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Sensitive Spectrophotometric Determination of Deltamethrin Using Leuco Malachite Green in Environmental Samples

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A spectrophotometric method for the determination of deltamethrin is reported. The method is based on hydrolysis of deltamethrin to form dibromochrysanthemic acid and phenoxybenzaldehyde cyanohydrin then phenoxybenzaldehyde cyanohydrin on further hydrolysis releases cynide which after bromination form cynogen bromide which reacts with potassium iodide-potassium iodate mixture in the presence of leuco malachite green to form a greenish blue coloured complex which is soluble in 70 % alcohol. The complex shows maximum absorbance at 620 nm. Beer's law obeyed over the concentration range of 10-50 µg in a final solution volume of 10 mL. The molar absorptivity of the coloured system is 7.72×10^4 L mol^{-1} cm^{-1} and Sandell's sensitivity is 1.0×10^{-3} µg cm^{-2}. The reproducibility assessed by carrying out seven days replicate analysis of a solution containing 10 µg of deltamethrin in a final solution volume of 10 mL. The standard deviation and relative standard deviation for the absorbance value were found to be 1.53×10^{-3} and 1 %, respectively. The proposed method is free from the interference of other toxicants. The analytical parameters were optimized and the method was applied to the determination of deltamethrin in various environmental samples.

Keywords: Spectrophotometry, Deltamethrin, Leuco malachite green.

INTRODUCTION

Deltamethrin is a synthetic pyrethroid insecticide with molecular formula ($C_{22}H_{19}Br_2NO_3$). Solubility in water is < 0.1 mg/L at 25 °C. Relative molecular mass of the compound is 505.2 g/mol [1]. It is one of the most effective insecticides known and is not only widely used in veterinary products to control lice, flies and ticks on cattle, sheep and pigs but also in agricultural formulation to control several insect pests on fruits, vegetables and field crops [2], due to its persistence, residual activity and low toxicity to mammals [3]. However, deltamethrin has been found to be very toxic to terrestrial invertebrates, fish and other aquatic organism [4]. Because of its liphophilc characteristics it can be highly absorbed by the fish gills, which partially explains the high sensitivity of these mammals to deltamethrin exposure in concentration up to a thousand times lower than in mammals [5,6]. However, after exposure, a verity of reversible symptoms such as paraesthesia, irritation of the skin and mucosa, headache, dizziness and nousea are reported [7].

The aim of the present work is to develop a rapid, simple and sensitive analytical method for the determination of widely used deltamethrin insecticide at trace levels. Up to now, few analytical procedure have been reported for the determination of deltamethrin residues, including high-performance liquid chromatography (HPLC) [8-10], gas chromatography-mass spectroscopy (GCMS) [11], gas chromatography with electron capture detection (GC-µECD) [12,13], photochemical-spectro-fluorometric [6] and NMR [6].

EXPERIMENTAL

All spectral measurements were made by a systronic UV-visible spectrophotometer model – 104 with matched silica. A systronic pH meter model – 335 was used for pH measurements. A Remi C-854/4 clinical centrifuge force of 1850 g with permanent swing out rotors was used for centrifugation. All reagents used were of AnalaR grade and Double Distilled water was used throughout the experiment.

