Spectrophotometric Determination of Malathion in Environmental Samples

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Abstract: A simple, rapid, sensitive, and precise spectrophotometric method for the determination of Malathion is described. The method is based on the decomposition of Malathion in the presence of alcoholic KOH. Dimethyldithiophosphate produced is made to react with Ammonium meta vanadate in Nitric acid with the formation of blue color. Acid degradation of too slow to be important under environmental reaction conditions. However, alkaline degradation is too fast to be a pathway in environmental condition. The products of alkaline degradation are temperature dependant. The absorbance maximum was observed at 760 nm. The Beers law is obeyed up to 11 ppm. Interference study was carried for other pesticides.

Keywords: Spectrophotometry, Malathion, Ammonium meta vanadate.

Introduction

The use of pesticides helped to significantly reduce crop losses and to improve the yield of crops such as corn, maize, vegetables, potatoes, and cotton. Worldwide the use of pesticides increased tremendously since the 1960s. Notwithstanding the beneficial effects of pesticides, their adverse effects on environmental quality and human health have been well documented worldwide and constitute a major issue that gives rise to concerns at local, regional, national, and global scales. Residues of pesticides contaminate soils and water, persist in the crops, enter the food chain and finally are ingested by humans with foodstuffs and water. Furthermore, pesticides can be held responsible for contributing to biodiversity losses and deterioration of natural habitats.

Malathion (*S*-1,2-bis(ethoxycarbonyl)ethyl-*O,O*-dimethyl-phosphorodithioate) is a widely used organophosphorus pesticide for the control of household and poultry pests, pests in vegetables, field crops, fruits, nuts, tea, coconut, cashew nuts, stored grains, and domestic animals.

Figure 1. Structure of malathion.

It has been the subject of many studies relating to its persistence and fate in soil, plants, and grains¹. A possible concern is that malathion being used in an outdoor environment, could enter a house or other building; however, studies by the EPA have conservatively estimated that possible exposure by this route is well below the toxic dose of malathion. Regardless of this fact, in jurisdictions which spray malathion for pest control, it is often recommended to keep windows closed and air conditioners turned off while spraying is taking place, in an attempt to minimize entry of malathion into the closed environment of residential homes. This pesticide can be determined by different methods.

Many procedures are reported in literature for determining Malathion in pure or formulated methods such as colorimetry²⁻⁶, Gas chromatography⁷⁻⁹, Infrared spectrophotometry¹⁰, and mass spectrometry¹¹ have been used. For example, it can be hydrolyzed quantitatively in alkaline media to dimethyldithiophosphate (DMDTP) which in the presence of Cu(II), Bi(III), and Mo(IV) or Methylene Blue forms complexes that can be extracted in organic solvents and measured spectrophotometrically¹²⁻¹⁵. To enhance the sensitivity, the DMDTP has been extracted with Rhodamine 6G as an ion pair into toluene and measured fluorometrically.¹⁶ Atomic absorption spectrometry has also been used for the indirect determination of malathion by formation and later extraction of the palladium chloride–malathion complex¹⁷. An environmentally friendly methodology has been developed for quality control analysis of emulsifiable concentrate pesticide formulations containing Malathion as active ingredient, using flow injection analysis (FIA)–Fourier transform infrared (FTIR) spectrometry¹⁸.

The spectrophotometric method developed by NORRIS *et al.*¹⁹ for the determination of malathion has been extensively employed and has been recommended as suitable for malathion residue analysis by the Malathion Panel, set up jointly by the Scientific Sub-Committee of the Inter –Departmental Advisory Committee on Poisonous Substances LUsed in Agriculture 2nd Food Storage, the Analytical methods committee of the Society or Analytical Chemistry and Association of British Manufacturers of Agricultural Chemicals²⁰.

In addition, it is the recommended method of the US Association of official Analytical Chemists²¹. Reddy *et al.*²² determined malathion by using gentian violet. Ayman²³ described a method based on oxidation of malathion with a slight excess of N-bromosuccinamide and determined the unreacted with amaranth dye. Due to its wide use and toxicity, several, spectrophotometric methods²⁴. Most spectrophotometric procedures involve the determination of organophosphorus insecticides by total phosphorus measurement.

