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Full Paper

Voltammetric Determination of Parathion at Sulphonated Polyaniline based Electrochemical Sensor

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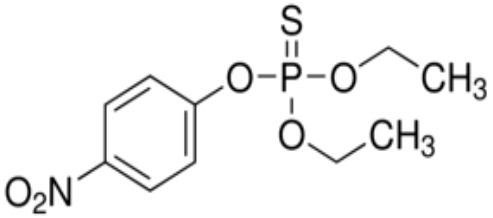
Abstract- A highly sensitive voltammetric method was developed for the determination of parathion in biological samples using sulphonatedpolyaniline modified glassy carbon electrode. The modified electrode was electrochemically fabricated by cyclic voltammetric method. Electrochemical reduction of parathion at modified electrode was investigated by cyclic voltammetry and differential pulse voltammetry. The instrumental parameters and reaction conditions were optimized for the development of stripping voltammetric procedure for the determination of parathion. A linear relationship was found between the peak current due to the reduction of nitro group to hydroxylamine and parathion concentration over the range from 1.0×10^{-8} to 2.0×10^{-5} M with detection limits of 1.5×10^{-9} M. The applicability of the proposed method was demonstrated by the determination of parathion in spiked human urine samples.

Keywords- Parathion, Sulphonated polyaniline, Glassy carbon electrode, Voltammetry, Human urine samples

1. INTRODUCTION

Parathion is a typical member of organophosphorous (OP) pesticide family which is widely used against various pests and insects.Parathion displays acute toxicity owing to its

irreversible inhibitory action on acetylcholine esterase that regulates central nervous system [1]. The indiscriminate use of OP pesticides has led to their accumulation in air, water and soil. Because of their toxicity, they pose serious hazards to health and environment even when present in trace levels [2]. Hence there is an urgent need for the rapid and accurate determination of OP pesticides for environmental and health protection.



Scheme1. Chemical structure of parathion

A number of analytical methods based on gas and liquid chromatography have been reported for the determination of parathion [3-6]. However these methods are laboratory oriented and involve sample pretreatment, extraction and clean up procedures. Electrochemical methods, on the other hand, offer fast, reliable and sensitive determination of OP pesticides. Amultitude of electrodes have been employed for the determination of parathion to improve sensitivity [7-11]. Conducting polymers are utilized as electrode modifiers due to their unique electrical conductivity, chemical stability, and enhanced catalytic activity owing to their high surface area. Polypyrrole, polyethylene dioxythiophene and polyaniline have been reported as electrode modifiers in the determination of biological molecules and pesticides [12-16]. Self-doped polyaniline has attracted increased attention lately as electrode modifier for the determination of ascorbic acid [17-19] and metals [20] owing to its well defined electrochemical properties with good electrical conductivity in neutral and alkaline solutions in contrast to polyaniline coated electrodes.

Although a large number of conducting polymer modified electrodes are reported, there is a demand for electrochemical sensors based on functionalized conducting polymers with good sensitivity, selectivity and stability. In the present work, sulphonated polyaniline modified glassy carbon electrode has been fabricated electrochemically using cyclic voltammetry. A highly sensitive differential pulse adsorptive stripping voltammetric procedure is developed for the determination of parathion in human urine samples with satisfactory results.

2. EXPERIMENTAL

2.1. Reagents and chemicals

Aniline (Aldrich) was distilled under vacuum and stored in dark before use and 2-aminobenzenesulphonic acid (Aldrich) was used as received. Parathion was obtained from Meghamani Industries Ltd, Paldi, Ahmedabad, India. Britton–Robinson buffer was prepared from 0.04 M solutions each of O-phosphoric acid, acetic acid, boric acid and the pH was adjusted using 0.2 M NaOH solution. All the chemicals and solvents used were of analytical grade obtained from Merck (Mumbai, India). A stock solution of parathion of concentration 1.0×10^{-3} M was made up in ethanol (AR-grade).

