

Research Article

Electrochemical Sensor for Determination of Parathion Based on Electropolymerization Poly(Safranine) Film Electrode

Xingyuan Liu

Department of Chemistry, Teachers' College of Simao, Puer, Yunnan 665000, China

Correspondence should be addressed to Xingyuan Liu, yunliuxy@sina.com.cn

Received 25 February 2011; Accepted 29 March 2011

Academic Editor: Aleksandar Radu

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Parathion has been determined with voltammetric technique based on a novel sensor fabricated by electropolymerization of safranine on a glassy carbon electrode (GCE). The electrochemical behavior of poly(safranine) film electrode and its electrocatalytic activity toward parathion were studied in detail by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). All experimental parameters were optimized, and LSV was proposed for its determination. In optimal working conditions, the reduction current of parathion at this poly(safranine)-modified electrode exhibited a good linear relationship with parathion concentration in the range of 3.43×10^{-8} to 3.43×10^{-5} mol L⁻¹. The detection limit was 1.0×10^{-8} mol L⁻¹. The high sensitivity and selectivity of the sensor were demonstrated by its practical application for the determination of trace amounts of parathion in fruit samples.

1. Introduction

Organophosphate pesticides (OPs) present a challenge for detection and identification in both gas and liquid phases. The most common methods involve preconcentration of the organophosphate on a solid phase and subsequent detection by high-performance liquid chromatography or gas chromatography (GC), often coupled to mass spectroscopy (MS) [1, 2]. Direct electrochemical methods for the detection of electroactive OPs compounds or applied electrochemical and gravimetric techniques in conjunction with enzymes have also been reported [3–10]. Electrochemical analysis based on chemically modified electrodes has proved a sensitive and selective method for the determination of OPs [5, 11, 12]. The electrochemical detection can be accomplished rapidly without tedious separation and might be suitable for continuous monitoring. OPs include a variety of toxic chemicals, for example, parathion, fenitrothion, and malathion. Like all OPs, parathion irreversibly inhibits the enzyme acetylcholinesterase (AChE) and is readily adsorbed through the skin. The determination of parathion and its substituted derivatives has, therefore, become increasingly important in environmental monitoring [13].

Recently, water-soluble dyes, such as methylene blue [14, 15], methylene green [16], carmine [17], brilliant cresyl blue [18], and other dye derivatives, have been widely used as mediators to catalyze the reduction or oxidation of organic molecules. Safranine is a water-soluble red-colored phenazine-type dye used widely in the paper and pharmaceutical industries. However, safranine polymer has rarely been used as a mediator to facilitate the electrochemical reaction of compounds.

In this work, a parathion sensor is fabricated by the electropolymerization of safranine on a glassy carbon electrode. A sensitive and selective electrochemical response has been obtained after incubating the sensors in phosphate buffer solution containing appropriate amount of parathion. This modified film electrode is used to determine parathion in real samples. The results suggest that the method has potential for practical determination.

2. Experimental

2.1. Reagents and Apparatus. Analytical grade parathion was purchased from Ehrenstorfer GmbH Company (Augsburg, Germany). Stock standard solution was prepared by dissolving parathion in ethanol and then storing it in the refriger-

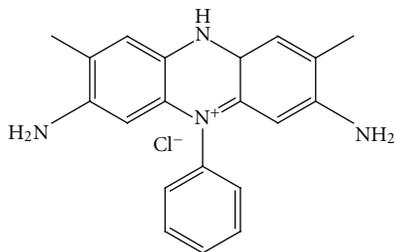


FIGURE 1: The molecular structure of safranine compounds.

ator. An aqueous solution was prepared daily by simple dilution of the stock solution with 0.100 mol L^{-1} phosphate buffer solution (PBS, pH = 6.0). Safranine (Figure 1) was obtained from Shanghai Reagent Company (Shanghai, China). All reagents are of analytical reagent grade unless stated otherwise. Double-distilled water is used throughout the experiment.