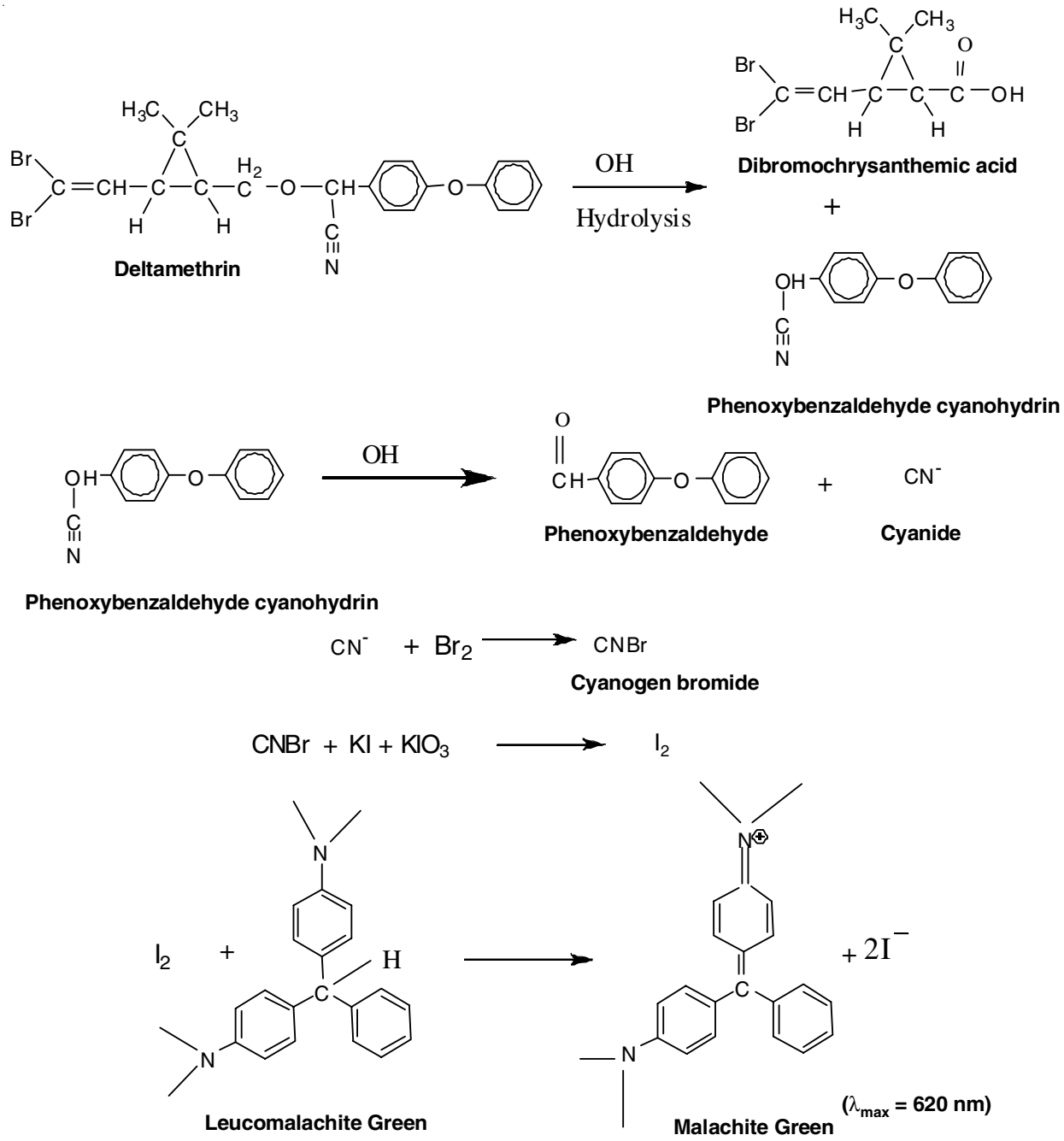
Deltamethrin [Isagro (Asia) Agrochemicals Pvt. Ltd.] A stock solution of 1 ppm deltamethrin is prepared in double distilled water. Working standard solution was prepared by appropriate dilution of stock. Sodium hydroxide (Loba Chemie, Mumbai) aqueous solution of 1 M concentration were prepared. The saturated solution of bromine in water was prepared. The solution was prepared daily. Formic acid solution was 90 %

(v/v). Potassium iodide (BDH) 0.1 mol L^{-1} aqueous solution and Potassium iodate (Merck) 0.2 mol L^{-1} aqueous solution were prepared. Leuco malachite green (Sigma-Aldrich) prepared in 1 litre flask added 100 mL water, 1.5 mL of 85 % phosphoric acid and 25 mg of leuco malachite green. Acetate Buffer (pH = 4.5) prepared by dissolving 13.6 g (1 M) sodium acetate trihydrate in 80 mL of water with acetic acid and mixture was diluted to 100 m with water [14].

