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A novel and sensitive kinetic method for the determination of malathion using chromogenic reagent

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ABSTRACT

A novel and sensitive kinetic spectrophotometric method for the determination of malathion has been developed. The method is based on the oxidation of malathion with slight excess of N-bromosuccinimide (NBS) at 30 °C where unconsumed NBS was monitored with safranine dye spectrophotometerically at λ_{max} 530 nm using fixed time procedure after 10 min of the reaction. The oxidized product was characterized as malaoxon by Fourier transformation infrared (FTIR) spectroscopy. Beer's law was obeyed in the concentration range of 0.025–0.25 μg mL^{-1}. Important analytical parameters such as time, temperature, reagents concentration, and acidity have been optimized for the reaction. Sandell's sensitivity and molar absorptivity for the reaction system were found to be 0.0003 μg cm^{-2} and 9.6×10^5 L mol^{-1} cm^{-1} respectively. The proposed method was successfully applied for the determination of malathion in different samples with satisfactory results. The results were compared with those obtained by GC–MS methods.

1. Introduction

Pesticides have played a major role in the improvement of agricultural production and in the control of many disease vectors in the area of public health. Pesticides are very much applied to reduce crop losses and to increase the production of crops such as corn, maize, vegetables, potatoes, and cotton. The use of pesticides increased worldwide many folds from the 1960s [1,2]. However, their harmful effects on environmental quality and human health have been observed and have become a prominent issue as a matter of great concern at local, regional, national and global levels [1,3]. The residues of pesticides retained in the crops through soil and water, enter the food chain and are consumed by human through foodstuffs and drinking water [3–5]. These retained pesticides also contribute to biodiversity losses and deterioration of natural habitats [6]. Therefore many researches relating to detection and determination of pesticides retention in soil, sediment, plant, vegetable, grain and water samples have regularly been carried out [7–19].

Organophosphorus pesticides (OPPs) are a class of chemicals i.e. organic esters of phosphoric acid, thiophosphoric acid and other phosphoric acids. Due to their high insecticidal activity, OPPs have widely been used in agriculture as insecticides and acaricides as the replacement for persistent organochlorinated pesticides [20–23]. However, they are toxic organic chemicals, which can irreversibly inhibit acetylcholinesterase that is essential for the function of the central nervous system [24,25].

Malathion i.e. di-ethyl2-[(dimethoxyphosphorothioyl)sulfanyl] butanedioate (Structure 1) is commonly referred to as OPP, is used as insecticides for insect control on fruits and vegetables. As malathion is being used in an outdoor environment, it easily enters in residential homes. However, studies by the United States Environmental Protection Agency (USEPA) have estimated that the exposure by this way is lesser than that of the toxic dose of malathion [8]. It is often recommended to keep windows closed and air conditioners turned off while spraying for pest control is carried out to minimize the entry of malathion into the closed environment like residential homes [2]. Malathion was first registered for use in the United States of America in 1956 by the United States Department of Agriculture (USDA), and it is now regulated by USEPA [18]. It is a non-systemic wide-spectrum organophosphate insecticide and one of the earliest organophosphate insecticides. It is used for the control of sucking and chewing insects on fruits and vegetables, and also to control mosquitoes, flies, household insects, animal parasites, etc. [18]. However, the pesticide, malathion, residue is a potentially serious hazard to human health, and thus its detection and control play an important role in minimizing risk to human [26,27].

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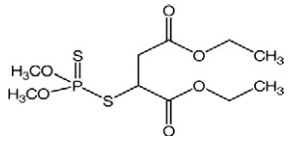


Structure 1. Chemical structure of malathion.

In the last few years many methods have been developed for the determination of various OPPs. The most widely used methods for its detection and determination are: gas chromatography (GC) [28–30], high-performance liquid chromatography (HPLC) [31,32], gas chromatography–mass spectrometry (GC–MS) [33], immune assay and fluorescence [34,35], chemiluminescence [36–38], electron-capture detector (ECD) [39], supercritical fluid extraction (SFE) and microwave solvent extraction (MSE) [40]. These methods are accurate and selective, but they require relatively expensive instrumentation and highly skilled technicians. Therefore, the development of inexpensive and sensitive method for the determination of malathion is still desirable.