All electrochemical experiments were carried out on a CHI 660C electrochemical workstation (CH Instrument Company, Shanghai, China) with a conventional three-electrode system. The working electrode was a GCE modified with electropolymerization of safranine. The auxiliary and reference electrodes were made of platinum wire and saturated calomel electrode (SCE), respectively.

2.2. Preparation of the Modified Electrode. The GCE (3.0 mm in diameter) was polished to a mirror finish with polish paper and alumina slurry and cleaned consecutively and thoroughly in an ultrasonic cleaner with 1 : 1 HNO_3 , alcohol, and redistilled water. Electropolymerization of safranine on the GCE was accomplished by cyclic voltammetry (CV) in PBS (pH 6.0) containing $2.0 \times 10^{-5} \text{ mol L}^{-1}$ safranine. A poly(safranine) film was formed on the electrode surface by sweeps between -1.6 and 2.0 V for 15 cycles at a scan rate of 0.1 V s^{-1} . The thickness of poly(safranine) film could be controlled by the number of scans. Figure 2 presents the voltammograms during scanning. In the first potential scan, a cathodic peak (a) was observed near a potential value of -0.45 V . Oxidation peak was hardly observed. Two obvious anodic peaks (b, c) appeared after the second scan. Moreover, with further scans, the redox peak increased gradually until a stable status is reached. These phenomena-illuminated safranine was deposited on the surface of GCE by electropolymerization mode. The redox couple (a and b) at -0.45 V is the redox process for safranine. The oxidation peak at $+1.5 \text{ V}$ is due to irreversible oxidation of the monomer. The likely chemical process is shown in Scheme 1.

2.3. Sample Preparation. The apple sample was obtained from the local market. Its pretreatment followed the recommended process in literature [19]. Briefly, the apple seedcase sample was mashed with a blender. Then, 25.0 g of pulp was mixed with 0.05 L acetonitrile and 1.5 g NaCl, and the organic phase was collected and evaporated on a steam bath. The final volume was adjusted to 0.005 L by adding appropriate amount of dichloromethane. Part of the sample

