Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 101 (2013) 54–58

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Kinetic-spectrophotometric determination of methyl parathion in water and vegetable samples

Neetu Tiwari *, Anupama Asthana, Kanchan Upadhyay

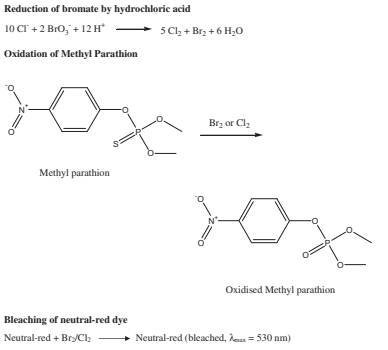
Department of Chemistry, Govt. V.Y.T. PG Autonomous College, Durg, Chhattisgarh 491 001, India

HIGHLIGHTS

- Based on a new kinetic approach.
- Simple, selective and sensitive.
- Applicable in different vegetable and water samples with satisfactory results.

GRAPHICAL ABSTRACT

Inhibitory effect of methyl parathion.



ARTICLE INFO

Article history:
Received 1 June 2012
Accepted 22 September 2012
Available online 29 September 2012

Keywords:
Methyl parathion
Potassium bromate
Neutral red
Spectrophotometry

ABSTRACT

A new selective and sensitive kinetic method has been developed for spectrophotometric determination of methyl parathion based on its inhibitory effect on the redox reaction between bromate and hydrochloric acid. The decolorization of neutral red by the reaction product was used to monitor the reaction spectrophotometrically at 530 nm by measuring the change in absorbance at the fixed time of 5 min after the initiation of the reaction. The variables affecting the rate of the reaction were investigated. Under the selected experimental conditions methyl parathion was determined in the range of 0.025–0.3 μg mL^{-1}. Sandell's sensitivity and molar absorptivity for the system were found to be 0.0004 μg cm^{-2} and 6.5×10^5 L mol^{-1} cm^{-1} respectively. The proposed method was applied for the determination of methyl parathion in different vegetable and water samples with satisfactory results. The results were compared with those obtained by GC–MS, very similar values were found by the two methods.

Introduction

Organophosphorus pesticides attained the growing importance in pest control because of their rapid decomposition and less likely accumulation in environment. They are still of great concern because of their high solubility in water, excessive usages and acute toxicity. Methyl parathion (O,O-dimethyl-O-(4-nitrophenyl) phosphorothioate) is one of the organophosphorus pesticides very effective against many pests in important crops, such as bulbs, cereals, fruits, vegetables, cotton, peanuts, soybean, potato, sugar cane, coffee, alfalfa, and pasture [1,2]. It act by contact, ingestion, and inhalation [3], and is well known inhibitor of acetylcholinesterase (essential for the operation of the central nervous system of the insects), therefore, producing serious damage and death [4]. It is classified in toxicological class 1 meaning that it is extremely dangerous for mammals. Detection of methyl parathion as environmental pollutant and their monitoring is important to minimize the potential hazards in human health [5,6].

* Corresponding author. Tel.: +91 9755888857.
E-mail address: neetuchem30@gmail.com (N. Tiwari).

1386-1425/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2012.09.084

Analysis of methyl parathion in environmental and biological samples is routinely carried out using analytical techniques, such as GC–MS [7–11], GC–PFPD [12], HPLC–DAD [13], and electrochemical methods [14–16]. Such analysis is generally performed at centralized laboratories, requiring extensive labor and analytical resources, and often results in a lengthy turn-around time. Spectrophotometry is considered the most convenient analytical technique because of its inherent simplicity, low cost, and wide availability in most of the laboratories. However, few spectrophotometric methods have been reported for its determination which is based on the estimation of phosphorus present in organophosphorus pesticides by reduction of molybdophosphoric acid to molybdenum blue by using reducing reagents [17–19], or based on the reduction of the nitro group present in parathion-methyl with zinc/HCl to form amino-parathion-methyl. The aminoparathion-methyl thus formed is diazotized and subsequently coupled with a coupling agent [20]. Reported spectrophotometric methods are indirect, less sensitive, or suffers from interference.