We have been interested in developing analytical methods for various analytes of environmental, biological and medicinal interests [41–53]. The search for a selective, rapid, accurate and economic method for the determination of toxic malathion led us to an investigation of its oxidation by N-bromosuccinimide (NBS). To the best of our knowledge no studies on analytical method have been reported on the determination of malathion based on its oxidation with NBS. Therefore, in continuation of our interest in developing analytical methods, the present method is based on the oxidation of malathion with slight excess of NBS where unconsumed NBS was monitored with safranine dye spectrophotometerically at λ_{max} 530 nm using fixed time procedure after 10 min of the reaction. The oxidized product of malathion was also characterized by Fourier transformation infrared (FTIR) spectroscopy. The proposed method is simple and inexpensive and was applied for the determination of malathion in vegetable and water samples with satisfactory results. The results obtained by the proposed method were also compared with those obtained by GC–MS methods.

2. Experimental

2.1. Reagents

All reagents used were of analytical grade and all the solutions were prepared in distilled deionized water. The stock solution of malathion (Northern Minerals Ltd., India) was prepared by dissolving 100 mg of insecticide (technical forms and formulations) in minimum amount of glacial acetic acid (E. Merck, Mumbai, India) and diluted to 100 mL with distilled deionized water. Working standards were prepared by appropriate dilution. N-bromosuccinimide (E. Merck, Mumbai, India) 5×10^{-2} mol L^{-1}, safranine (E. Merck, Mumbai, India) 1×10^{-2} mol L^{-1} and hydrochloric acid (E. Merck, Mumbai, India) 2 mol L^{-1} were also prepared in distilled deionized water.

Table 1
Determination of malathion in pesticide free vegetable samples under the conditions: HCl (2.0 mol L^{-1}), NBS (5×10^{-2} mol L^{-1}), safranine (1×10^{-2} mol L^{-1}) and malathion (1 μg mL^{-1}) at 30 °C.

Samples[a]	Amt. added (μg)	Amt. found (μg)[b]	Recovery (%)
Cauliflower	30.0	28.55	95.16
	50.0	48.67	97.34
	70.0	69.21	98.87
Cabbage	30.0	29.10	97.00
	50.0	49.32	98.64
	70.0	68.93	98.47
Spinach	30.0	28.83	96.10
	50.0	48.88	97.76
	70.0	69.01	98.58

[a] Amount of sample: 25 g.
[b] Mean of three replicate analysis.

2.2. Apparatus

A Systronics spectrophotometer 166 with 1 cm quartz cuvette was used for absorbance and spectral measurements. PerkinElmer Spectrum RX-I FTIR and GC–MS (JEOL-JMS, Mate-MS system at Bose Institute, Centenary Campus, Kankurgachi, Kolkata) were used in spectrum and data comparison. A thermostatic water bath model MSW-273 (MAC Macro Scientific Works Pvt. Ltd., India) was used to control the temperature of the reaction system. The pH measurements were made with Systronics digital pH meter model 335.

2.3. Procedure

2.3.1. Preparation of calibration curve

Aliquots of standard solution containing 0.025–0.25 μg mL^{-1} of malathion were transferred into a series of 10 mL calibrated flasks, to which 1 mL of NBS and 2 mL of 2 mol L^{-1} HCl solution were added in sequence. The solution was mixed and kept for 10 min at 30 °C with occasional shaking followed by the addition of 1 mL of safranine solution and mixed thoroughly. A blank without pesticide was prepared in the similar manner. The absorbance was measured at 530 nm against the reagent blank using fixed time procedure after 10 min of the reaction. The decrease in absorbance of dye i.e. safranine corresponding to the consumed oxidant reflected the malathion concentration. The calibration curve was prepared by plotting the decrease in absorbance of safranine against concentration of the malathion.