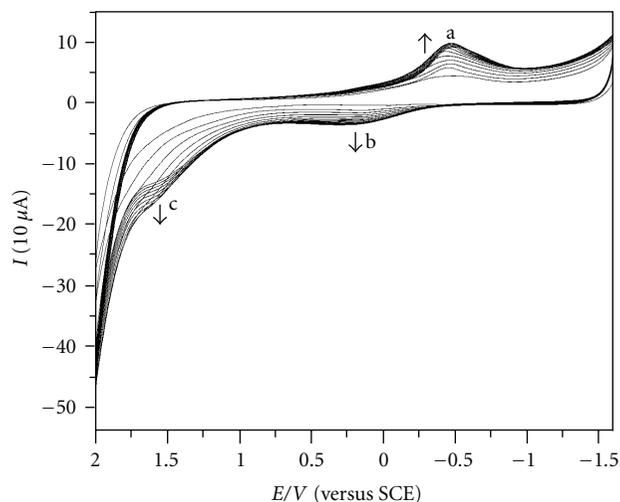


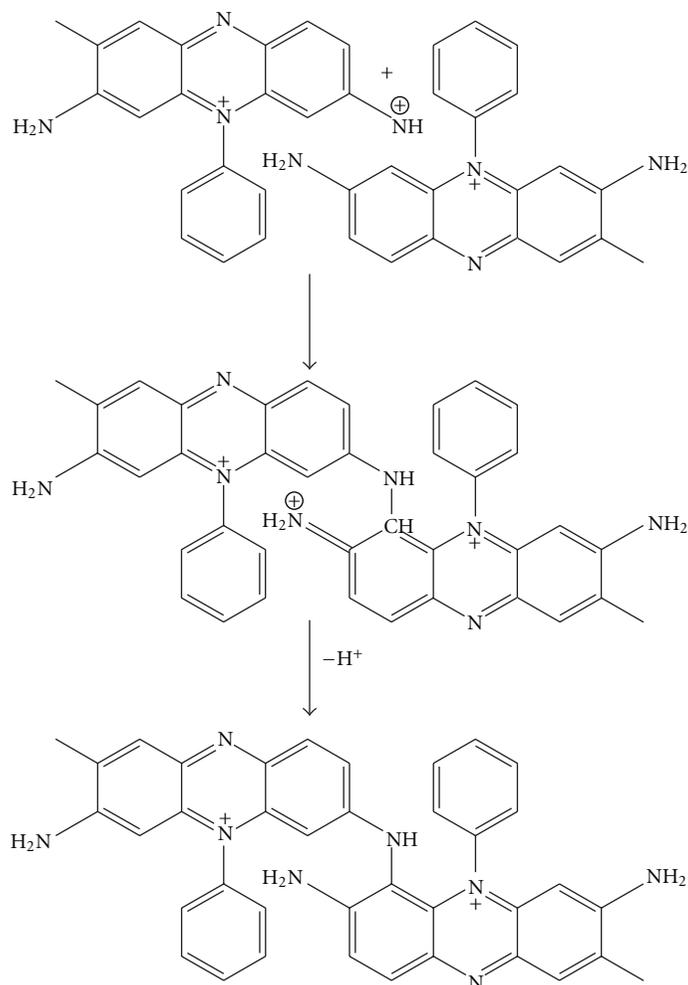
FIGURE 2: Cyclic voltammograms of $2.0 \times 10^{-5} \text{ mol L}^{-1}$ safranine at the GCE in PBS (pH 6.0) at a scan rate of 100 mV s^{-1} .

solution was transferred to PBS (pH 6.0). It was then spiked with a known amount of parathion stock solution. This was used for the electrochemical determination.

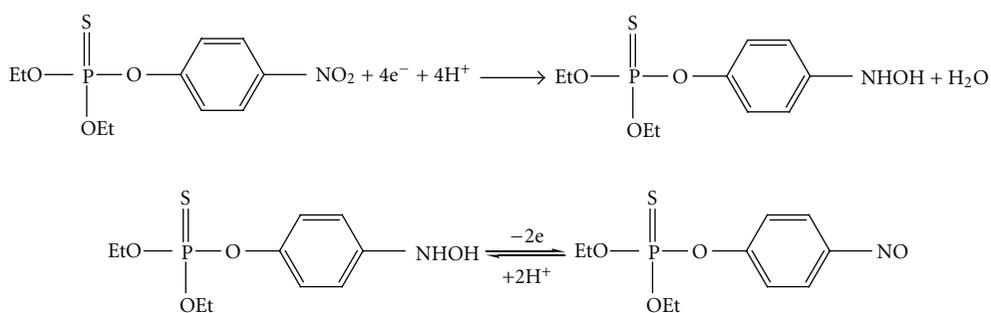
2.4. Analytical Procedure. An electrochemical cell containing 0.01 L supporting electrolyte (0.1 mol L^{-1} PBS, pH 6.0) and a specific amount of standard parathion solution were used to perform electrochemical measurements. The solution was deaerated with nitrogen for 10 min. The accumulation step was carried out under open circuit with stirring. The stirrer was stopped after 80 s, and the solution was left for 5 s to become quiescent. A linear sweep voltammogram from -1.20 to 0.40 V was recorded. The reduction peak current, measured at approximately -0.60 V in LSV, was applied for the electrochemical determination. After each measurement, the poly(safranine) film electrode was reactivated by successive cyclic potential sweeps between -1.0 and 0.6 V at 0.1 V s^{-1} in PBS (pH 6.0). All experiments were carried out at room temperature.

