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Indirect Spectrophometric Determination of Fly-Fighter Insecticide in Agricultural & Environmental Samples.

Etesh K. Janghel [1*], Santosh Sar[2] and Yasmeen Pervez[3**]
Department of Applied Chemistry
Ashoka Institute of Technology & Management[1]
Gram- Torankatta, Post-Somni, Rajnandgaon (Chhattisgarh) - 491441, India
Bhilai Institute of Technology[2], Bhilai House, Durg (C.G.), 491002, India
Chhatrapati Shivaji Institute of Technology[3**], Balod Road, Durg (Chhattisgarh) 491001, India.
* To whom correspondence should be addressed
** E mail: dr.ypervez@gmail.com, eteshkumarjanghel@gmail.com

Abstract
Indirect spectrophotometric method is developed for the determination of widely used organophosphorus insecticide Fly-Fighter. The method is based on alkaline hydrolysis of Fly-Fighter to dichloroacetaldehyde followed by benzoic acid in alkaline medium. The absorption maxima of the reddish-brown dye formed is measured at 510 nm. Beer's law is obeyed over the concentration range of 2.3 to 25 µg in a final volume of 25 ml (0.092-1.00 ppm). The molar absorptivity, Sandell's sensitivity and correlation coefficient were found to be $1.8x10^4$ l $mole^{-1}cm^{-1}$, 0.002 µg cm^{-2} and 09989 respectively. The lower limit of detection is about 0.001. The standard deviation and relative standard deviation were found to be ± 0.002 and 1.98% respectively. The method is simple sensitive and free from interferences of other pesticides and diverse ions. Other organophosphorous pesticides do not interfere with the proposed method. The method is simple, fast and has been satisfactorily applied to the determination of Fly-Fighter in agricultural & environmental samples.
Key Words : Spectrophotometer, Fly-Fighter, Benzoic Acid Agricultural, Environmental Samples.

Introduction

Fly-Fighter is an organophosphate compound used to control household, public health, and stored product insects. It is effective against mushroom flies, aphids, spider mites, caterpillars, thrips, and white flies in greenhouse, outdoor fruit, and vegetable crops. Fly-Fighter s is used to treat a variety of parasitic worm infections in dogs, livestock, and humans. Fly-Fighter can be fed to livestock to control botfly larvae in the manure. It acts against insects as both a contact and a stomach poison. It is used as a fumigant and has been used to make pet collars and pest strips. It is available as an aerosol and soluble concentrate. Unfortunately, its ready access has resulted in its increased misuse in homicidal and suicidal poisoning cases. Hence the need has therefore arisen for a rapid and reliable method for the detection and determination of Fly-Fighter in environmental materials. Consequently characterization of this insecticide is necessary in forensic toxicology [1-2].

Fly-Fighter [2, 2-dichlorovinyl dimethylphosphate] is highly toxic to mammals and human beings. It is readily absorbed through the skin, because it is volatile. Inhalation is the most common route of exposure. Dermal absorption and ingestion also occurs causing acute toxicity . The acute oral LD_{50} for rats is 55-56 mg/kg body weight and FDA for milk of 0.02 ppm. [3-4].

The wide applicability and high toxicity of Fly-Fighter, numerous instrumental methods have been described for the detection/determination of Fly-Fighter, such as automated analyzer analysis [5], pH-sensitive fluorescence probe [6], fluorimetry [7], polarography [8], tandem mass spectrometry [9], thin-layer chromatography [10-11], high performance liquid chromatography [12], gas-liquid chromatography [13], mass spectrometric method [14] gas chromatography _ flame thermionic detection[16], and some updated instrumental methods such as biosensors methods i.e., amperometric enzymatic biosensors[17], flow - injection analysis[18], etc**.**

Different spectrophotometric methods have been reported for the determination of Fly-Fighter [16-21]. The methods described are generally based on alkaline hydrolysis of Fly-Fighter to produce dichloroacetaldehyde followed by reaction with reagents like resorcinol[15], 2,4 dinitrophenylhydrazine[16], J-acid[17], phloroglucinol[18]and diphenyl semicarbazide [19] and diazotized p-amino acetophenone[20]. Some of these methods have poor sensitivity and higher blank problem. The cholinesterase[21], methods are non selective as all organophosphorus pesticides interfere with the method.

