



A novel nanosilver/nafion composite electrode for electrochemical sensing of methyl parathion and parathion

A. Kumaravel, M. Chandrasekaran *

Central Electrochemical Research Institute, Karaikudi 630 006, Tamil Nadu, India

ARTICLE INFO

Article history:

Received 31 July 2009

Received in revised form 29 October 2009

Accepted 2 November 2009

Available online 6 November 2009

Keywords:

Nanosilver/nafion electrode
Organophosphorus pesticides
Electroanalytical sensor

ABSTRACT

A novel nanosilver/nafion composite electrode was fabricated and used for sensing methyl parathion and parathion for the first time. This electrode offers lower reduction potential and higher sensing current. Reproducible response for four successive measurements was observed. The maximum sensing current was obtained in 30 s for various concentrations of pesticides.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Organophosphorus pesticides are widely used in agricultural production [1]. Their presence in water and food poses hazard to human health [2]. Due to high toxicity of organophosphorus pesticides, rapid detection of these toxic agents becomes increasingly important for homeland security and health protection [3–5]. Analysis of these pesticides in an environment is routinely carried out by using gas chromatography and mass spectrometry [6]. Such analysis is generally performed at centralized laboratories, requiring extensive labor, analytical resources and often results in a lengthy analysis time. Biological methods such as immunoassay have also been reported [7]. However, long analysis time and extensive sample handling with multiple washing steps limit the application under field conditions. So we need fast, reliable and economically viable methods for their detection in the environment and also in the agro-food products. Electroanalytical sensors are an alternative and viable method because of its compact nature, easy handling in field trials, low cost, low power requirements and also produce selective responses within a very short time [8]. The voltammetric and amperometric methods have been used for the determination of pesticides in crops, pharmaceutical products and environmental samples [9–11]. Among the organophosphorus pesticides, the nitro aromatic organophosphorus pesticides, such as methyl parathion (MP) and parathion (P) exhibit good redox activities at the electrode surface. Electrochemical reactions of most of these pesticides show sluggish electrode kinetics [12], as they are very large organic molecules, resulting electrode fouling.

This affects the performance of the electrode during electrochemical measurements. In recent times this problem has been overcome by applying suitable modifiers such as hexadecane [13], clay [14], stearic acid [15], crown sol gel film [16], ZrO_2 [17] and bismuth film [18] on the electrode surface, hence improving the performance of the electrode for methyl parathion and parathion sensing. Nafion film modification gave a better selectivity and mass transfer for parathion detection [19]. This polymer film selectively preconcentrates the analyte of interest [20] thus improving the sensitivity and the selectivity [21,22]. Metal and semiconductor nanoparticles in the construction of sensing devices have received considerable attention in recent years because of its unique electrocatalytic, chemical and electrical properties [23]. Silver nanoparticles deposited on the glassy carbon electrode (GCE) produced better electro catalytic activity for the reduction of hydrogen peroxide [24] and benzyl chloride [25]. Silver nanoparticles have a higher reducibility than bulk silver and it shows a higher electro reductive activity in the determination of thiocyanate [26]. In the present investigation, a novel approach was adopted by electrochemical co-deposition of silver nanoparticles with nafion film on GCE for the sensing of methyl parathion and parathion. The silver/nafion co-deposited film on GCE offers better properties than silver or nafion deposited individually. The silver/nafion film on GCE is highly stable and gave reproducible results for four successive electrochemical measurements. Cyclic voltammetry, differential pulse voltammetry and amperometry techniques were used. The experimental results showed that the nanosilver/nafion composite electrode not only exhibited strong electro catalytic activity but also exhibited good reproducibility. The reliability of the sensor was also checked with analytical data obtained in HPLC method.

* Corresponding author. Tel.: +91 4565 227550; fax: +91 4565 227779, 227713.
E-mail address: yemchand@yahoo.com (M. Chandrasekaran).