2.2. Instrumentation

Electrochemical measurements were carried out using Metrohm E-506 Polarecord (Herisau, Switzerland) in combination with Metrohm 663 VA stand and with 612 VA scanner. A three electrode system housing self-doped polyaniline modified glassy carbon electrode (3 mm diameter) as working electrode, a Ag/AgCl/KCl electrode as a reference electrode and a Pt wire as counter electrode was used. An Elico LI-120 pH meter was used to determine the pHof the B-R buffer solutions.

2.3. Preparation of SPAN modified glassy carbon electrode

Before modification, the glassy carbon electrode (GCE) was polished with alumina slurry on a polishing cloth, rinsed with triple distilled water and dried and anodic potential of +1.6 V was applied to the electrode for 6 minutes in 0.1 M sulphuric acid. Then the potential of the electrode was scanned between -0.5 to +1.5 V for 15 minutes until a voltammogram was obtained with reduced background currents. Sulphonated polyaniline (SPAN) film was electrodeposited from a solution of aniline and2-aminobenzenesulphonic acid (1:5) using cyclic voltammetry in 0.5 M sulphuric acid. A potential sweep from -0.2 V to +0.9 V was applied to the working electrode at a scan rate of 50 mVs^{-1}. An optimum value of 20 potential cycle sweeps was selected based on the high peak currents for parathion (not shown). With the increase in number of cycles, the polymer thickness also increases reducing the charge transfer at the electrode interface [19]. SPAN modified glassy carbon electrode so obtained was washed with double distilled water, dried at room temperature and used for subsequent studies.

2.4. Voltammetric determination of parathion

A standard solution of parathion of concentration 1×10^{-5} M was prepared by dilution of the stock solution with double distilled water. 1.0 mL of the standard parathion solution, 9.0 mL of Britton – Robinson buffer of pH 2.5 was taken into the electrolytic cell. The solution was purged with nitrogen gas for 15 minutes before the experiment. Parathion was determined at

SPAN/GCE using differential pulse adsorptive stripping voltammetry (DP-AdSV). The potential of the electrode was scanned between 0.0 and -0.8 V *vs*. Ag/AgCl. Parathion exhibited maximum peak current at -0.56 V in BR buffer of pH 2.5. The voltammograms for blank, parathion at GCE and parathion at SPAN/GCE were shown in Fig. 1.

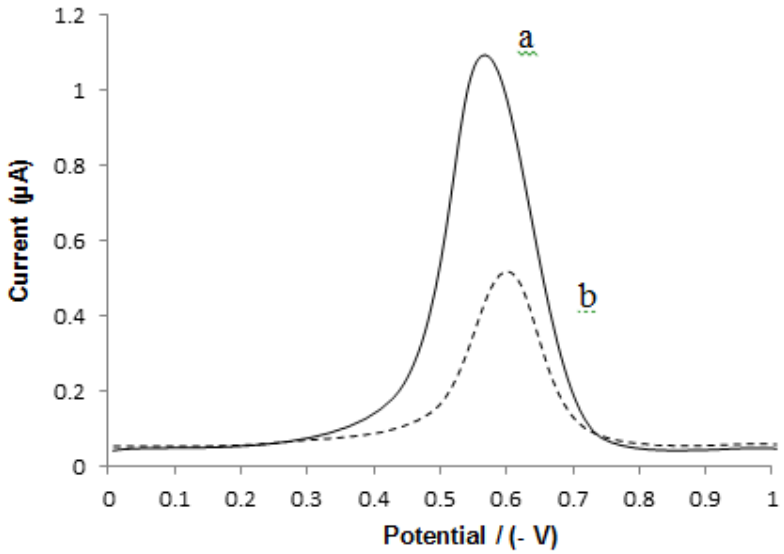


Fig. 1. Differential pulse adsorptive stripping voltammograms of parathion (1 µM) at a) SPAN/GCE and b) bare GCE

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetric study of parathion at SPAN/GCE

An aliquot of standard solution containing 1×10^{-5} M of parathion in Britton - Robinson buffer of pH 2.5 was taken in electrolytic cell and cyclic voltammogram was recorded by scanning potential from 0.0 to -0.7 V *vs*. Ag/AgCl at a scan rate of 20 mV s^{-1}. At pH 2.5, parathion exhibited maximum peak current at -0.56 Vat SPAN/GCE due to the reduction of nitro group of parathion to hydroxyl amine as reported earlier [7].