2.3.2. Determination of malathion pesticide spiked samples

To check the recoveries of malathion pesticide, vegetable samples free from malathion pesticides, were taken and fortified with a known amount of the malathion pesticide and kept for 24 h. The vegetable samples were then washed with ethanol. Twenty different percentage proportions of ethanol were tested for the extraction of malathion. The extraction was not completed as long as alcohol was less than 85% but above 85% alcohol, no change in malathion concentration was observed. Thus 85% of ethanol was used for the best extraction recovery results. The washings from different samples were collected and evaporated to dryness and residue was dissolved in 0.1% acetic acid. Aliquots of these washings were used for the determination of malathion pesticide by the proposed method. The recovery results have been summarized in Table 1. The proposed method was successfully applied for the determination of malathion in vegetable samples.

3. Results and discussion

As shown in reaction Scheme 1, malathion reacts with N-bromosuccinimide in the presence of acidic medium to form malaoxon (oxidized form of malathion). Thus the malathion was reacted with excess NBS and the unconsumed NBS was then determined by decrease in color intensity of safranine i.e. by measuring absorbance at 530 nm.

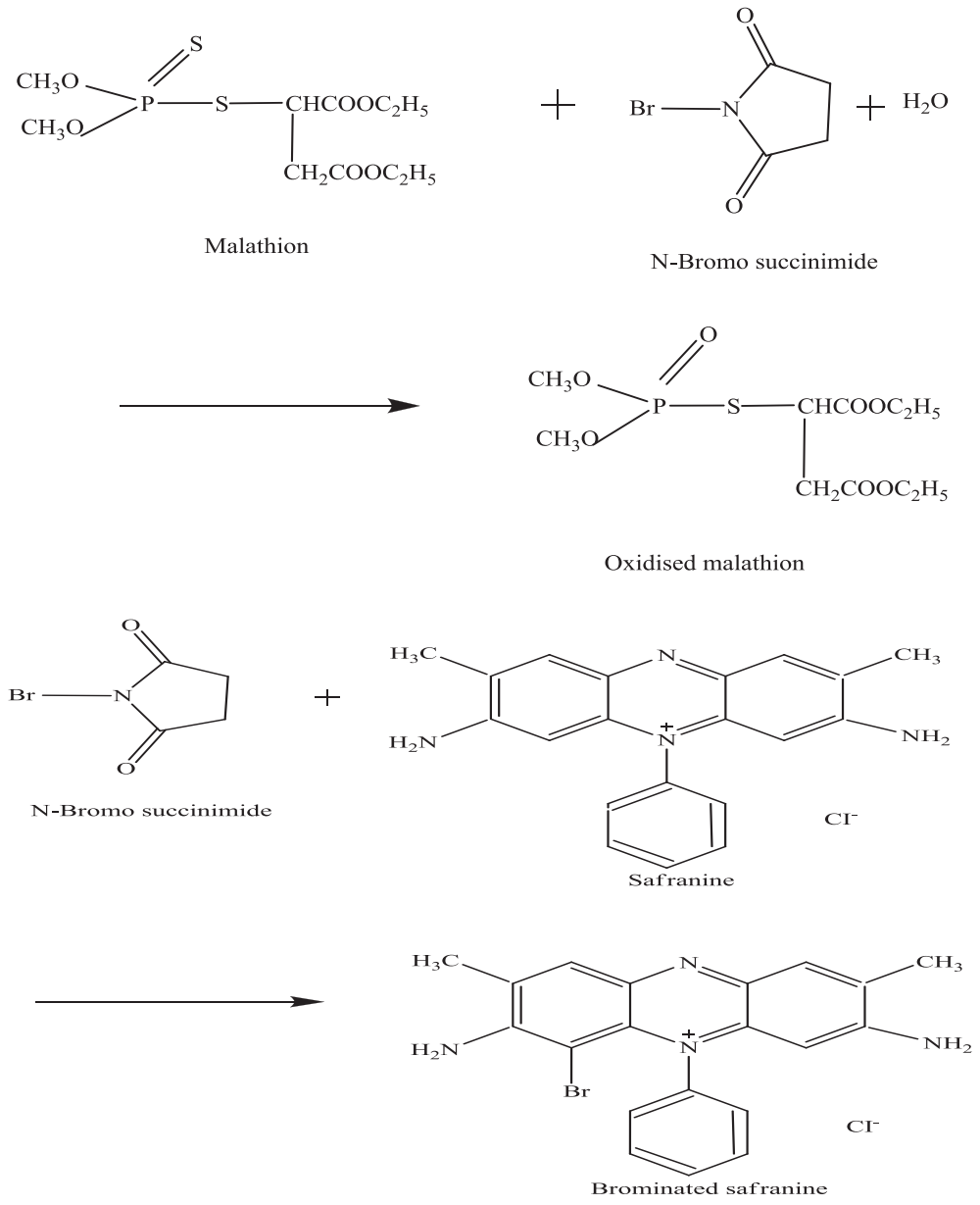
3.1. FTIR characterization of the oxidized product of malathion