In these paper fast, simple and sensitive spectrophotometric method is described for the determination of Fly-Fighter, where Fly-Fighter is hydrolysed to give dichloroacetaldehyde, which is further reacted with benzoic acid to produce a reddish-brown dye with maximum absorbance at 510 nm(Fig-1). The reagents is selective for Fly-Fighter, amongst the organophosphorus group. The colour system obeys Beer's law in the range

of 0.092-1.00 ppm of Fly-Fighter. The method has been applied to the determination of Fly-Fighter in various samples of polluted water, vegetables, soil, foliages and environmental samples.

The technique can be applied as a useful method for simple and rapid analysis. The features of the method are its sensitivity and stability of the colour formed. The results of trace of the target substance is not interfered by presence of other pesticides, especially other phosphorous pesticides.

Experimental

Apparatus

A systronics UV-Vis spectrophotometric model 104 with matched silica cells was used for all spectral measurements. A systronic pH meter model 335 was used for pH measurements. A Remi C-854/4 clinical centrifuge force of 1850 g with fixed swing out rotors was used for centrifugation.

Reagents

All reagents used were of Anala R grade or of the best available quality. Double distilled deionised water was used throughout.

Fly-Fighter (Hindustion Ciba-Geigy Bombay, India): A stock solution of 1mg ml^{-1} was prepared in ethanol. Working standard solution were prepared by appropriate dilution of the stock standard solution with ethanol.

Sodium hydroxide: A 1.0 mol l^{-1} aqueous solution was used.

Hydrochloric acid: A 0.001 mol l^{-1} aqueous solution was used.

Benzoic Acid (E. Merck, Germany): 0.2% (m/v) solution of the reagent was prepared by dissolving 0.2 gm of benzoic acid in 100ml ethanol.

Procedure

An aliquot of the test solution containing 2.3 to 25 µg of Fly-Fighter was taken in a 25 ml graduated tube and to it 1.0 ml of 1.0 mol l^{-1} sodium hydroxide was added. The solution was kept for 30 min at room temperature for complete hydrolysis. Then 1 ml of benzoic acid was added, shaken thoroughly and pH was adjusted to 9.0-9.5 by adding 0.001 mol l^{-1} hydrochloric acid. The solution was kept for 45min for full colour development. A reddish-brown monomethine dye is obtained [16-21] The solution was then diluted to the mark with water and absorbance was measured at 510 nm against a reagent blank.

Determination of Fly-Fighter in water

River water samples, receiving run off water from agricultural fields, sprayed with dichlovos were collected. These samples were extracted with 2 × 25 ml portions of diethyl ether. Ether solution was evaporated to dryness and residue was dissolved in 50 ml of ethanol. Aliquot were than analysed as described above and in parallel by reported method [19]. Table-3.

Determination of Fly-Fighter in soil and vegetables

Various samples such as soil, cauliflower and tomato were collected from the fields where dichlorvos was used as an insecticide. The samples were weighed (50g) crushed and extracted with 2 × 25 ml portions of diethyl ether. Diethyl ether was then evaporated to dryness and residue was dissolved in 50ml of ethanol. Aliquot were than analysed as described above and in parallel by reported method [19]. Table-3.

RESULTS AND DISCUSSION

Spectral characteristics : The reddish-brown dye formed in the proposed reaction shows maximum absorption at 510 nm.(Fig. 2) All spectral measurements carried out against deionised water as the reagent blank showed negligible absorption at this wavelength. The colour system obeys Beer's law in the range of 2.3 to 25 µg of Fly-Fighter in 25 ml of final solution at 510nm(Fig.-3). The molar absorptivity, Sandell's sensitivity and correlation coefficient were found to be $1.8x10^4$ l $mole^{-1}cm^{-1}$, 0.002 µg cm^{-2} and 09989 respectively.