The reduction reaction involves $4e^-/4H^+$ and it is irreversible since no peak was observed on reverse scan. Cyclic voltammograms of parathion obtained at SPAN modified GCE (-0.56 V) and at bare GCE (-0.6 V) are included in the Fig. 2. It is evident that the peak current is doubled and peak potential decreased negatively by 40 mV for parathion at SPAN/GCE compared to bare GCE. The increase in peak current and decrease in peak potential may be due to the increase in the electroactive surface area and electrical conductivity by modifying

the glassy carbon electrode surface with sulphonated polyaniline film and electrostatic interaction between negatively charged polyaniline and protonated parathion.

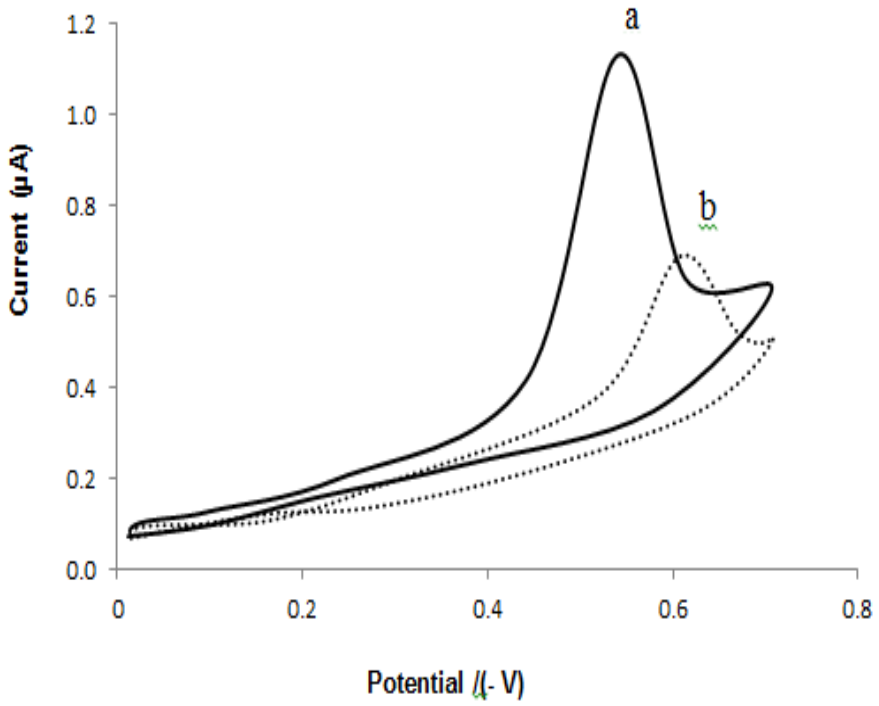


Fig. 2. Cyclic voltammograms of parathion (0.1 µM) from 0.0 V to -0.8 V at scan rate of 20 mV s^{-1} at a) SPAN/GCE and b) bare GCE

3.2. Effect of pH

PH is one of the important parameter in the voltammetric measurement of pesticides. The effect of pH was investigated over the range of 2-10 and the maximum peak current was obtained at pH 2.5 (Fig. 3A). As pH increases, peak potential shifted to negative values indicating proton participation in the reduction reaction. The equation of the plot Ep *vs.* pH (Fig. 3B) was obtained as E_p=-0.042 pH-0.393 (R^2=0.995) with slope of 42 mV/pH indicating equal proton and electron participation during the electrochemical reduction which is in agreement with Nernst equation.