The chemical bonds in malathion are potentially reactive under different suitable reaction conditions giving different products. Thus, various possible pathways have been shown resulting in sulfur–carbon bond cleavage proceeding through an elimination reaction that gives O, O-dimethyl phosphorodithioic acid and diethyl fumarate [54]. Diethyl thiomalate and O,O-dimethyl phosphorothionic acid are obtained due to phosphorus–sulfur bond cleavage by water or hydroxide, which would be in equilibrium with its tautomer, O,O-dimethyl

phosphorothiolic acid [54]. It has also been reported that carboxyl ester hydrolysis gives two possible products, malathion α- and β-monoacids [55]. Another potential reaction under suitable conditions would be the oxidation of the sulfur–phosphorus double bond to give malaoxon and is shown in Scheme 1 (first reaction) [56]. The detection of the oxidized product (malaoxon) was performed by its FTIR. The FTIR spectrum of malathion was recorded in 450–4000 cm^{-1} region and is shown in Fig. 1. The bands located at 3436 cm^{-1}, 1730 cm^{-1}, and 1030 cm^{-1} are the most intense ones. The signal at 3436 cm^{-1} is due to the stretching of O–H bond (hydroxyl group). The absorption around 2350 cm^{-1} and 2062 cm^{-1} is due to the CH_3 group and stretching of S–H bond respectively. Absorption at 1730 cm^{-1} is due to the stretching of carbonyl of the ester group and at 1637 cm^{-1} is due to C=C group. The absorptions around 1453 cm^{-1} and 1365 cm^{-1} are due to the various vibrational modes of $-CH_2$ and $-CH_3$ groups. The intense band at 1030 cm^{-1} is due to stretching of $P-OCH_3$ group and at 690 cm^{-1} is due to P–S bond. The oxidation of malathion was confirmed by measuring the decrease in the intensity of these bands.

3.2. Spectral characteristics and method validation

The maximum absorption (λ_{max}) of safranine was found to be at 530 nm against deionized water (Fig. 2). As shown in Fig. 3, Beer's law was obeyed over the malathion concentration range of 0.025 to 0.25 μg mL^{-1}. The molar absorptivity and Sandell's sensitivity were found to be 9.6×10^5 L mol^{-1} cm^{-1} and 0.0003 μg cm^{-2}, respectively where stability of safranine color was 24 h. The coefficient of determination (R^2) evaluated by least square regression analysis was found to be 0.999 (Fig. 3). To check the precision of the method, three different concentrations of malathion (within the calibration limits) were analyzed in five replicates during the same day (intra-day precision) and five consecutive days (inter-day precision). The relative standard deviation values of



Scheme 1. Reaction of malathion with N-bromosuccinimide and reaction of NBS with safranine.