The proposed new kinetic method is based on the inhibitory effect of methyl parathion on the decolorization reaction of neutral red by bromate in acidic medium of hydrochloric acid. The method is simple, selective, sensitive, and can be easily applied for the determination of methyl parathion in different vegetable and waste water samples. The results were compared with those obtained by GC–MS; similar values were found by the two methods.

Experimental

Reagent solutions and apparatus

All chemicals used were of analytical reagent grade and solutions were prepared from doubly distilled water. Methyl parathion (Bayer, India Ltd.) stock solution (1000 μg mL^{-1}) was prepared in ethanol. Potassium bromate (Merck, Mumbai, India) aqueous solution of 6.0×10^{-3} mol L^{-1} was prepared, and stored in amber colored bottle. Neutral red (Merck, Mumbai, India) aqueous solution of 7.0×10^{-3} - mol L^{-1} was prepared. A 2 mol L^{-1} aqueous solution of HCl (Merck, Mumbai, India) was prepared. A Varian Cary 50 Bio UV–Visible Spectrophotometer was used for spectral measurements, pH measurements were made with Systronics digital pH meter 335.

Recommended procedure

All the solutions and distilled water were kept in a thermostate water bath at 30 °C for 15 min for equilibration before starting the experiment. An aliquot of the solution containing 0.025–0.3 μg mL^{-1} methyl parathion was transferred into a 10 mL volumetric flask and 0.3 mL of 6.0×10^{-3} mol L^{-1} potassium bromate, 0.6 mL of 2 mol L^{-1} hydrochloric acid were added and the solution was diluted up to 5 mL and kept for 2 min and then 0.5 mL of 7.0×10^{-3} mol L^{-1} neutral red solution was added and solution was diluted to the mark with distilled water. Time was measured just after the addition of neutral red. The mixture was mixed and a portion of the reaction mixture was transferred into spectrophotometric cell. The reaction was followed by recording the absorbance against water at 530 nm from 0.5 to 5.0 min after the initiation of the reaction. Then a calibration graph of the difference between the decrease in absorbance of the blank minus that of the sample ($\Delta A_{blank} - \Delta A_{sample}$) at a fixed time vs. methyl parathion concentration was constructed.

Determination of methyl parathion in water and vegetable samples

The proposed method was applied satisfactorily to the determination of pesticides in waste water and vegetable samples. To check the recoveries, various samples free from methyl parathion were taken and treated with a known amount of the pesticide, and kept for ~24 h. The samples were then washed with ethanol and washings were collected. Aliquots of these washings were used for the determination of methyl parathion by the proposed method. The recoveries are given in Table 1.

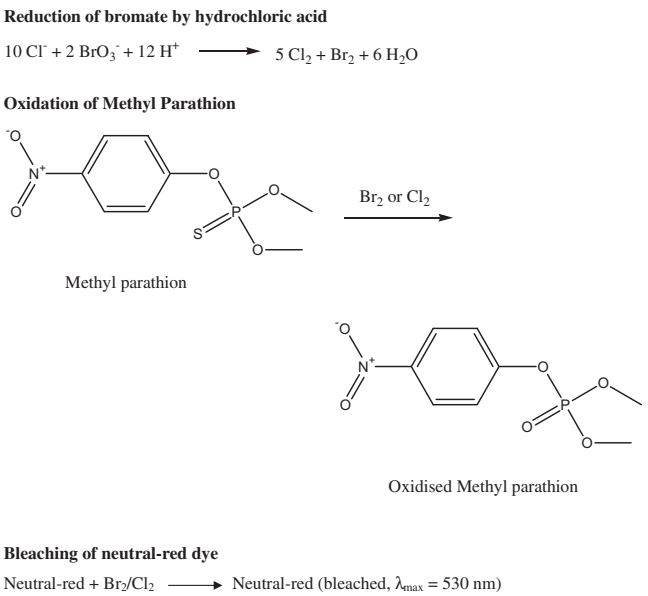
Table 1
Recoveries from environmental samples.