The proposed method has been successfully applied for the determination of malathion in water and vegetables. The vegetable samples collected from various places near sabbavaram area, Visakhapatnam District, Andhra Pradesh, India.

Experimental

A Jasco (Model Uvidec-610 UV-VIS Spectrophotometry with 1 cm matched quartz cuvettes was used for all absorbance measurements. Standard Solution: 1000-ppm solution of Malathion in acetone was prepared by dissolving 0.1 g of known Malathion standard in 100 mL acetone. Stock Solution: - Stock solutions were prepared by dissolving 5 mg of malathion in 50 mL of water. All other chemicals were of analytical grade and provided from Merck.

Procedure

Method I

An aliquot of the malathion stock solution and 1ml potassiumhydroxide and 2 mL of ethylalcohol were introduced into a 25 mL standard flask and made up to volume with nitric acid and with water. The resultant mixture was heated at 50-70°C. The resulting absorbance of the blue color was measured at 760 nm employing all reagents. The experiments were repeated with different volumes of standard malathion solution and a calibration curves were prepared the color reaction obeys Beer's law from 0.01 to 11 mg/10 mL of malathion.

Method II

Water samples (5 mL), 5 g of finely ground vegetable samples (5 g) were spiked with known amount of the working standard solution of malathion. Aliquots of the washed extracts of endosulfan were evaporated off under suction. To the residue, 5 mL of acid reagent and 1 mL of alcoholic potassium hydroxide solutions were added. 5ml of ammonium meta vanadate was added and analyzed by the proposed method. Suitable volume of aliquot was analyzed according to the proposed and reference method. The results are tabulated in tables 1 and 2.

Table 1. Determination of malathion in water and vegetables.

S.NO	Samples	Amount of Malathion($\mu\text{g/mL}$) ^{**}	
		Proposed Method	Reference method ²⁵
1	water	1.63 $\pm$ 0.01	1.61 $\pm$ 0.01
2	Vegetables		
	Cauliflower	5.12 $\pm$ 0.02	5.06 $\pm$ 0.02
	Potato	6.1 $\pm$ 0.03	6.0 $\pm$ 0.05
	Spinach	11.0 $\pm$ 0.05	11.23 $\pm$ 0.01

^{**} mean $\pm$ standard deviation(n=5).

Table 2. Optical characteristics and precision data.

λ_{max} , nm	760 nm
Color	blue
Beer's law range	0.5-11 $\mu\text{g/mL}$
Detection limit	0.13 $\mu\text{g/mL}$

Results and Discussion

Spectral Characteristics

Acid degradation of too slow to be important under environmental reaction conditions. However, alkaline degradation is too fast to be a pathway in environmental condition. The products of alkaline degradation are temperature dependant.

The absorption spectra of the reaction product of malathion with ammonium meta vanadate shown in Figure 2 with maximum absorption at 760 nm. A temperature range of 50-70°C is selected for the reaction. Beer's law was obeyed and the linearity graph is shown in Figure 3 in the concentration range of 0-01-11 mg/10 mL of malathion.

Figure 2. Absorption maximum of malathion with ammonium metavanadate.

Figure 3. Absorbance versus concentration graph of malathion.

Effect of Color Producing Reagent

The rate of formation of complex in solution is generally rapid (45 seconds in color reaction) changes in spectrum or color are associated with a transfer/interchange of electrons when such molecules undergo properly oriented collisions. The absorbance of the developed color was stable for more than three hours.

Sensitivity

The results for the determination of malathion are shown in tables 1 and 2 which reveal the sensitivity, validity and repeatability of the method. The method is also reasonably precise and accurate, as the amount taken from various samples is known and the amount found by the above procedure does not exceed the relative standard derivative of 0.74%. The optimization has been done at lower analyte concentration. The method has been applied for the determination of malathion in various water and vegetable samples. The various samples were collected from sabbavaram areas in Visakhapatnam District, Andhra Pradesh, India. The various vegetables collected are cauliflower, potato, spinach, *etc.* The proposed method is simple, selective, sensitive, and rapid, offers the advantage of high sensitivity.

Conclusion

The spectrophotometric method for the determination of malathion is simple, reliable, sensitive and less time consuming. The color reaction is selective for malathion. The advantage of the present procedure is that it does not require many solvents, where as the HPCL procedures are long, tedious, and expensive, involving many reagents and solvents showing high RSD value.

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