2. Experimental

2.1. Instrumentation

Computer controlled Autolab PGSTAT 30 (Eco Chemie, Netherlands) electrochemical system was used. Silver/naftion coated GCE (Tokai GC 3 mm diameter) served as a working electrode. Platinum wire and saturated calomel electrode (SCE) served as the counter electrode and reference electrode, respectively. X-ray diffraction (XRD) patterns were recorded in a PANalytical diffractometer Model PW3040/60 X'pert PRO operating with Cu K α radiation ($k = 0.15406$ nm) generated at 40 kV and 20 mA. Scans were done at 3° min^{-1} for 2θ values between 20° and 90° . SEM was done with a Hitachi Model S-3000H with 10 kV (acceleration voltage). HPLC was done with an LC-10AT pump and SPD-10A detector (Shimadzu, Japan) at 254 nm with a Shimpack CLC ODS-18 column. Electrochemical experiments were carried out in a 10 ml glass cell at $30 \pm 1^\circ \text{C}$. Prior to electrochemical measurements, the solutions were deoxygenated by purging with pure nitrogen for 15 min.

2.2. Reagents

Methyl parathion and parathion were purchased from Accu-Standard, USA. Stock solutions of methyl parathion (2070 μM) and parathion (2540 μM) were prepared from methanol. Working solution was prepared daily by dilution with Britton–Robinson buffer (B–R) of pH 2.56. The B–R buffer solution of pH 2.56 was prepared by adding 15 ml of 0.2 M sodium hydroxide solution into 100 ml of a mixed acid, containing 0.04 M of each boric, orthophosphoric and acetic acids. Nafion (5 wt.% in aliphatic alcohols and water mixture), were purchased from Sigma–Aldrich (St. Louis, MO, USA). Silver nitrate and other reagents used were of analytical reagent grade and double distilled water was used to prepare solutions.

2.3. Preparation of silver/naftion modified GCE

The GCE was hand polished with the fine emery paper (1/0.2/0.3/0.4/0) rinsed thoroughly with double distilled water and cleaned successively in 10% NaOH solution, 1:1 HNO $_3$ –H $_2$ O (v/v) and methanol, each for 2 min and dried in air. Nafion and silver composite was deposited on GCE by using graphite plate as anode and GCE as cathode by applying 1 V constant cell voltage for 2 min from the solution containing 0.1 ml (5 wt.%) nafion and 10 ml of 1 mM silver nitrate with stirring. Modified GCE was washed with water, dried in air and used.

3. Results and discussion

3.1. Surface morphology of silver/naftion composite modified GCE

SEM images of GCE and the modified GCE are shown in Fig. 1A, B and C. From the figure, it can be found that in the absence of nafion, silver particles are agglomerated (Fig. 1B) and there is no uniform deposition. From the Fig. 1C, it can be found that when silver is deposited in the presence of nafion a uniform deposition is observed. To determine the approximate crystallite size, XRD patterns of the silver/naftion composite were obtained as shown in Fig. 2. All XRD peaks are indexed with the JCPDS file [27]. The two major peaks observed at 38.11° and 44.31° can be assigned to the diffraction from the (1 1 1) and the (2 0 0) planes, respectively, of the face-centered cubic lattice of Ag (0). The silver particle size is calculated from the Scherrer equation [28]. The crystallite size is found to be less than 50 nm.

3.2. Cyclic voltammetric response of MP and P at silver/naftion modified electrode

Cyclic voltammograms were recorded for the addition of 10.2 μM methyl parathion. One sharp irreversible diffusion controlled reduction peak was observed at -168 mV (Fig. 3d) at 100 mV s^{-1} . Parathion possessed similar structure with methyl parathion, reduced at -218 mV (Fig. 4). This single peak observed is due to $4e^-$ transfer reduction of nitro group into hydroxylamine group [9]. The peak potential shifted 406 mV anodically and the peak current increased by 71.13% for methyl parathion and the peak potential shifted 242 mV anodically and current increased by 33.59% for parathion at silver/naftion composite modified GCE when compared with cyclic voltammogram obtained at bare GCE under identical conditions. Only 20 mV anodic shift and 30% current increase was reported during the reduction of methyl parathion at bismuth film modified electrode under similar conditions [17]. The shift in the reduction potential is due to the electro catalytic activity of the silver nanoparticles [22] and the increase in current response is due to the presence of nafion film on the electrode surface. Nafion has a structure of hydrophobic fluorocarbon chain and hydrophilic $-\text{SO}_3$ groups, enables to attract the protonated pesticides molecules [12,13] via the ion exchange model. The protonated form of pesticide molecules in acidic solutions easily penetrate through the nafion membrane and reach the electrode surface. Hence, the concentration of the pesticide molecules near the electrode surface gets increased. As a result, the enhanced reduction current is obtained. The enhanced current and the lower reduction potential on silver/naftion composite GCE are qualitatively equal to those observed for electrodes coated with the individual components (Fig. 3b and c). According to our best of knowledge, there was no report for such a drastic potential shift and current increase for the reduction of methyl parathion and parathion. A linear relationship between the peak current and the concentration was obtained. The detection limit 0.4515 μM for methyl parathion and 0.00103 μM for parathion were estimated ($S/N = 3$).