Sample	Amt. added (μg)	Amt. found (μg)[a]	Recovery (%)	RSD (%)
Vegetable sample[b]				
Cauliflower	5	5.13	102.52	0.296
	10	10.11	101.06	0.205
	15	15.11	100.75	0.127
Tomato	5	4.94	98.8	0.32
	10	9.96	99.56	0.208
	15	14.97	99.8	0.106
Spinach	5	4.92	98.4	0.455
	10	9.94	99.4	0.159
	15	14.94	99.57	0.139
Waste water sample[c]				
A	5	4.89	97.92	0.47
B	10	9.97	99.68	0.165
C	15	14.96	99.72	0.129

[a] Mean of five replicate analyses.
[b] Amount of sample, 10 g (free from methyl parathion).
[c] Volume of sample, 5 mL (free from methyl parathion).

Results and discussion

The reaction of bromate with hydrochloric acid produces chlorine and bromine. The produced bromine and chlorine react with neutral red and the reaction causes oxidative decolorization. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of the reaction mixture at 530 nm. Methyl parathion can be oxidized with the product of the reaction (bromine and chlorine) in aqueous medium and by oxidative desulfuration, paraoxon is formed [21–24] as shown in reaction Scheme 1. The induction period of the indicator reaction increases with increasing methyl parathion concentration. The increase in induction period affects the change in absorbance with time so the



Scheme 1. Inhibitory effect of methyl parathion.

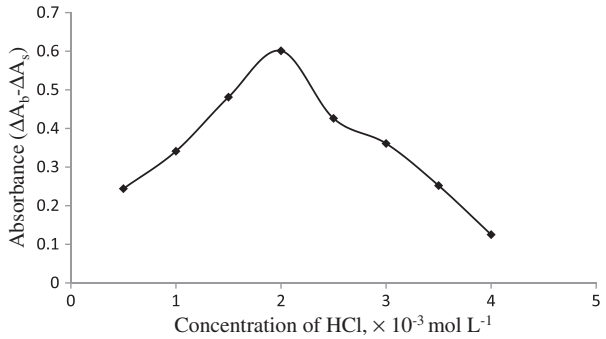


Fig. 1. Effect of HCl concentration on the sensitivity. Condition – methyl parathion: 0.2 μg mL^{-1}; neutral red: 7×10^{-3} mol L^{-1}; potassium bromate: 6×10^{-3} mol L^{-1}; temperature: 30 °C.

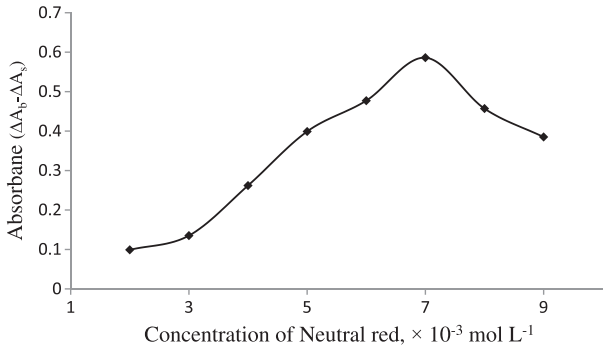


Fig. 3. Effect of neutral red concentration on the sensitivity. Condition – methyl parathion: 0.2 μg mL^{-1}; hydrochloric acid: 2 mol L^{-1}; potassium bromate: 6×10^{-3} mol L^{-1}; temperature: 30 °C.

calibration graph was plotted between the decrease in absorbance of the blank minus that of the sample ($\Delta A_{blank} - \Delta A_{sample}$) at a fixed time vs. methyl parathion concentration.

Effect of acid concentration

The effect of hydrochloric acid concentration on obtaining maximum sensitivity was investigated with 6×10^{-3} mol L^{-1} potassium bromate, and 7×10^{-3} mol L^{-1} neutral red at 30 °C (Fig. 1) over the range of 0.5–4 mol L^{-1}. In order to find the optimum concentration of hydrochloric acid, the absorbance changes for the blank reaction (the reaction in the absence of methyl parathion) at a fixed time of 5 min were measured as a function of HCl concentration. The results have been shown in Fig. 1. The difference between the change in absorbance for the blank and sample reaction shows a maximum at 2.0 mol L^{-1} HCl, therefore, a final concentration of 2.0 mol L^{-1} acid was selected as optimum.