3. Results and Discussion

3.1. Electrochemical Behavior of the Parathion Sensor. Cyclic voltammetric response of $1.9 \times 10^{-5} \text{ mol L}^{-1}$ parathion on the sensor is shown in Figure 3. On the first cycle, only a cathodic peak (Pc) at around -0.60 V and anodic peak (P1a) at -0.03 V are observed. In the subsequent cathodic potential sweeps, another new reductive peak (P1c) appears at -0.08 V . A well-defined redox couple at approximately -0.05 V is found to increase at the expense of the decrease of the reductive peak at around -0.60 V . According to the currently accepted mechanism [5, 11, 12], the reduction peak (Pc) should be attributed to a four-electron transfer reduction of the nitro group ($\varphi\text{-NO}_2$) to give the hydroxylamine derivative. It can be reoxidized to the nitroso compound at a more positive potential (P1a). Under subsequent cycling, the nitroso group is reversibly



SCHEME 1



SCHEME 2

reduced to respective hydroxylamine (P1c). Therefore, the redox behaviour of parathion at the poly(safranin) film electrode included the following steps (see Scheme 2).

Typical cyclic voltammograms of parathion at a bare GCE (curve a) and a poly(safranin) film-modified GCE (curve b) are shown in Figure 4. It is apparent that poly(safranin) film results in much better catalysis of parathion reduction than the bare GCE. In addition, a

significant increase in the redox peak currents of parathion at the sensor also clearly observed. With regard to the sensitivity for the determination of parathion, the reductive peak (IPC) is selected for quantitative analysis.

Figure 5 shows linear sweep voltammograms of $3.43 \times 10^{-5} \text{ mol L}^{-1}$ parathion in pH 6.0 PBS solution at a bare glassy carbon electrode (curve a) and a poly(safranin)-modified electrode (curve b). A small reduction peak at

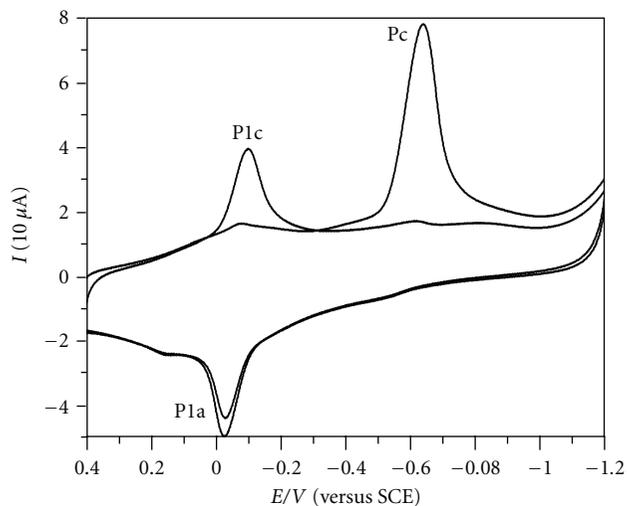


FIGURE 3: Cyclic voltammograms of $1.9 \times 10^{-5} \text{ mol L}^{-1}$ parathion in pH 6.0 PB solution at the poly(safranine) film-modified electrode. Scan rate: 100 mV s^{-1} .

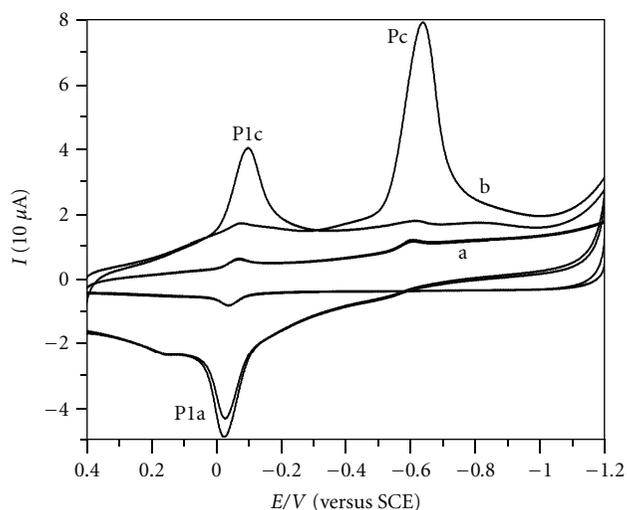


FIGURE 4: Cyclic voltammograms of $1.9 \times 10^{-5} \text{ mol L}^{-1}$ parathion at a bare GCE (a) and a poly(safranine) film-modified electrode (b) in pH 6.0 PB solution. Scan rate: 100 mV s^{-1} .