Procedures: An aliquot of the test solution containing 10 to 50 µg of deltamethrin was taken in a 10 mL graduated tube and to it 5 mL 1 N sodium hydroxide solution was added and allowed to stand for 10 min for complete hydrolysis and than 0.5 mL bromine water was added and shakes well for 10 min. Then add 2 drops of formic acid to remove excess of bromine. Then 0.5 mL potassium iodide-potassium iodate mixture and 1 mL leuco malachite green was added and leave for 15 min for complete colour development. A greenish blue coloured dye obtained. The solution was then diluted with 70 % alcohol and absorbance was measured at 620 nm against a reagent blank (**Scheme-I**).

Determination of deltamethrin in water samples: River water samples, receiving run-off water from agricultural fields sprayed with deltamethrin, were collected. These sample were extracted with 2 × 25 mL portion of diethyl ether. The ether solution was evaporated to dryness and the residue was dissolved in 50 mL of ethanol.

Determination of deltamethrin in soil and vegetables: Various samples such as water, soil, potato, rice and cauliflower



Scheme-I: Colour reaction of deltamethrin

were collected from the field. The samples were weighed (25 g), crushed and extracted with 2 × 25 mL portion of diethyl ether. The ether solution was evaporated to dryness and the residue was dissolved in 50 mL of ethanol.

RESULTS AND DISCUSSION

The absorption spectrum of greenish blue colour dye shows maximum absorbance at 620 nm. The reagent blank had negligible absorbance at this wavelength (Fig. 1). All spectral measurements carried out against double distilled water as the reagent blank shows negligible absorption at this wavelength. The colour system obeys the Beer's law in the range of 10 to 50 µg of deltamethrin in 10 mL of final solution at 620 nm (Fig. 2). The standard deviation and relative standard deviation for the absorbance value were found to be 1.53 × 10^{-3} and 1 %, respectively.

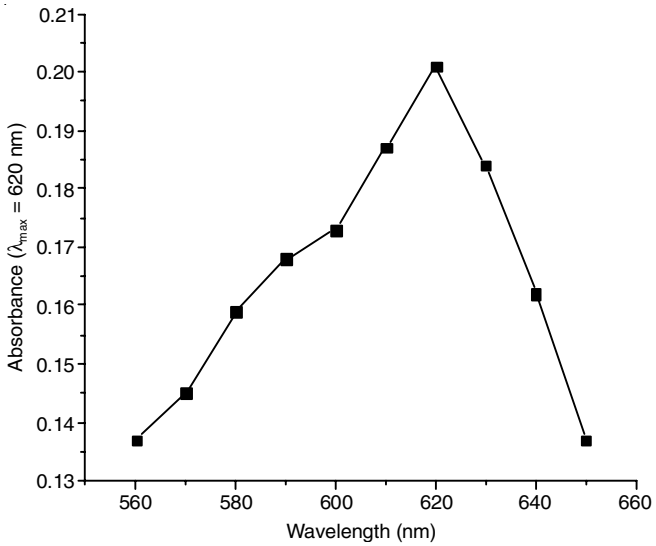


Fig. 1. Absorption curve for deltamethrin

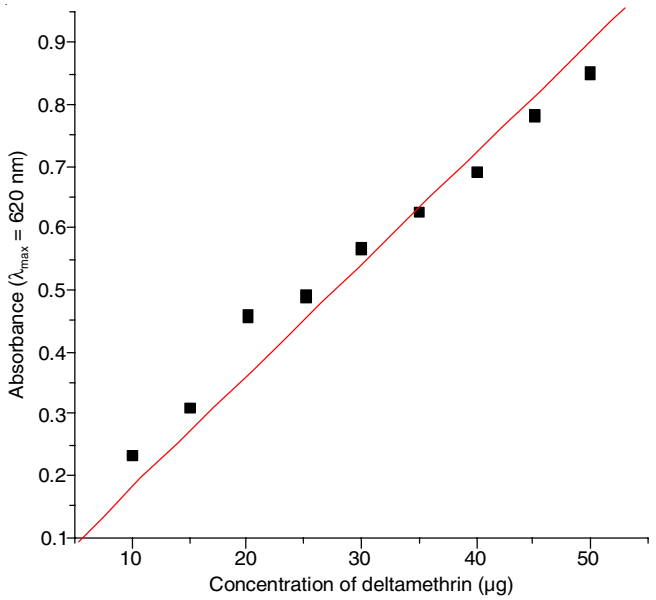


Fig. 2. Calibration curve for deltamethrin

Effect of temperature and pH: It was found that 30 min was required for full colour development the colour was stable for several days. At higher temperature the absorbance value increases (Fig. 3). The effect of pH on the colour reaction was studied and it was found that constant absorbance values were obtained at the pH range of about 2-3 was found for complete hydrolysis of the pesticides. At higher pH absorbance value decreases (Fig. 4).