Effect of potassium bromate concentration

The effect of potassium bromate concentration on the reaction rate was studied with 2.0 mol L^{-1} hydrochloric acid and 7.0×10^{-3} mol L^{-1} neutral red at 30 °C. Potassium bromate concentration in the range of 2×10^{-3} to 10×10^{-3} mol L^{-1} was investigated. An increase in bromate concentration causes a decrease in the induction period. It was also observed that the calibration range differed according to the concentration of bromate hence the concentration of bromate was selected on the basis of the rate of the reaction of bromate with HCl. As the rate of production of Cl_2 and Br_2 increases by increasing HCl and bromate concentration, this causes an increase in the rate of the reaction of Cl_2 and Br_2 with methyl parathion and therefore decreases the induction period. An increase in the production rate of Cl_2 and Br_2 also cause an increase in the rate of reaction with neutral red and therefore the slope of the absorbance changes after the initiation of the reaction. A good sensitivity was observed at final concentration of 6.0×10^{-3} mol L^{-1} (Fig. 2).

Effect of neutral red concentration

The influence of neutral red concentration on the sensitivity of the reaction was studied in the range of 2×10^{-3} to 10×10^{-3} mol L^{-1} with 6.0×10^{-3} mol L^{-1} potassium bromate and 2.0 mol L^{-1} hydrochloric acid at 30 °C. The results show that by increasing the neutral red concentration up to 7.0×10^{-3} mol L^{-1} the sensitivity increases, whereas a greater amount of reagent decreases sensitivity, thus 7.0×10^{-3} mol L^{-1} neutral red was selected for the study (Fig. 3).

Effect of temperature and time

The effect of temperature on the inhibitory reaction was studied in the range of 10–70 °C with the optimum of the reagent concentrations. The results showed that as the temperature increases up to 30 °C the sensitivity increases, whereas higher temperature value decreases the sensitivity ($\Delta A_{blank} - \Delta A_{sample}$). Therefore, 30 °C was selected for further study and 5.0 min time was suitable for the study of inhibitory reaction (Fig. 4).

Effect of foreign species

To evaluate the analytical applicability of the proposed method, the method was applied to determination of methyl parathion in

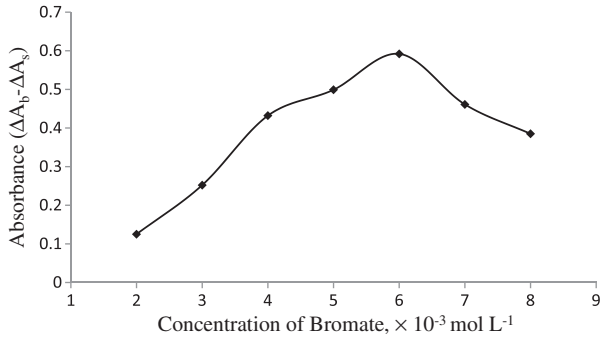


Fig. 2. Effect of bromate concentration on the sensitivity. Condition – methyl parathion: 0.2 μg mL^{-1}; hydrochloric acid: 2 mol L^{-1}; neutral red: 7×10^{-3} mol L^{-1}; temperature: 30 °C.

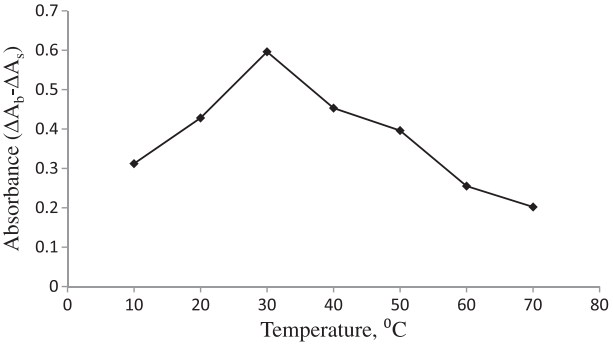


Fig. 4. Effect of temperature on the sensitivity. Condition – methyl parathion: 0.2 μg mL^{-1}; neutral red: 7×10^{-3} mol L^{-1}; hydrochloric acid: 2 mol L^{-1}; potassium bromate: 6×10^{-3} mol L^{-1}.