-0.60 V can be seen at the bare glassy carbon electrode. However, the reduction peak current of parathion increases significantly when the poly(safranine) film-modified GCE is employed. The remarkable peak current enhancement was undoubtedly attributed to the extraordinary properties of the polymer film, such as its three-dimensional distribution mediators and strong adsorption ability. In Figure 1, phenazine groups are present in the chemical structure of safranine. Thus, these are also present in the structure of poly(safranine). Moreover, a phenyl group is present in the structure of parathion. Therefore, during the process of preconcentration, parathion can be accumulated in the surface of the electrode via “ π - π ” hydrophobic interaction and/or hydrogen bonding with the poly(safranine) film to

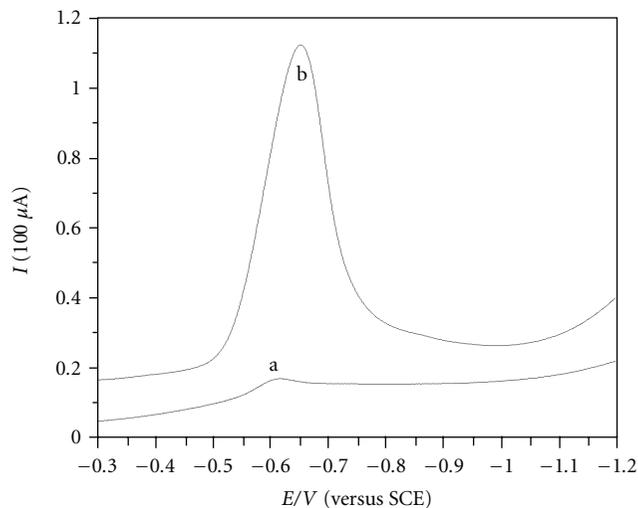


FIGURE 5: Linear sweep voltammograms of $3.43 \times 10^{-5} \text{ mol L}^{-1}$ parathion at a bare GCE (a) and a poly(safranine) film-modified electrode (b) in pH 6.0 PB solution. Scan rate: 100 mV s^{-1} .

enhance the current response. These results suggest that the sensor exhibits strong adsorptive ability and subtle electronic properties for parathion.

3.2. Influence of Scan Rate. The effect of scan rate on the reduction of parathion was investigated by linear sweep voltammetry in the range of 0.01 – 0.2 V s^{-1} . A good linear relationship between the reduction peak current (I_{pc}) and scan rate was observed in the range studied. The regression equation was $I_{pc} (\mu\text{A}) = 0.151 v (\text{mV s}^{-1}) + 6.172$ ($r = 0.998$). The reduction peak current increases linearly with v for scan rates between 0.01 and 0.2 V s^{-1} . This electrochemical behavior reflected an adsorption process of parathion at the polymer film electrode and indicated that the electrode reaction is predominantly adsorption controlled in a confined thin film.

3.3. Influence of Solution pH. The influence of the solution pH on the reduction peak potential was examined by LSV. The reduction peak potential (E_{pc}) shifts negatively with increasing pH values. The relationship between the E_{pc} and the solution pH obeys the following equation: $E_{pc} = -0.052 \text{ pH} - 0.379$ ($r = 0.998$). A slope of 52 mV/pH suggests that the transfer number of protons and electrons is equal in the reduction reaction of parathion.