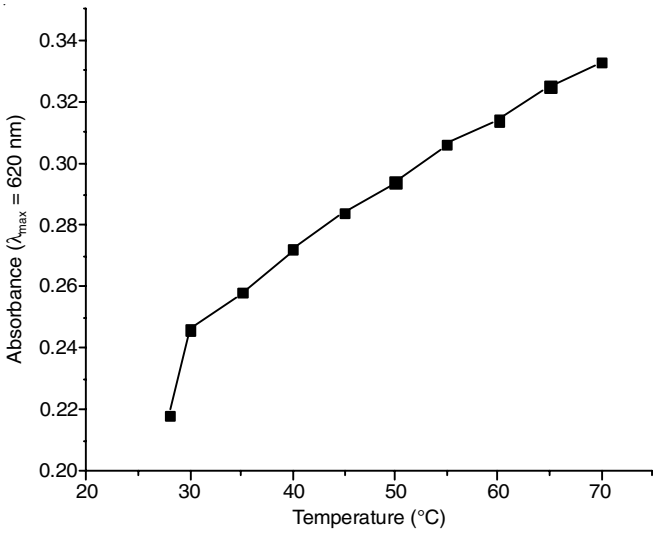


Fig. 3. Effect of temperature

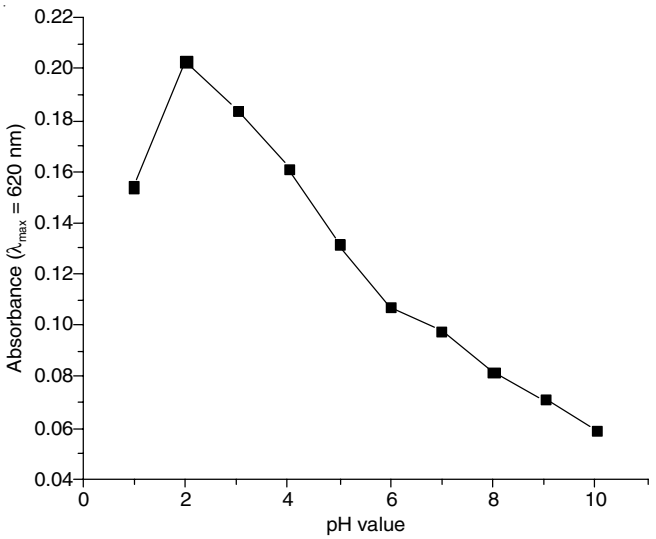


Fig. 4. Effect of pH

Effect of mixture of KI + KIO_3: It is observed that concentration of KI + KIO_3 increases then absorbance value increases (Fig. 5).

Effect of bromine: It is observed that when concentration of bromine increases absorbance value also continuously increases (Fig. 6).

Effect of foreign species: The effect of common foreign species and pesticides were studies to assess the validity of the method. Known amount of foreign species and pesticides were added to the standard solution containing 10 µg of deltamethrin in 10 mL of final solution prior to hydrolysis and the solution was analyzed by the proposed method. The method was found to be free from interferences of most of the foreign species and pesticides (Table-1).