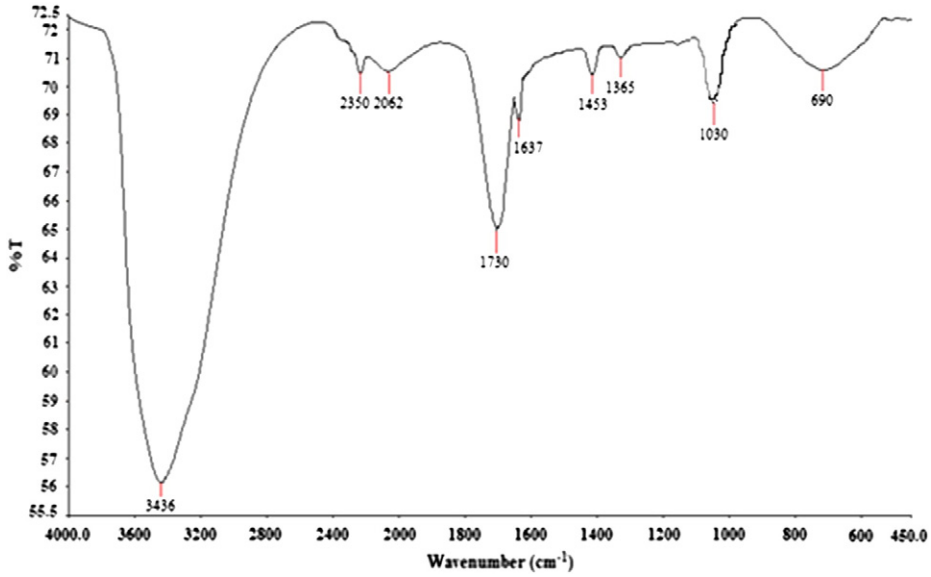


Fig. 1. FTIR spectrum of malathion pesticide.

intra-day (0.61–2.40%) and inter-day (0.48–1.04%) studies showed that the precision of the proposed method was very good.

3.3. Effect of acid concentration

The effects of various acids of same concentration such as hydrochloric acid, sulfuric acid, acetic acid, and nitric acid were studied. The hydrochloric acid was found to be the most suited for the oxidation of malathion by NBS. Thus the effect of [HCl] on obtaining maximum sensitivity was investigated with 5×10^{-2} mol L^{-1} NBS and 1×10^{-2} mol L^{-1} safranine for reaction at 30 °C and is shown in Fig. 4. The results showed that 2.0 mL of 2.0 mol L^{-1} hydrochloric acid gave the best result in the determination of malathion. Thus 2.0 mL of 2.0 mol L^{-1} hydrochloric acid was selected for further study in the determination of malathion.

3.4. Effect of N-bromosuccinimide concentration

The effect of NBS concentration on the oxidation of malathion was investigated with 2.0 mol L^{-1} hydrochloric acid and 1×10^{-2} mol L^{-1} safranine at 30 °C. The effect of [NBS] was studied by varying [NBS] in the range 1.0×10^{-2} to 7.0×10^{-2} mol L^{-1} and the results obtained are shown in Fig. 5. According to the results, 5.0×10^{-2} mol L^{-1} NBS concentration was required for complete oxidation of malathion and thus selected for further study.

3.5. Effect of safranine concentration

The effect of safranine concentration was investigated in the range 1.0×10^{-1} to 5.0×10^{-2} mol L^{-1}. This study was conducted in the presence of 2.0 mol L^{-1} HCl and 5.0×10^{-2} mol L^{-1} NBS at 30 °C and the results are shown in Fig. 6 where a decrease in absorbance was observed with an increase in [safranine]. This may be due to the aggregation of the dye at higher concentration. According to the results, 1.0×10^{-2} mol L^{-1} safranine concentration was selected throughout the study.

3.6. Effects of temperature, time and pH

The effect of temperature on the reaction was studied by varying in the range of 10 to 50 °C under the optimized reagent's concentrations. As shown in Fig. 7, temperature range of 25–50 °C had no pronounced effect on the oxidation reaction so the temperature 30 °C was selected and maintained throughout the study. It was also found that 10 min was required for the complete oxidation of malathion as no change in

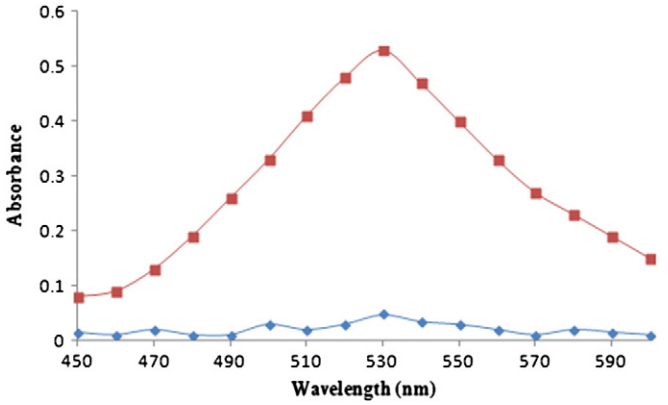


Fig. 2. Absorption spectrum of reagent blank (no peak) and spectrum of the reaction system containing HCl (2.0 mol L^{-1}), NBS (5×10^{-2} mol L^{-1}), safranine (1×10^{-2} mol L^{-1}), and malathion (1 μg mL^{-1}) at 30 °C.