3.3. Differential pulse voltammetric (DPV) response of MP and P at silver/naftion modified electrode

DPV was recorded with the following optimized instrumental settings: modulation amplitude 40 mV, modulation frequency 30 Hz and modulation step 4 mV. Figs. 5 and 6 show the DPV response of methyl parathion and parathion, respectively. Inset shows the calibration graphs. The peak current and the concentration were linear for the concentration ranging from 0.3001 μM to 1.444 μM for methyl parathion and 0.103–0.6179 μM for parathion, respectively. The detection limits were found to be 0.0874 μM for methyl parathion and 0.0835 μM ($S/N = 3$) for parathion, respectively.

3.4. Amperometric response of MP and P at silver/naftion modified electrode

Amperometric method was used to examine the sensitivity of silver/naftion modified GCE towards the sensing of methyl parathion and parathion. Figs. 7 and 8 show the amperometric $i-t$ curve obtained for methyl parathion and parathion, respectively. The current increased for each addition and a steady state current was measured. The amperometric current response increased linearly with increasing concentration from 0.2 μM to 1.00 μM for methyl parathion and parathion. The detection limits were found to be 0.2815 μM for methyl parathion and 0.2659 μM for parathion, respectively.

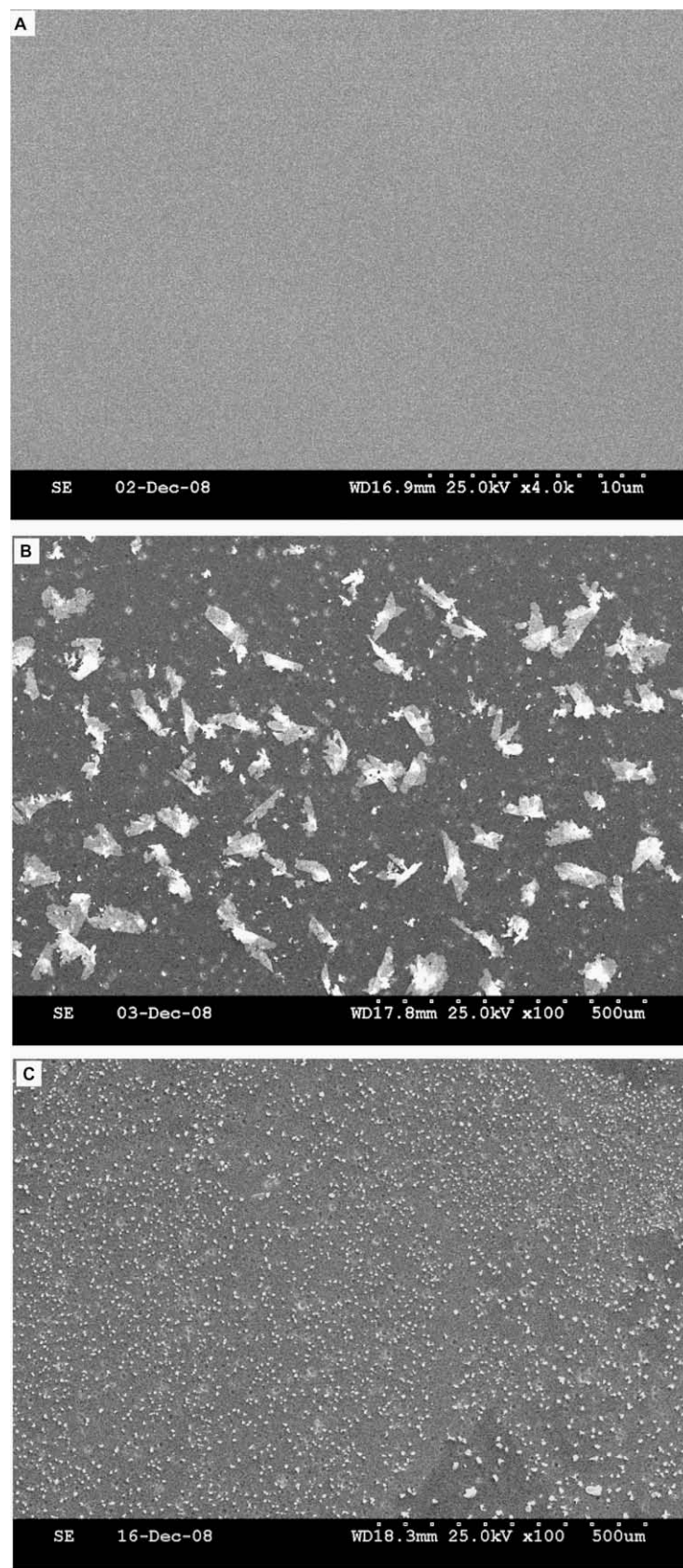


Fig. 1. SEM images of bare GCE (A), silver modified GCE (B), silver/nafion composite modified GCE (C).

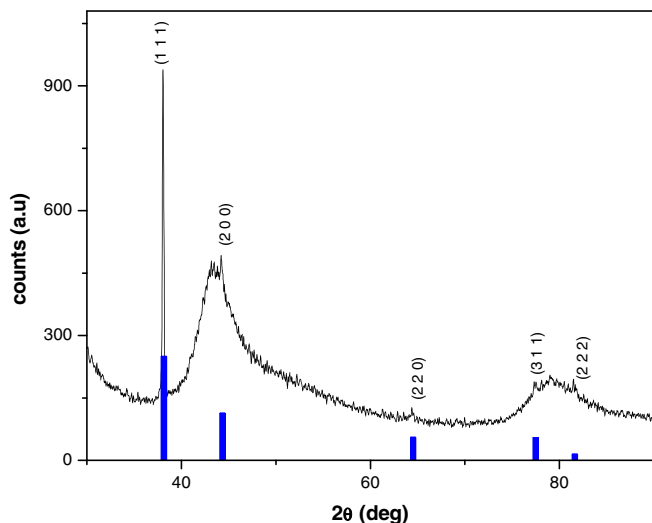


Fig. 2. XRD pattern of silver/nafion composite modified GCE.

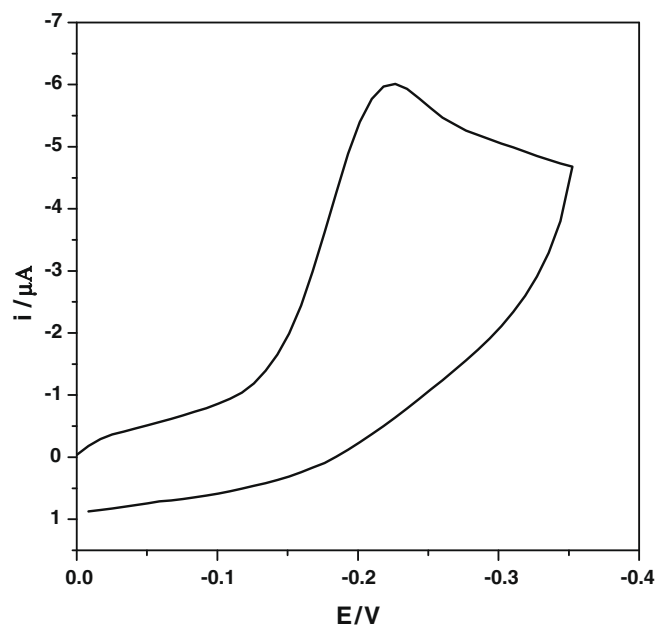


Fig. 4. Cyclic voltammogram for 10.2 μM parathion at silver/nafion modified GCE in 2.56 pH B–R buffer at 100 mV s^{-1} .