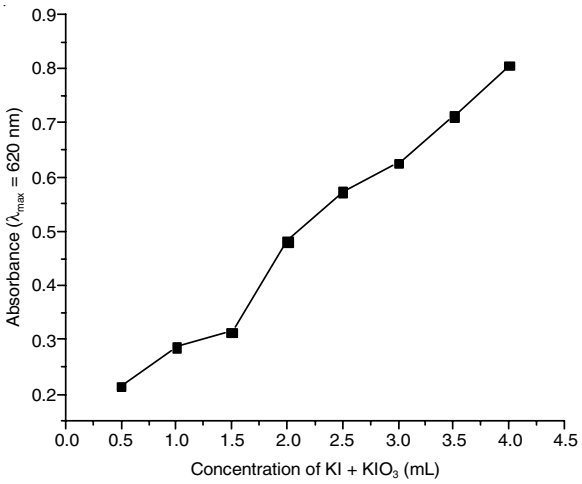


Fig. 5. Effect of KI + KIO_3

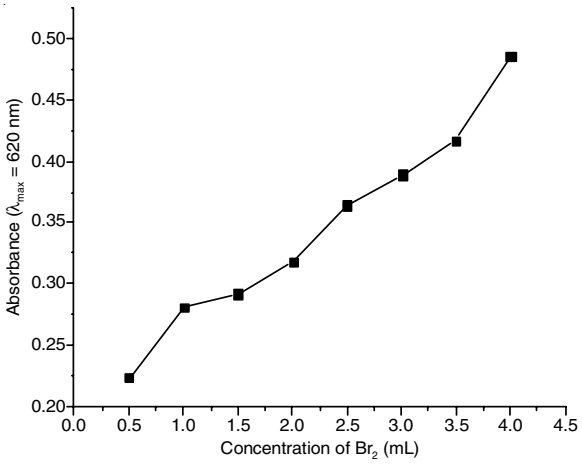


Fig. 6. Effect of bromine

TABLE-1
TOLERANCE LIMIT OF FOREIGN SPECIES

Foreign species	Tolerance limit (μg mL^{-1})	Foreign species	Tolerance limit (μg mL^{-1})
Dicholorovo	1400	SO_4^{2-}	800
Thiochloprid	1300	Fe^{2+}	750
Isoprothiolane, Benzene	1100	Zn^{2+}	600
Cypermethrin	1000	Cu^{2+}	500
Pryridine	500	Mg^{2+}	400

Conclusion

The proposed method is low-cost, rapid, more selective and sensitive for the determination of deltamethrin. The advantage of the proposed method is mainly its sensitivity, simplicity and higher stability of the coloured solution. The proposed method can successfully be applied for the determination of deltamethrin residue in water, soil and vegetables (Tables 2 and 3).

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TABLE-2
DELTAMETHRIN DETERMINATION IN VARIOUS ENVIRONMENTAL AND AGRICULTURAL SAMPLES

Sample	Deltamethrin added (μg/mL)	Total deltamethrin found by proposed method (μg/mL)	Recovery (% ± RSD)
Water*	5	5.40	97.70 ± 0.27
	10	10.73	96.80 ± 0.30
Soil**	5	5.20	97.50 ± 0.36
	10	9.81	90.20 ± 1.16
Rice**	5	5.27	95.13 ± 0.26
	10	9.91	91.26 ± 0.40
Beans**	5	5.61	97.36 ± 1.04
	10	10.82	96.10 ± 0.27
Potato**	5	5.53	94.20 ± 1.11
	10	10.97	96.00 ± 0.77

Recovery was calculated as the total amount found/amount added × 100. Values are mean ± RSD for three determinations. *Sample taken = 25 mL, **Sample taken = 10 g.

TABLE-3
DETERMINATION OF DELTAMETHRIN IN VARIOUS WATER SAMPLES

Sample**	Deltamethrin added (μg/mL)	Total deltamethrin found by proposed method (μg/mL)	Recovery (% ± RSD)*
Sample 1	5	4.52	98.00 ± 0.323
	10	9.5	95.00 ± 0.473
Sample 2	5	3.97	95.00 ± 0.481
	10	9.79	97.50 ± 0.429
Sample 3	5	4.17	96.00 ± 0.164
	10	9.12	91.20 ± 0.444
Sample 4	5	4.17	96.00 ± 0.180
	10	11.13	91.00 ± 0.50
Sample 5	5	4.52	98.00 ± 0.177
	10	9.65	96.50 ± 0.470

*Recovery was calculated as the amount found/amount added × 100. Values are mean ± RSD for three determinations. **Sample taken = 25 mL.

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