Table 2
Effect of diverse ions (concentration of methyl parathion 0.2 μg mL^{-1}).

Foreign species	Tolerance limit (μg mL^{-1})[a]
Pyrethroid pesticides, atrazine	400
Carbamate pesticides	250
Phorate	200
PO_4^{3-}, CH_3COO^-	100
Cr(VI)	50
K^+, Na^+, Ba^{2+}, Ca^{2+}, NH_4^+, Mg^{2+}, Mn^{2+}, Cu^{2+}, Cr^{3+}, Al^{3+}, Zn^{2+}, Co^{2+}, Cd^{+2}, Fe^{3+}, Pb^{2+}, As(V), NO^{3-}, SO_4^{2-}	20
Phenol	10
NO_2^-	5
SO_3^{2-}, Fe^{2+}, Mo(VI)	4
Chlorpyrifos, endosulfan malathion, dimethoate	1.5

[a] Tolerance limit causing ±2% variation in absorbance value.

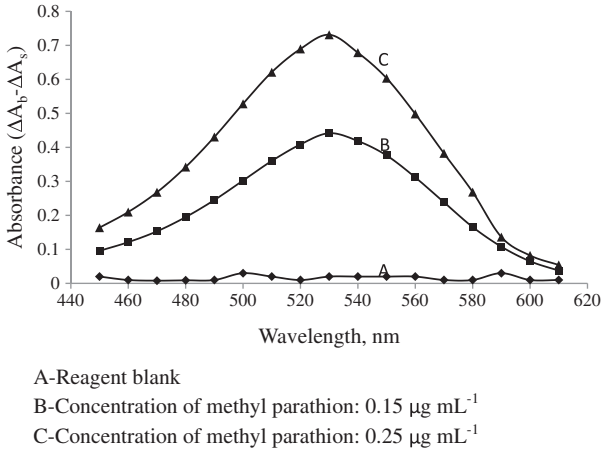


Fig. 5. Absorption spectra of the dye.

various samples. The influence of various ions, several organic and inorganic compounds and pesticides was examined under the optimum conditions with the developed method. The effect of various interferences on the determination of 0.2 μg mL^{-1} of methyl parathion concentration was studied. A variation of ±2% in the absorbance value was considered tolerable. The results are given in Table 2, it was found that sensitivity of the reaction was not affected by most of interferences.

Spectral characteristics and method validation

The absorption spectra of colored product showed a maximum absorbance at 530 nm (Fig. 5). The reagent blank had negligible absorbance at this wavelength. Beer's law was obeyed over the concentration range of 0.025–0.3 μg mL^{-1} (Fig. 6). The molar absorptivity and Sandell's sensitivity are given in Table 3. The slope, intercept, and the correlation coefficient were calculated by least squares regression analysis (Table 3). The detection limits (DL = 3.3 σ/S) and quantitation limits (QL = 10 σ/S) (where 'S' is the slope of the calibration curve and σ is the standard deviation of blank), SD of slope and intercept values calculated are given in Table 3.

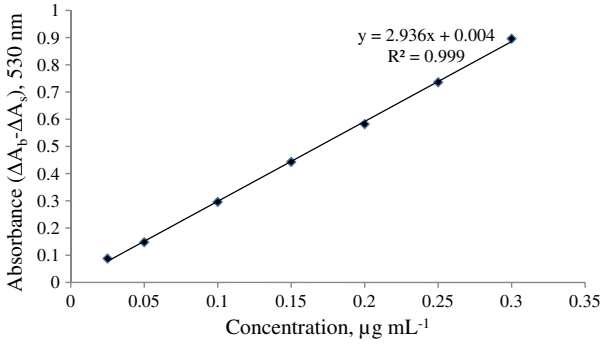


Fig. 6. Calibration data for the determination of methyl parathion.

Table 3
Spectral characteristics, precision and accuracy of the proposed method.