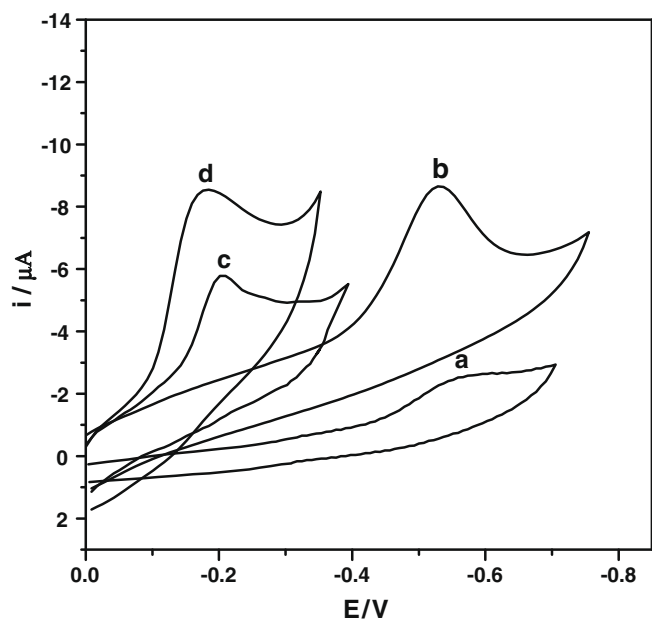


Fig. 3. Cyclic voltammograms for 10.2 μM methyl parathion at: (a) bare GCE, (b) nafion modified GCE, (c) silver modified GCE, and (d) silver/nafion composite modified GCE in 2.56 pH B–R buffer at 100 mV s^{-1} .

3.5. Reproducibility and stability of silver/nafion modified electrode

A series of six repetitive measurements were done for the fixed concentration of 10.2 μM methyl parathion and parathion yielded reproducible peak currents with the relative standard deviations of 3.2% for methyl parathion and 4.2% for parathion, respectively. This electrode offers maximum sensing current in 30 s for various concentrations of pesticides. The stability was checked after the fresh modification, the same electrode was used for four successive measurements. The results were reproducible with the relative standard deviations of 5.2% for methyl parathion and 3.1% for parathion. This reveals that the composite film was highly stable.

The analytical utility of the above methods was assessed by applying it to the determination of methyl parathion and parathion in the water sample collected from CECRI premises. The analyzed sample contained no methyl parathion and parathion, so they

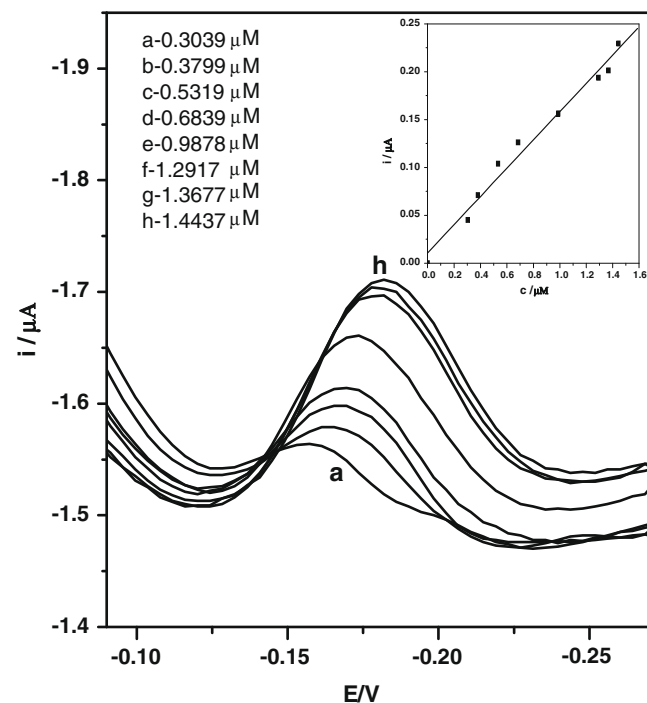


Fig. 5. Differential pulse voltammograms of methyl parathion at various concentrations in 2.56 pH B–R buffer; modulation amplitude, 40 mV; modulation frequency, 30 Hz; modulation step, 4 mV. Inset shows the calibration graph.

had to be spiked with the analyte at a certain concentration. Then it was extracted by using dichloromethane. The results are summarized in the Table 1. The recovery rate obtained is well comparable with the recovery rate obtained from HPLC. So this proposed silver/nafion composite film electrode and the voltammetric procedures for methyl parathion and parathion sensing would be useful for environmental applications.

