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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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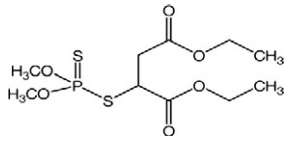

Structure 1. Chemical structure of malathion.

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