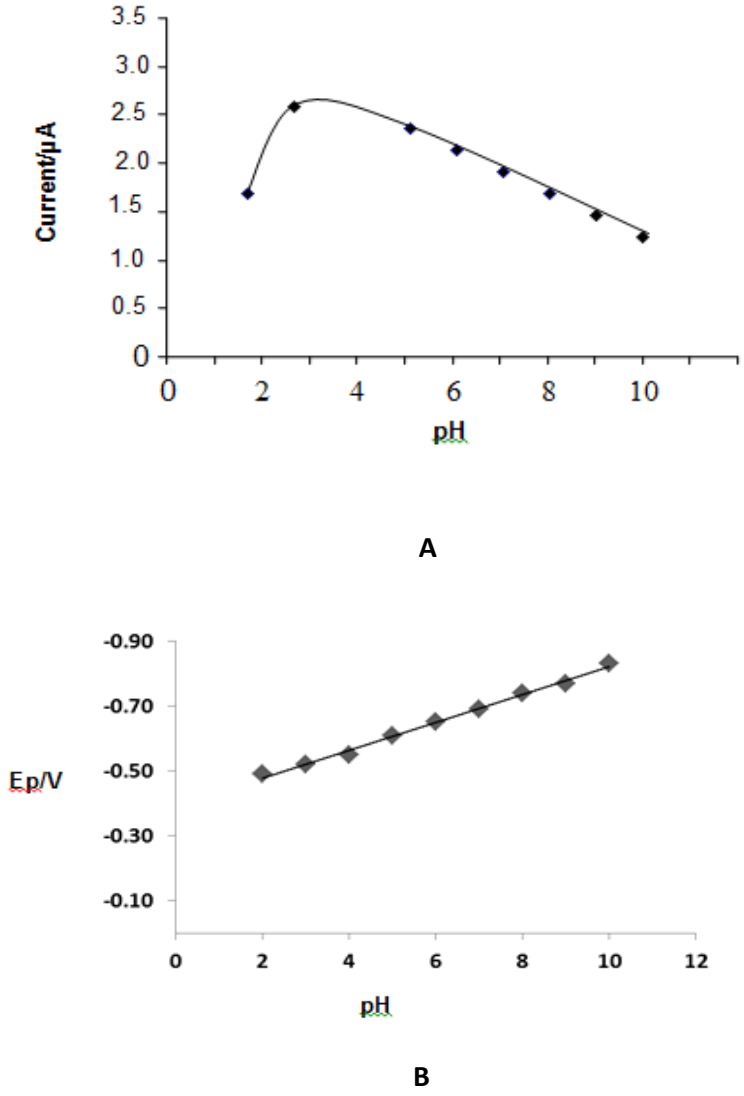
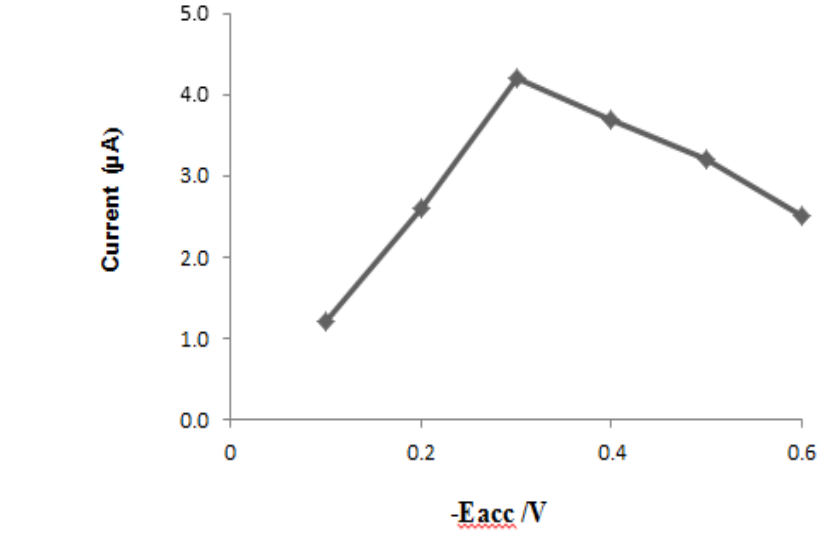