Parameters	Results
λ_{max} (nm)	530
Range of Beer's law (μg mL^{-1})	0.02–0.3
Molar absorptivity (L mol^{-1} cm^{-1})	6.5×10^5
Sandell's sensitivity (μg cm^{-2})	0.0004
Relative standard deviation (%)	
Intra-day	0.54–2.65
Inter-day	0.39–4.89
Limit of detection (μg mL^{-1})	0.009
Limit of quantification (μg mL^{-1})	0.028
SD of slope	0.047
SD of intercept	0.004
Regression equation ($Y = bx^a + a$)	
Slope (b)	2.94
Intercept (a)	0.005
Correlation coefficient	0.999

[a] Concentration in μg mL^{-1}.

To check the precision of the method three different concentrations of methyl parathion (within the working limits) were analyzed in seven replicates during the same day (intra-day precision) and seven consecutive days (inter-day precision). The RSD (%) values range of intra-day and inter-day studies showed that the precision was good for the method (Table 3).

Determination of kinetic parameters

The reaction rate of bromate with hydrochloric acid in the presence of methyl parathion was determined at four different temperatures. A plot of ln *K versus 1/T* gives a straight line, from which the energy of activation $\Delta E^{\neq}$ was calculated according to the Arrhenius equation:

$$K = A \cdot e^{-\Delta E^{\neq}/RT}$$

where K is the reaction rate constant and R is the gas constant. The other thermodynamic parameters were calculated at 30 °C. The enthalpy of activation ($\Delta H^{\neq}$) was calculated using the relation:

$$\Delta E^{\neq} = \Delta H^{\neq} + RT$$

The entropy of activation ($\Delta S^{\neq}$) was obtained from the equation:

$$A = KT/h \cdot e^{(R+\Delta S^{\neq}/R)}$$

where K and h are rate constant and Planck's constant, respectively.

The free energy of activation ($\Delta G^{\neq}$) was calculated according to equation:

Table 4
Kinetic parameters for the decolorization of neutral-red at 30 °C.

A (s^{-1})	$\Delta E^{\neq}$ (kJ/mol)	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (J/mol K)	$\Delta G^{\neq}$ (kJ/mol)
1.15×10^5	38.10	35.59	−628.05	225.88

Table 5
Application of the method for determination of methyl parathion in real samples.

Sample	Methyl parathion found (μg)[a]		
	Proposed method	Reported method [17]	GC–MS method [25]
Agricultural waste water[b]			
A	4.14 (0.029)	3.95 (0.039)	4.57 (0.011)
B	3.58 (0.064)	3.19 (0.041)	3.81 (0.009)
Vegetable samples[c]			
Cauliflower	3.09 (0.019)	2.96 (0.032)	3.33 (0.016)
Tomato	4.21 (0.039)	3.99 (0.061)	4.71 (0.018)
Spinach	3.98 (0.026)	3.88 (0.061)	4.06 (0.021)

[a] Mean ± standard deviation ($n = 5$).
[b] Volume of sample, 5 mL (from field where methyl parathion has been sprayed).
[c] Amount of sample, 10 g (from field where methyl parathion has been sprayed).

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$$

The results are given in Table 4.

Applications

Determination of methyl parathion in waste water samples

Water samples were collected from nearby runoff agricultural field where methyl parathion was sprayed as a pesticide. Water was filtered through a Whatman no. 40 filter paper and the aliquot of the filtrate was analyzed as described above. Results were compared with reported spectrophotometric [17] and GC–MS method [25] (Table 5).

Determination of methyl parathion in vegetable samples

Various samples of foliages and fruits were collected from agricultural field where methyl parathion was sprayed. The samples were weighed, macerated with ethanol and deionised water (1:1) and then filtered through a thin cotton cloth. The filtrate was centrifuged at 1850*g* for 10 min. The filtrate which was greenish yellow due to the presence of organic matter from plant was passed through a silica gel column (10×1 cm) to remove chlorophyll and other interfering materials. The column was washed with 10 mL ethanol. Washings were collected and analyzed as recommended above by the proposed method. Results were compared with reported spectrophotometric [17] and GC–MS method [25] (Table 5).