Optimization of conditions : Hydrolysis of Fly-Fighter to dichloroacetaldehyde was studied at different temperatures and alkalinity. It was observed that alkaline conditions were required for the hydrolysis. Maximum hydrolysis was observed with 1.0 mol l^{-1} sodium hydroxide at temperature of 20-25^oC as it gave maximum absorbance values, good stability and quantitative results. It was observed that 1ml of benzoic acid was sufficient for complete colour reaction.

Effect of time and temperature : The effect of pH on the colour reaction was studied and it was found that constant absorbance values were obtained at pH range of ~ 9.0-9.5 and no buffer solution was required to stabilize the colour. The maximum absorbance of the dye was obtained at 25^0C. The coloured species remain stable for more then 12 hr, under optimum conditions.

Precision of the method was checked by the replicate analysis of working standard solution containing 3 µg ml^{-1} of Fly-Fighter in 25 ml final solution over a period of 7 days. The standard deviation and relative standard deviation were found to be ± 0.002 and 1.98% respectively.

Effect of foreign species : The effect of common foreign species and pesticides were studied to assess the validity of the method. Known amounts of foreign species and pesticides were added to the standard solution

containing 3 µg of dichlorvos prior to hydrolysis and the solution was analysed by the proposed method. The method was found to be free from interferences of most of the foreign species and pesticides. (Table-1)

Application

The proposed method has been applied satisfactorily to the determination of Fly-Fighter in various samples of water, vegetables, and soil. The results are in a good agreement with the reported method (19). To check the recoveries, known amount of Fly-Fighter were added to these samples and then analysed by the proposed as well as the reported method [19](Table-3). The recoveries were found to be 91 to 99%.

Conclusion

The proposed method has been compared with other spectrophotometric methods and found to be more sensitive and selective (Table-2). This method is a good alternative to some of the reported costly instrument method. The advantage of the proposed method is mainly its sensitivity, simplicity and selectivity and higher stability of the coloured solution. The proposed method has been successfully applied for the determination of Fly-Fighter in water, soil and vegetables.

Acknowledgement

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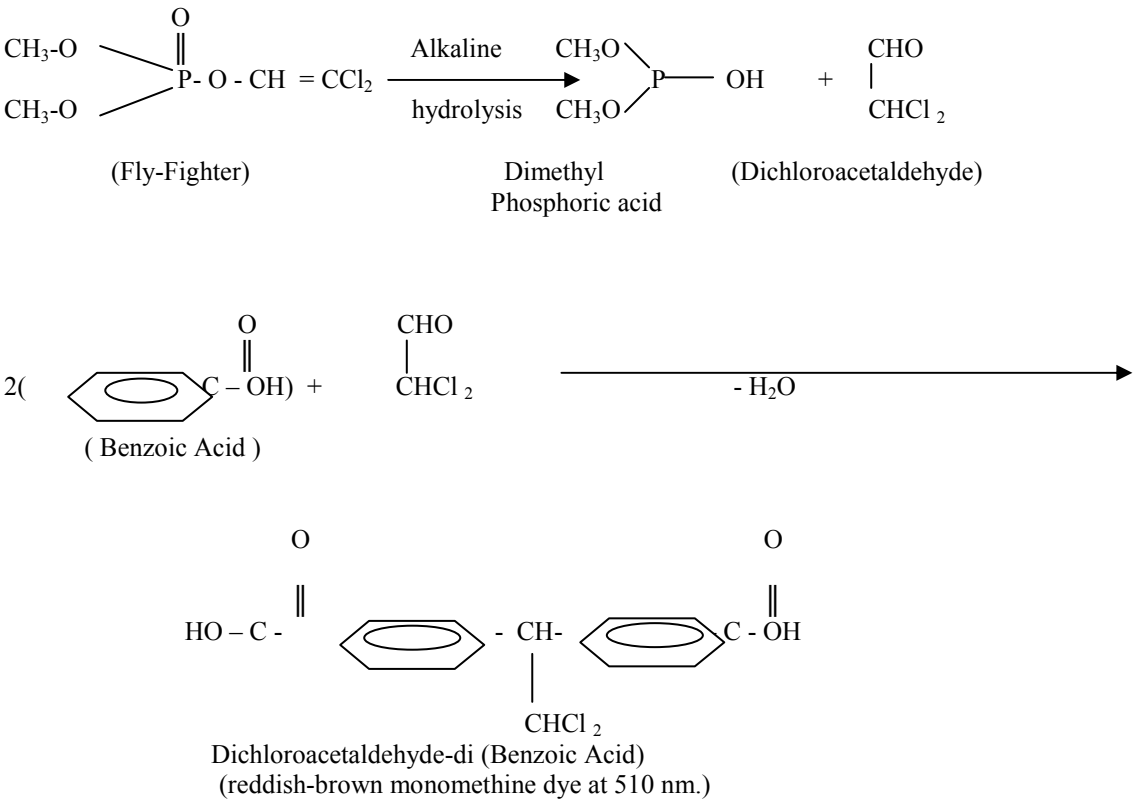