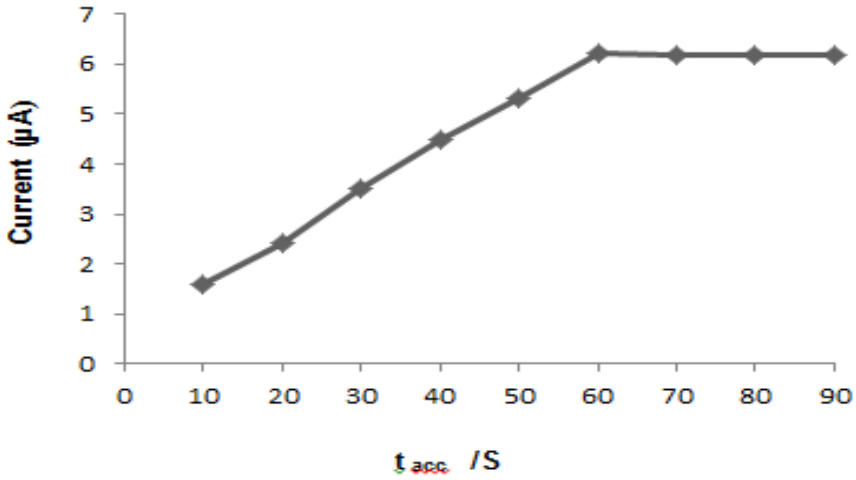
Fig. 3. A: Effect of pH on the peak current of parathion (1µM) at SPAN/GCE; **B:** Effect of pH on the peak potential of parathion (1µM) at SPAN/GCE

3.3. Effect of accumulation potential and time

The influence of accumulation potential on the peak signal was studied at SPAN/GCE in the range of 0.0 to –0.6 V for parathion of conc. 1 µM. It is evident (Fig. 4A) that the maximum peak current was obtained at -0.3 V *vs*. Ag/AgCl because of increased adsorption of the parathionover the micro porous structure of sulphonated polyaniline film characteristic of conducting polymers. The influence of accumulation time on current signal was studied at SPAN/GCE for parathion (1 µM) (Fig. 4B). The peak current increases with accumulation time, reaching a maximum value at 60 s and then it becomes constant above 60 s. Therefore, the optimum accumulation time selected for the measurement was 60 s.



A



B

Fig. 4. A: Effect of accumulation potential on peak current of parathion (1 µM) at SPAN/GCE; **B:** Effect of accumulation time on peak current of parathion (1 µM) atSPAN/GCE

3.4. Effect of scan rate

The scan rate was varied from 20 to 250 $mVs^{-1}$and a line was plotted between peak current (Ip) *vs.* square root of scan rate ($\nu^{1/2}$) (Fig. 5). The value of Ip increases linearly with $\nu^{1/2}$ indicating that the electrode reaction is diffusion controlled. The linear equation was given by $Ip\,(\mu A) = 0.862\ \nu^{1/2}\ (mV\,s^{-1}) + 0.028$ with R^2=0.999. At low scan rates 2-20 mVs^{-1}

peak current increases linearly with scan rate (not shown) indicating adsorption component of the reduction reaction. It can be explained that at low scan rates adsorption of analyte within polymer film plays a major role in peak signal generation while at high scan rates diffusion of the analyte to the electrode interface dominates the electrochemical reduction [15]. Hence the overall reduction is diffusion controlled with adsorption factor involved. An optimum scan rate of 20 mVs^{-1} was selected for the voltammetric determination of parathion.

