, viz., blood and urine, are analyzed after digestion in nitric acid and hydrogen peroxide as described before. All results of data are summarized in Table 1.

Table 1. Determination of Lead in tap water, lotion and biological samples

.	CPME	Reference[a]
Tap Water[b], ng/ml	34.36±0.23	33.88±0.54
Lotion[b], μg/ml	1.92±0.002	1.86±0.79
Human Blood[b], μg/ml	65±1.562	66.0±0.48
Human Urine[b], μg/ml	2.5± 0.04	2.76±0.66

[a] Graphite furnace atomic absorption spectrometer
[b] Average of three determinations.

It is concluded that the new and simple carbon paste electrode modified with chitosan has been shown to offer comparable performance to the more expensive glassy carbon electrode for the practical use to analysis Pb^{2+} ions at trace concentrations in real samples by anodic striping voltammetry with high sensitivity and selectivity.

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