Fig 1. Proposed reaction for formation of coloured species.

The colour reaction involves the following steps.

1. Hydrolysis of Fly-Fighter to its corresponding aldehyde.
2. Coupling of aldehyde with benzoic acid under alkaline condition to form reddish-brown dye at 510 nm.

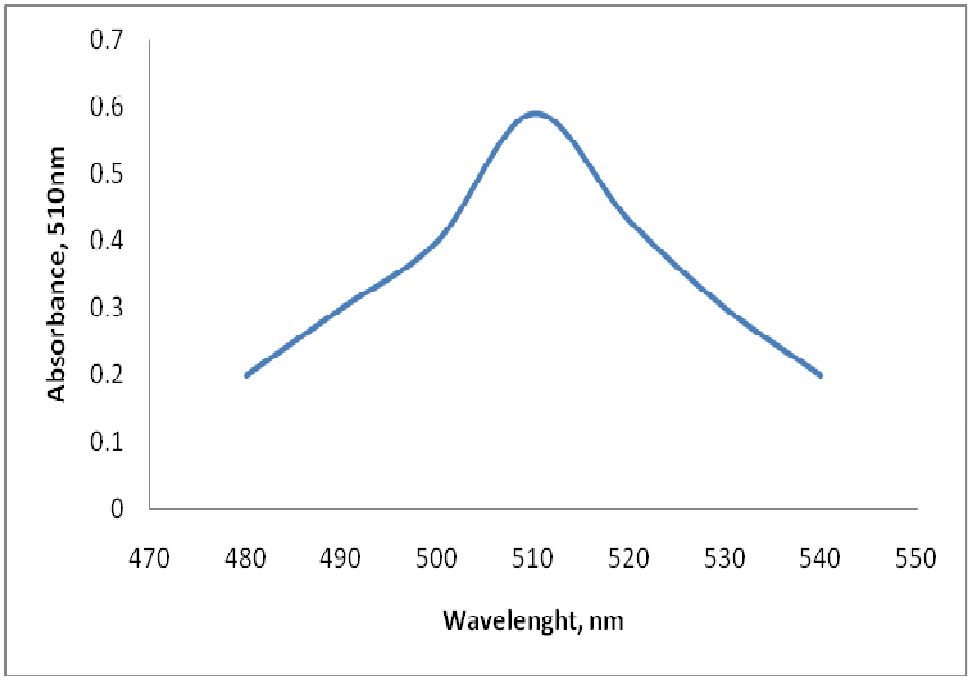

Fig. 2 Absorption spectra of the dye formed

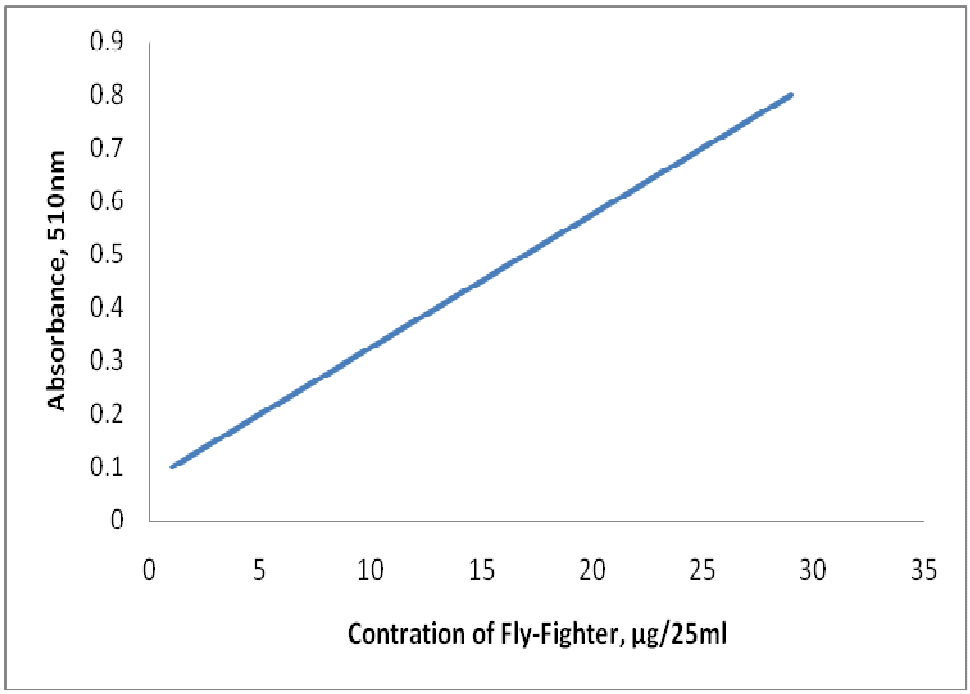

Fig-3 Beer's law of Fly-Fighter

Table-1:-Effect of various pecticides and pollutants. (Concentration of Fly-Fighter 3 µg in 25ml).

Foreign species	Tolerance limit* ppm	Foreign species	Tolerance limit* ppm
BHC,DDT	5500	SO_4^{--}	2200
Benzene, ether	2400	CO_3^{--}	1050
Malathion	1600	NO_2^{-}	900
2; 4-D, 2:4:5-T	1100	NO_3^{--}	750
Cyanide	600	Cu^{2+},Pb^{2+}	450
Kelthane, Fluoride,chloroform	200	Sb^{3+},	300
		Ca^{2+},Mg^{2+},Cd^{2+}	200
Parathion	100	K^{+}, Cl^{-}	150

* The amount causing an error of ± 2% in absorbance value.

Table-2:-C**omparison with other reported reagents.**

Reagent	λmax	Beer's law range ppm	Interference
Resorcinol(15)	490	1-20	Dye unstable high reagent blank