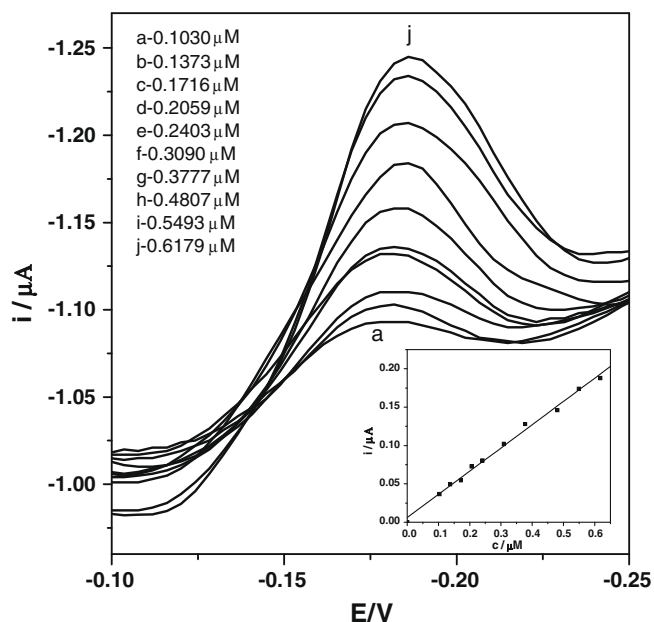


Fig. 6. Differential pulse voltammograms of parathion at various concentrations in 2.56 pH B–R buffer; modulation amplitude, 40 mV; modulation frequency, 30 Hz; modulation step, 4 mV. Inset shows the calibration graph.

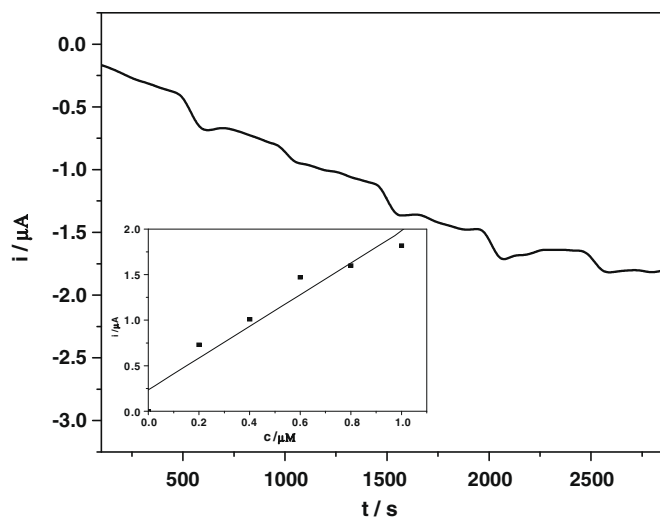


Fig. 7. Amperometric response of methyl parathion for the successive addition of 0.2 μM at the silver/naftion composite modified GCE in 2.56 pH B–R buffer. Inset shows the calibration graph.

4. Conclusion

A novel silver/naftion composite film modified GCE reported in the present work is more suitable for the sensing of methyl parathion and parathion pesticides. Minimum amount of energy is enough to bring out the reduction process. This composite electrode gave high sensing current when compared with bare GCE and bismuth film modified GCE which improves the sensitivity of the electrochemical sensors. Moreover, the electrode once modified which can be used for four successive reproducible measurements. This proposed electrochemical sensing methodology is thus expected to open new opportunities for the sensing of methyl parathion and parathion in the environment.

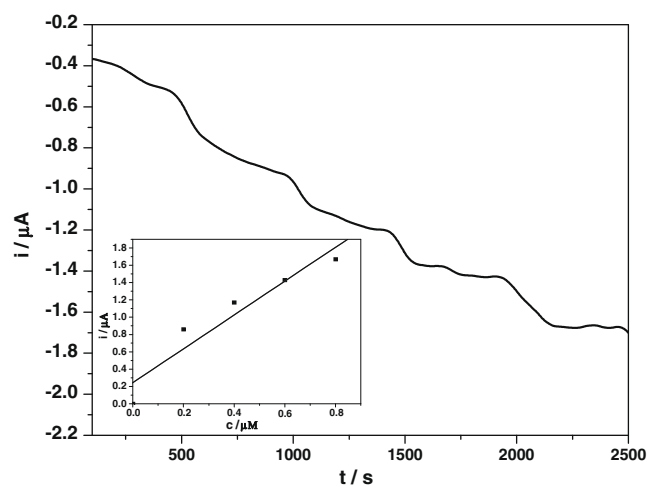


Fig. 8. Amperometric response of parathion for the successive addition of 0.2 μM at the silver/naftion composite modified GCE in 2.56 pH B–R buffer. Inset shows the calibration graph.