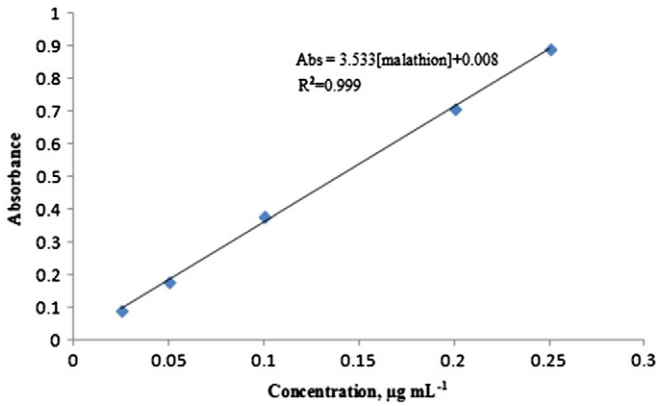


Fig. 3. Calibration data for the determination of malathion, under the conditions: HCl (2.0 mol L^{-1}), NBS (5×10^{-2} mol L^{-1}), safranine (1×10^{-2} mol L^{-1}), and malathion (1 μg mL^{-1}) at 30 °C.

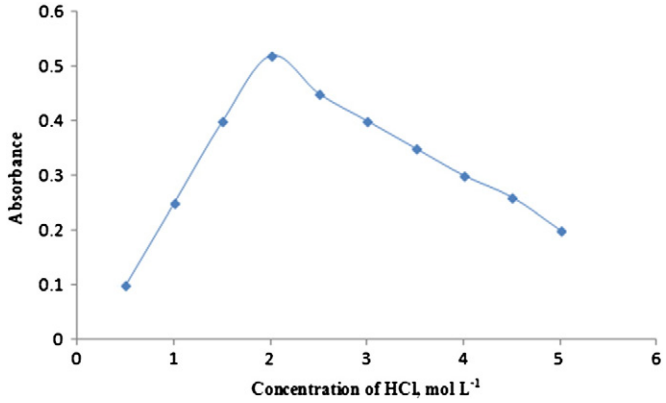


Fig. 4. Effect of HCl concentration under the conditions: NBS (5×10^{-2} mol L^{-1}), safranine (1×10^{-2} mol L^{-1}), and malathion (1 μg mL^{-1}) at 30 °C.

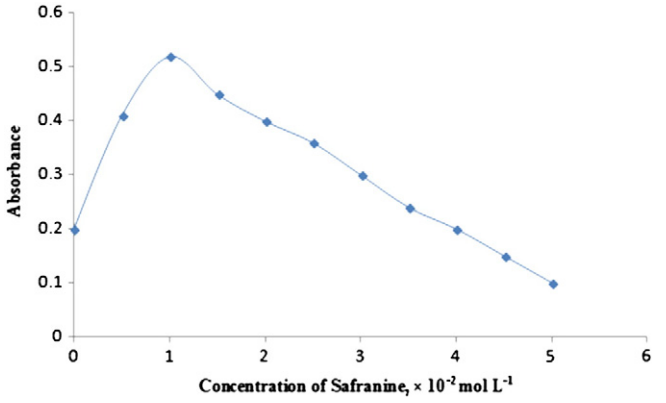


Fig. 6. Effect of safranine concentration under the conditions: HCl (2.0 mol L^{-1}), NBS (5×10^{-2} mol L^{-1}), and malathion (1 μg mL^{-1}) at 30 °C.

absorbance was observed after 10 min. The effect of pH is shown in Fig. 8 which clearly shows the highest absorbance change at pH ~3.0–3.5. Thus under the optimum conditions, the absorbance was measured at pH 3.0–3.5.