2,4-dinitrophenyl hydrazine(16)	580	3.4-27.5	Less sensitive
Chlolinesterase(21)	412	20	Interference of other organophosphorus pesticides.
J-acid(17)	470	1-10	Less sensitive
Phloroglucinol(18)	475	0.4 -4	Less sensitive
Diphenyl semicarbazide(DPC)(19)	490	0.17-1.36	Less sensitive
Benzoic acid (present method)	510	0.092-1.00	High sensitivity

Table-3:- Results of analysis of real samples and recovery from spiked samples.

Sample	Fly-Fighter Originally Found*		Fly-Fighter Added(µg) (b)	Total Fly-Fighter Found by Proposed* method (c)	Difference (c-a)	Recovery % $\frac{(c-a)}{b} \times 100$
	Proposed method (µg) (a)	Reported method (µg) (19)				
Agricultural waste water [a]	6.12	5.98	10	15.98	9.86	98.6
	4.69	4.63	20	23.95	19.26	96.3
Soil [b]	5.01	4.83	10	14.29	9.28	92.8
	6.06	4.98	20	25.46	19.4	97.0
Cauliflower [c]	5.46	5.14	10	15.28	9.82	98.20
	5.98	5.46	20	25.64	19.66	98.30
Tomoto [d]	7.16	6.76	10	16.89	9.73	97.30
	5.56	4.32	20	25.49	19.93	99.65

* Mean of three replicate analysis.
a = Water sample 250ml.
b, c and d = Sample 50gm (taken from a field where Fly-Fighter had been sprayed)

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