The effect of pH on the peak current of parathion is displayed in Figure 6. The reduction peak current (I_{pc}) is also significantly affected by solution pH. In this sensing system, the peak current increases with the increasing solution pH when the pH of the solution is less than 5.5 and larger than 4.5. A maximum response is observed between 5.5 and 6.5. The best results, with respect to the current enhancement and shape, are obtained at pH 6.0 phosphate buffer.

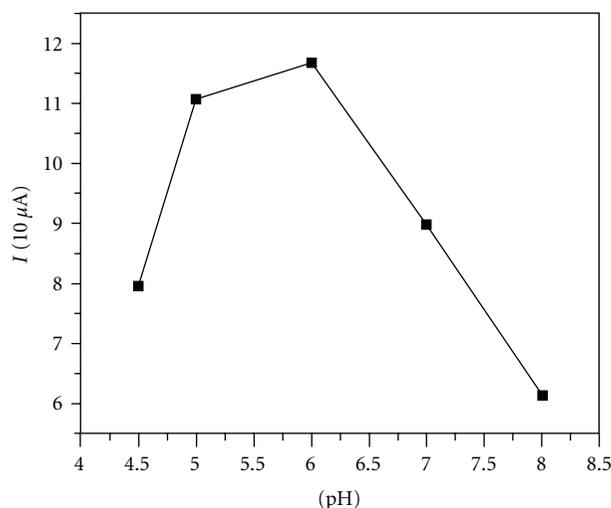


FIGURE 6: Effects of pH on the peak current of $3.43 \times 10^{-5} \text{ mol L}^{-1}$ parathion at a safranin modified electrode. Scan rate: 100 mV s^{-1} .

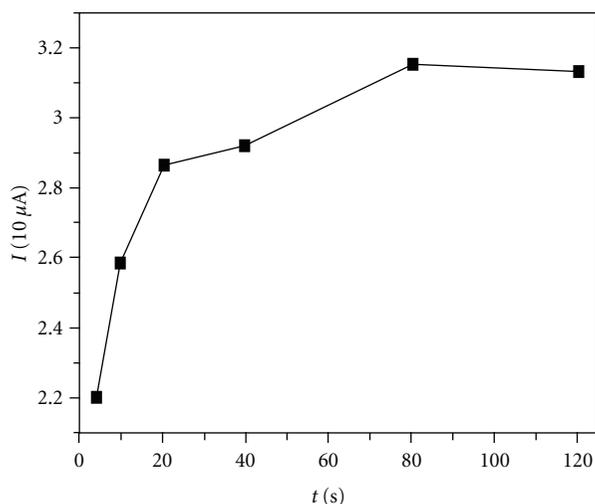


FIGURE 7: Effect of the accumulation time on the peak current in pH 6.0 PB solution containing $5.0 \times 10^{-7} \text{ mol L}^{-1}$ parathion. Scan rate: 100 mV s^{-1} .

3.4. Influence of Accumulation Time and Accumulation Potential. Effects of accumulation time on the reduction peak current of $5.0 \times 10^{-7} \text{ mol L}^{-1}$ parathion were investigated by LSV, and the results are illustrated in Figure 7. The peak current increased with the accumulation time in the range of 4–80 s. This indicated the occurrence of adsorptive accumulation of parathion on the surface of the modified electrode. However, further increase in accumulation time did not increase the amount of parathion at the electrode surface owing to surface saturation. Therefore, 80 s was selected as optimum accumulation time for the determination of parathion on the sensor.

Voltammetric responses to $5.0 \times 10^{-7} \text{ mol L}^{-1}$ parathion were used to investigate the effect of accumulation potential on the determination of parathion. The peak current almost does not vary with changing accumulation potential from