3.7. Effect of foreign species

In order to evaluate the analytical applicability of the proposed method, the influences of various ions, several organic and inorganic compounds and pesticides were also examined under the optimum conditions by the proposed method. The effect of expected interfering species was studied on the determination of 0.1 μg mL^{-1} malathion in the reaction mixture. A variation of ±2% in the absorbance value was considered tolerable. The results with tolerance limits of various expected interfering species are shown in Table 2. It was found that sensitivity of the determination based on proposed reaction system was not affected by most of the interfering species.

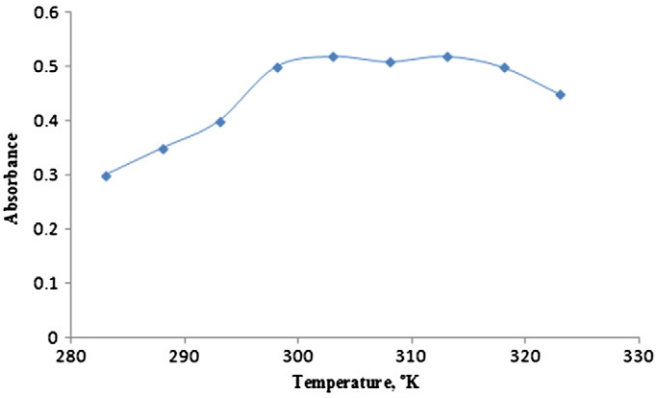


Fig. 7. Effect of temperature on the sensitivity of the reaction system under the conditions: HCl (2.0 mol L^{-1}), NBS (5×10^{-2} mol L^{-1}), safranine (1×10^{-2} mol L^{-1}), and malathion (1 μg mL^{-1}) at 30 °C.

4. Applications

To evaluate the applicability of the proposed method to the real samples, malathion was determined in various vegetable and water samples.

4.1. Determination of malathion in vegetable samples

Various vegetable samples were collected from treated agricultural field i.e. where malathion was sprayed. The malathion was estimated in random sampling. The samples were weighed, macerated with ethanol and deionized water (1:1) and then filtered through a thin cotton cloth. The filtrate was centrifuged at 1850 *g* for 15 min. Due to the presence of organic matter in the plants, the greenish yellow filtrate was passed through a silica gel column 1 × 10 cm (diameter × length) to remove chlorophyll and other interfering materials. The column was eluted with 10 mL ethanol. Washings were collected and analyzed for malathion concentration by the proposed method. The results were compared with reported GC–MS method [57] and are reported in Table 3.

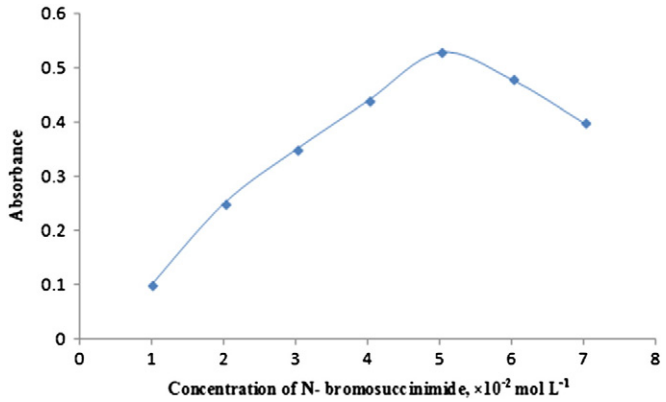


Fig. 5. Effect of N-bromosuccinimide concentration under the conditions: HCl (2.0 mol L^{-1}), safranine (1×10^{-2} mol L^{-1}), and malathion (1 μg mL^{-1}) at 30 °C.

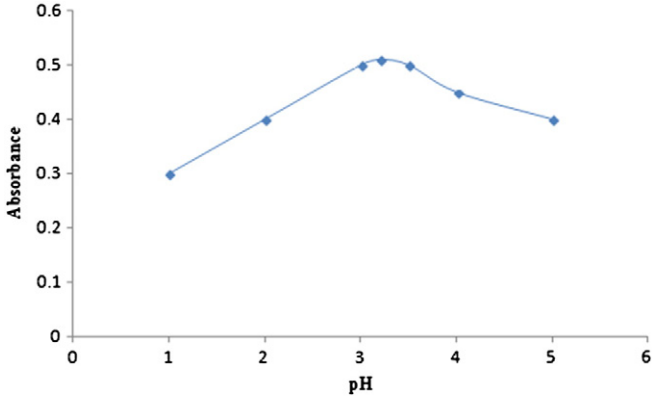


Fig. 8. Effect of pH on the reaction system under the conditions: HCl (2.0 mol L^{-1}), NBS (5×10^{-2} mol L^{-1}), safranine (1×10^{-2} mol L^{-1}), and malathion (1 μg mL^{-1}) at 30 °C.