Conclusion

Although many sophisticated techniques; GC, HPLC, voltametry, etc. are available but the factors such as the low cost of the instrument, ease of handling, and almost no maintenance have caused spectrophotometry to remain a popular and inevitable technique, particularly in the laboratories of developing countries. Most of the spectrophotometric methods reported for the determination of methyl parathion suffer from drawbacks including reagent cost, instability of color, interference, low sensitivity and selectivity. The proposed spectrophotometric method is based on a new kinetic approach which is more sensitive, simple and selective as compared with reported spectrophotometric methods. The easy availability of the reagent and freedom from a large group of interfering species are some advantages of the method. As the method is based on the kinetic study it can be further applied for simultaneous determination of different organophosphorus pesticides by partial least square method.

Acknowledgment

The authors are thankful to Government V.Y.T. PG Autonomous College, Drug for laboratory facilities.

References

[1] G.M. Castanho, C.M.P. Vaz, S.A.S. Machado, J. Braz. Chem. Soc. 14 (2003) 594–600.
[2] D. De Souza, S.A.S. Machado, Electroanalysis 18 (2006) 862–872.
[3] Compendio de Defensivos Agricolas, fifth ed., Organizacao Andrei Editora Ltda, Sao Paulo, 1996.
[4] A. Mulchandani, W. Chen, P. Mulchandani, J. Wang, K.R. Rogers, Biosens. Bioelectron. 16 (2001) 225–230.
[5] P.F. McInnes, D.E. Anderson, D.J. Hoff, M.J. Hooper, L.L. Kinkel, Environ. Toxicol. Chem. 15 (1996) 544–552.
[6] P. Mulchandani, C.M. Hangarter, Y. Lei, W. Chen, A. Mulchandani, Biosens. Bioelectron. 21 (2003) 523–527.
[7] M. Filho, F.N. Santos, P.A.P. Pereira, Talanta 81 (2010) 346–354.
[8] M. Filho, F.N. Santos, P.A.P. Pereira, Microchem. J. 96 (2010) 139–145.
[9] F.M. Rodrigues, P.R.R. Mesquita, L.S. Oliveira, F.S. Oliveira, A.M. Filho, P.A. Pereira, J.B. Andrade, Microchem. J. 98 (2011) 56–61.
[10] L.J. Qu, H. Zhang, J.H. Zhu, G.S. Yang, H.Y. Aboul-Enein, Food Chem. 122 (2010) 327–332.
[11] G. Wu, X. Bao, S. Zhao, J. Wu, A. Han, Q. Ye, Food Chem. 126 (2011) 646–654.
[12] Y. Wang, R. Du, Forensic Sci. Int. 198 (2010) 70–73.
[13] C. Wu, N. Liu, Q. Wu, C. Wang, Z. Wang, Anal. Chim. Acta 679 (2010) 56–62.
[14] C. Li, Z. Wang, G. Zhana, Colloids Surf. B 82 (2011) 40–45.
[15] H. Parham, N. Rahbar, J. Hazard. Mater. 177 (2010) 1077–1084.
[16] X. Tan, B. Li, K.Y. Liew, C. Li, Biosens. Bioelectron. 26 (2010) 868–871.
[17] S. Sunita, V.K. Gupta, J. Ind. Chem. Soc. 65 (1987) 114–117.
[18] Z.M. Getenga, J.I.O. Jandiiko, S.O. Wandigo, E. Beck, Bull. Environ. Contam. Toxicol. 64 (2000) 359–369.
[19] J. Raju, V.K. Gupta, Microchem. J. 39 (1989) 166–171.
[20] P. Shivhare, J. Raju, V.K. Gupta, Microchem. J. 42 (1990) 283–287.
[21] Q. Zhang, S.O. Pehkonen, J. Agric. Food Chem. 47 (1999) 1760–1766.
[22] Y. Magara, T. Aizawa, N. Matumoto, F. Souna, Water Sci. Technol. 30 (1994) 119–128.
[23] J.G. Wu, D.A. Laird, Environ. Toxicol. Chem. 22 (2003) 261–264.
[24] H.S. Lee, Y.A. Kim, Y.A. Cho, Y.T. Lee, Chemosphere 46 (2002) 571–576.
[25] A. Aguera, L. Piedra, M.D. Hernando, A.R. Fernandez-Alba, M. Contreras, Analyst 125 (2000) 1397–1402.