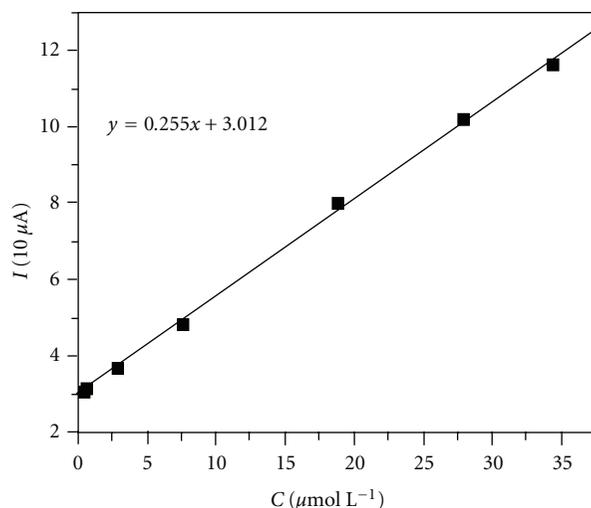


FIGURE 8: Calibration curve for the determination of parathion at the poly(safranin) film electrode ($n = 10$).

–0.9 to 0.3 V, revealing that the accumulation potential has no obvious effect on the reduction peak current of parathion at the modified electrode. The accumulation of parathion was therefore carried out under open circuit.

3.5. Analytical Characterization. Figure 8 shows the calibration curve of the sensor for the determination of parathion. Calibration of the sensor is carried out using the established current response. Under the optimized conditions, the sensor exhibits a linear relationship between the peak current and the concentration of parathion in the range of 3.43×10^{-8} to $3.43 \times 10^{-5} \text{ mol L}^{-1}$. The linear regression equation is $I_p (10 \mu\text{A}) = 3.012 + 0.255 C (\mu\text{mol L}^{-1})$, with a correlation coefficient of 0.9997. The detection limit is $1.0 \times 10^{-8} \text{ mol L}^{-1}$. The relative standard deviation (RSD) of 3.2% for $1.0 \times 10^{-7} \text{ mol L}^{-1}$ parathion ($n = 10$) implies good reproducibility.

The stability of the sensor is examined in PBS containing $1.0 \times 10^{-7} \text{ mol L}^{-1}$ parathion by means of voltammetry. The test results show that the current responses of the sensor remain the same after storage at room temperature for at least 2 weeks. The sensor therefore exhibits a good stability.

Several organic and inorganic species in the environmental samples can potentially contribute to the interference with the parathion sensor detection scheme. The selectivity of the sensor is determined by measuring the change in the sensor response in the presence of foreign compounds. The experimental results show that a 10-fold concentration of Pb (II), Cd (II), Mn (II), Cu (II), Co (II), Fe (III), Zn (II), Ca (II), Mg (II), ascorbic acid, and dopamine has little effect on the current response of $1.0 \times 10^{-7} \text{ mol L}^{-1}$ parathion. At a 1:1 ratio malathion, diazinon, and O,O-dimethyl- α -hydroxybenzyl phosphate, no observable difference in the voltammetric response is obtained for the determination of $1.0 \times 10^{-7} \text{ mol L}^{-1}$ parathion.

TABLE 1: Analytical results of apple samples and recovery test.

Sample	Spiked ($\mu\text{mol L}^{-1}$)	Found ($\mu\text{mol L}^{-1}$)	Recovery (%)
1	0	0	0
2	0.3	0.293	97.7
		0.143	104.7
		0.207	102.3
3	0.6	0.589	98.2
		0.596	99.3
		0.614	102.3
4	1	1.072	107.2
		1.018	101.8
		0.983	98.3

Applications of the Sensor. The sensor was used to determine parathion in fruit samples with the recommended procedure [19]. A standard addition method was adopted to estimate the accuracy. The measurement results are shown in Table 1. We can see that the recovery of the spiked parathion is good in fruit samples. Obviously, interferences in fruit samples are negligible.

4. Conclusions

Based on an electropolymerization of safranin film, a voltammetric sensor has been successfully fabricated for the determination of parathion. The successful determination of parathion spiked into fruit samples suggested that it was a promising electrochemical device for the detection of parathion in environmental samples.

Acknowledgment

The project was supported by the Research Foundation of Education Bureau of Yunnan Province, China (Grant no. 09C0237).

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