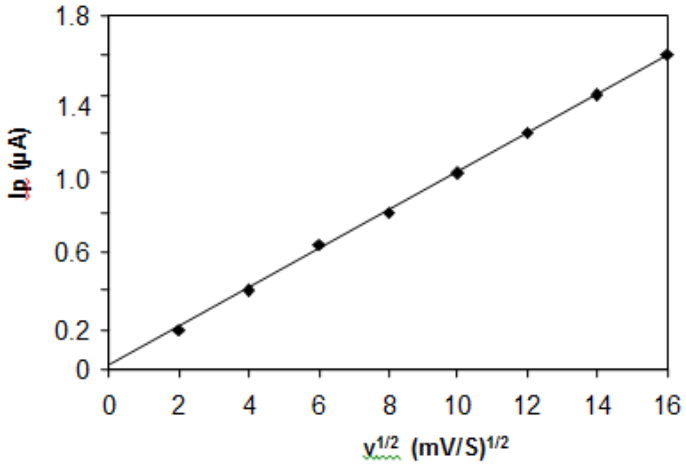


Fig. 5. Effect of square root of scan rate on peak current of parathion (0.1 µM)

The effect of pulse amplitude on peak current was studied from 10–100 mV. Maximum peak current was obtained at 50 mV and was selected for the subsequent determination of parathion. The optimum values of step potential and rest period were 4 mV and 5 s respectively. An optimum stirring rate of 1500 rpm was selected for voltammetric determination of parathion.

3.5. Calibration plot

A calibration curve was plotted between peak current and concentration of parathion over the range of 1.0×10^{-8} to 2.0×10^{-5}M. It was observed that the peak current increases linearly with the concentration of parathion.The linear regression equation is given by $Ip\,(\mu A) = 0.9758\,C\,(\mu\,M) + 0.0352$ with regression coefficient R^2=0.989. The detection limit(LOD=3 s/m) of parathion was found to be 1.5×10^{-9} M where 's' is the standard deviation of intercept and 'm' is the slope of the calibration curve**.**

3.6. Interference studies

The influence of nitro organophosphate pesticides and electro active biomolecules on the peak current of parathion of concentration 1.0×10^{-6}M was studied. It was found that in 5-fold excess concentration of methyl parathion and fenitrothion, the peak signal of parathion had increased by2%. Moreover 10-fold excess concentration of o-, m- and p-nitrophenol and

nitrobenzene had 3% increases in the peak signal. Furthermore, it was found that 50-fold excess concentration of dopamine, ascorbic acid, uric acid, vitamin E and xanthenes had no influence on the current response of parathion. These studies revealed good selectivity of SPAN/GC electrode towards the determination of parathion.

3.7. Stability and reproducibility of the SPAN/GCE

The electrode was stored in air for three weeks in order to test the stability of the signal. It was observed that 85 % of the signal response was retained suggesting good stability of the electrode. The reproducibility of the electrode was determined by the conducting a series of five measurements on a single day (Intra-day) and single measurement on five consecutive days (Inter-day) for parathion of concentration 1μM. The RSD values for intra-day reproducibility and inter-day reproducibility were 2.8% and 3.4% respectively indicating the adequate reproducibility of the electrode. Compared to a few different modified electrodes reported in literature, the present electrode system has low detection limits and wide linear range as given in Table 1.

Table1. Comparison of analytical merits of different modified electrodes for parathion

S. No.	Modified Electrode	Linear range	Detection limits	Technique	[Ref.]
1	Nafion/GCE[a]	1 μM -15 μM	50 nM	DPV[b]	7
2	NanoTiO_2self assembled film/GCE	5.0×10^{-8}M - 1.0×10^{-5} M	1×10^{-8}M	DPV	8
3	Poly (Carmine)/GCE	5.0×10^{-8} M - 1.0×10^{-5} M	1×10^{-8} M	LSV[c]	9
4	Stearic acid/GCE	1.016 μM - 6.096 μM	0.7929μM	DPV	10
5	NanoAg/Nafion/GCE	0.103 μM - 0.6179 μM	0.0835 μM	DPV	11
6	SPAN/GCE	1.0×10^{-8} M - 1.0×10^{-5} M	1.5×10^{-9}M	DPV	Present work