Table 1

Recovery study of methyl parathion and parathion in water samples.

	Recovery rate (%)			
	CV	DPV	Amperometry	HPLC
Methyl parathion	86.15	91.51	95.82	92.75
Parathion	97.65	98.58	99.44	97.76

Number of sample assayed is 6.

Acknowledgement

The authors gratefully acknowledge the financial support from the Department of Science and Technology, New Delhi, India.

References

- [1] M.V. Russo, L. Campanella, P. Avino, *J. Chromatogr. B* 780 (2002) 431.
- [2] I. Palchetti, A. Cagnini, M. Del Carlo, C. Coppi, M. Mascini, A.P.F. Turner, *Anal. Chim. Acta* 337 (1997) 315.
- [3] J. Wang, *Anal. Chim. Acta* 507 (2004) 145.
- [4] Y. Lin, E. Lu, J. Wang, *Electroanalysis* 16 (2004) 3.
- [5] J. Wang, M. Pumera, G. Collins, A. Mulchandani, Y. Lin, K. Olsen, *Anal. Chem.* 74 (2002) 1187.
- [6] J. Sherma, *Anal. Chem.* 65 (1993) 40.
- [7] J. Miller 1, D. Lenz, *J. Appl. Toxicol.* 21 (2001) S23.
- [8] C.M.A. Brett, *Pure Appl. Chem.* 73 (2001) 1969.
- [9] E.M. Garrido, C. Delerue-Matos, J.L.F.C. Lima, A.M.O. Brett, *Anal. Lett.* 37 (2004) 1755.
- [10] G.D. Liu, Y.H. Lin, *Electrochem. Commun.* 7 (2005) 339.
- [11] Y.N. Ni, P. Qiu, S. Kokot, *Anal. Chim. Acta* 516 (2004) 7.
- [12] A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980.
- [13] C. Xu, K. Wu, S. Hu, D. Cui, *Anal. Bioanal. Chem.* 373 (2002) 284.
- [14] P. Manishankar, G. Selvanathan, C. Vedi, *Appl. Clay Sci.* 29 (2005).
- [15] A. Navaratne, N. Susantha, *Anal. Lett.* 33 (2000) 1491.
- [16] C. Li, C. Wang, B. Guan, Y. Zhang, S. Hu, *Sens. Actuat. B* 107 (2005) 411.
- [17] G.D. Liu, Y.H. Lin, *Anal. Chem.* 77 (2005) 5894.
- [18] D. Du, X. Ye, J. Zhang, D. Liu, *Electrochim. Acta* 53 (2008) 4478.
- [19] J.M. Zen, J.J. Jou, A.S. kumar, *Anal. Chim. Acta* 396 (1999) 39.
- [20] Z. Hu, C.J. Seliskar, W.R. Heineman, *Anal. Chim. Acta* 369 (1998) 93.
- [21] J.M. Zen, F.S. Hsu, N.Y. Chi, S.Y. Huang, M.J. Chung, *Anal. Chim. Acta* 310 (1995) 407.
- [22] J. Wang, R. Li, *Talanta* 36 (1989) 279.
- [23] X. Luo, A. Morrin, A.J. Killard, M.R. Smyth, *Electroanalysis* 18 (2006) 319.
- [24] C.M. Welch, C.E. Banks, A.O. Simm, R.G. Compton, *Anal. Bioanal. Chem.* 382 (2005) 12.
- [25] A.A. Isse, S. Gottardello, C. Maccato, A. Gennaro, *Electrochem. Commun.* 8 (2006) 1707.
- [26] G.F. Wang, M.G. Li, Y.C. Gao, B. Fang, *Sensors* 4 (2004) 147.
- [27] P.A. Swarthmore, Joint Committee on Powder Diffraction Standards Diffraction data file: JCPDS International Center for Diffraction Data, 1991.
- [28] V. Radmilovic, H.A. Gasteiger, P.N. Ross, *J. Catal.* 154 (1995) 98.