Table 2
Effect of foreign species on the determination of malathion pesticides (0.1 μg mL^{-1}) under the reaction conditions given in Table 1.

Foreign species	Tolerance limit (μg mL^{-1})[a]
SO_4^-, CO_3^-, CH_3COO^-, benzene	1000
Fe^{2+}	580
Se^{4+}	500
Aniline	250
Cr^{3+}	200
Zn^{2+}[b]	100
Dithiocarbamate pesticides	40
Carbamate pesticides	15
Br^-[c], I^-[c]	10
Phenol	8

[a] Causing (±) 2% error in absorbance value,
[b] Masked with 0.1% EDTA solution,
[c] Removed by the addition of nitric acid as well as boiling the solution.

Table 3
Application of the method for the determination of malathion (μg)[a] in real samples under the reaction conditions given in Table 1.

Samples	Proposed method	GC–MS method [57]
Cauliflower[b]	4.67 ± 0.02	4.98 ± 0.03
Cabbage[b]	3.87 ± 0.02	4.00 ± 0.02
Spinach[b]	4.23 ± 0.03	4.66 ± 0.06
Agricultural waste water A[c]	4.56 ± 0.01	5.00 ± 0.02
Agricultural waste water B[c]	3.34 ± 0.06	3.73 ± 0.03

[a] Mean ± standard deviation of five replicated.
[b] Amount of vegetable sample, 10 g from field where malathion was sprayed.
[c] Volume of water sample, 5 mL from field where malathion was sprayed.

4.2. Determination of malathion in water samples

Two water samples were collected from the agricultural field where malathion was used as a pesticide. Water was filtered through a Whatman filter paper no. 40. The filter paper was washed repeatedly with deionized distilled water collecting filtrate. The collected aliquot of the filtrate was analyzed by proposed procedure as described in Section 4.1. Results were compared with GC–MS method [57] and are given in Table 3.

5. Conclusion

The oxidation efficiency of NBS in aqueous solution has shown that the selective oxidation of malathion to malaoxon can be achieved based on which a reliable and rapid method for the determination of malathion has been proposed. The method was found to be more sensitive, simple and selective as compared with literature reported spectrophotometric methods for the determination of malathion pesticides [2,21,58–61] (Table 4). The less time consumption, rapidity, stability and easy availability of the reagent and freedom from a large group of interfering species are some distinct advantages of the proposed method Table 4. The proposed method was applied for the determination of malathion in various vegetable and water samples with satisfactory results. The results were compared with those obtained by GC–MS methods (Table 3).

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Table 4
Comparison of the proposed method with other spectrophotometric methods for the determination of malathion.

Reagents	Medium	λ_{max}	Beer's law range (ppm)	Remarks	[Ref]
Ammonium metavanadate	Acidic/alkaline	760	11.00	Less sensitive	[2]
Ammonium molybdate/methylene blue	Acidic	640	0.02–0.16	Extractive, required more solvent	[21]
Rhodamine B	Acidic	558	0.1–1.00	Zn^{2+}, Cu^{2+}, Mn^{2+}, Cd^{2+}, Ni^{2+}, phenol had interference	[58]
Chromotrope 2R/rhodamine 6G/amaranth	Acidic	528 525 520	0.1–4.20	Costly reagents used	[59]
Guaiacol	Acidic/alkaline	470	0.6–8.00	Time consuming	[60]
Malonyl dihydrazide	Acidic	820 780	0.45–3.20	Extractive, interfere with ions	[61]
NBS and safranine	Acidic	530	0.025–0.25	Oxidized product was characterized by FTIR. More sensitive, selective and free from interference of Cr^{3+}, Br^- and pesticides	Present method

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