[a]GCE= glassy carbon electrode, [b]DPV= differential pulse voltammetry, [c]LSV= linear sweep voltammetry

3.8. Application of the developed method for human urine samples

The proposed method was directly applied for the determination of parathion in spiked human urine samples using standard addition method. The urine samples were diluted 25 times with double distilled water and spiked with parathion at two different concentration levels, 10 and 20 $\mu g L^{-1}$ respectively. An aliquot of the sample solution was directly transferred into the electrolytic cell containing BR buffer of pH 2.5 and parathion concentration was determined using the developed voltammetric method. Differential pulse voltammograms obtained for urine sample-1 spiked with 10 and 20 $\mu g\ L^{-1}$ and unspiked sample were illustrated in Figure 6. The validity of the voltammetric method was tested by using a recovery test. The maximum recoveries were 99.75 % and 99.80 % with relative standard deviation of 2.04 % and 1.98 % respectively for two human urine samples as shown in Table 2.

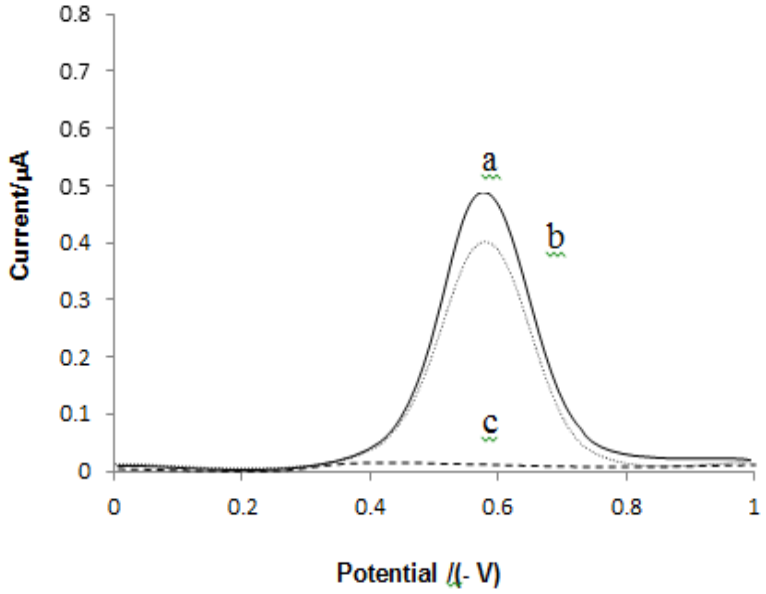


Fig. 6. DPV curves for sample urine -1 spiked with parathion at a) 10 $\mu g\ L^{-1}$ and b) 20 $\mu g\ L^{-1}$ with c) unspiked sample

Table 2. Determination of parathion in spiked human urine samples

Samples	Added($\mu g\ L^{-1}$)	Found*($\mu g\ L^{-1}$)	Recovery (%)	RSD (%)
Urine-1	10.0	9.96	99.60	1.95
	20.0	19.95	99.75	2.04
Urine -2	10.0	9.98	99.80	1.98
	20.0	19.85	99.25	2.09

*Average of five replicate determinations

4. CONCLUSION

Sulphonated polyaniline modified glassy carbon electrode was developed for the determination of parathion in biological samples. Fabrication of electrode is based on simple, low cost, electrochemical method and the stripping voltammetric method developed shows high sensitivity, selectivity, good stability and reproducibility. Moreover the SPAN electrode is quite useful for biological samples as it retains electrochemical activity at slightly alkaline pH values. A wide range of linearity was observed between peak current and concentration of parathion over the range from 1.0×10^{-8}M to 2.0×10^{-5}M with R^2=0.989. The limits of detection were found to be 1.5×10^{-9} M. The proposed method was successfully appliedwithout sample extraction and preconcentration steps for the determination of parathion in human urine samples with recoveries in the range of 99.25 to 99.80%.

Acknowledgements

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