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Research Paper

Analytical Studies for the Determination of Dicofol Pesticide with p-nitroaniline Reagent

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Abstract: *Method is based on Fujiwara Reaction an easy, impressible, sensitive spectrophotometric determination, explained for simple analysis of organochlorine pesticide dicofol on trace levels. Dicofol on its alkaline hydrolysis gives chloroform which react with pyridine produce pink colour Schiff base of glutaconic aldehyde. In the present method pink colour is discharged with adding acetic acid followed by the addition of p-nitroaniline reagent, reddish yellow colour dye obtained. To obtain the maximum sensitivity the effective reaction variables were optimised. The coloured complex shows absorption maxima at 410 nm. Under optimised experimental conditions calibration graph was linear over the range of 0.2 to 2.0 µg ml$^{-1.}$ The molar absorptivity and Sandal's sensitivity were found to be 4.2×10^{6} molL^{-1} cm^{-1} 4.131×10^{-5} µg cm^{-2} respectively. Also calculated the standard and relative standard deviation for the present method was 2.12×10^{-3} µg ml^{-1} and 0.47%. The interfering effect of various species was also investigated. The present method has been applied and checked for the determination of dicofol in various environmental samples.*

Keywords: Dicofol, spectrophotometry, Fujiwara Reaction, Environmental samples.

Introduction

Organochlorine compounds (OCs) are normally used as the agricultural pesticides. However, their high toxicity and long-lasting sustainability in nature make them the potential liquid and terrestrial contaminants, and they should be used under strict limits. Dicofol (DCF) 2, 2, 2-trichloro-1, 1-bis (4-chlorophenyl) ethanol is a non systemic acaricide broadly used for controlling mites that harm cotton, fruit trees and vegetables[1,2].Since dicofol has an analogous structure to DDT, it is related with similar concerns to DDT such as its persistence, bioaccumulation, residual period, acute toxicity, and neurological damage in humans and animals. Its toxicity, capacity for endocrine disturbances and carcinogenicity had a strong influence on the environment and human health[3,4]. Thus a selective, sensitive and convenient method for dicofol determination in fruits and vegetables is highly desirable. In 2013 dicofol was planned to be classified as persistent organic pollutant POP[5,6]. Due to its widespread use and toxicity a variety of methods have been illustrate for the deduction of dicofol such as gas chromatography, high-performance liquid chromatography (HPLC), and liquid chromatography–tandem mass spectrometry (LC–MS/MS), Dispersive liquid–liquid microextraction (DLLME)[7-10] etc. Some of these techniques suffer from poor sensitivity, analyses are limited to laboratory facilities and expensive due to its analytical cost. To overcome these drawbacks a rapid and sensitive method has been proposed for the determination of dicofol. Spectrophotometry is considered the most suitable analytical technique because of its inherent simplicity, low cost and wide accessibility in most laboratories.

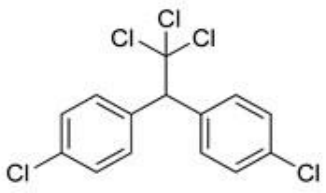


Figure 1: Structure of Dicofol (DCF)

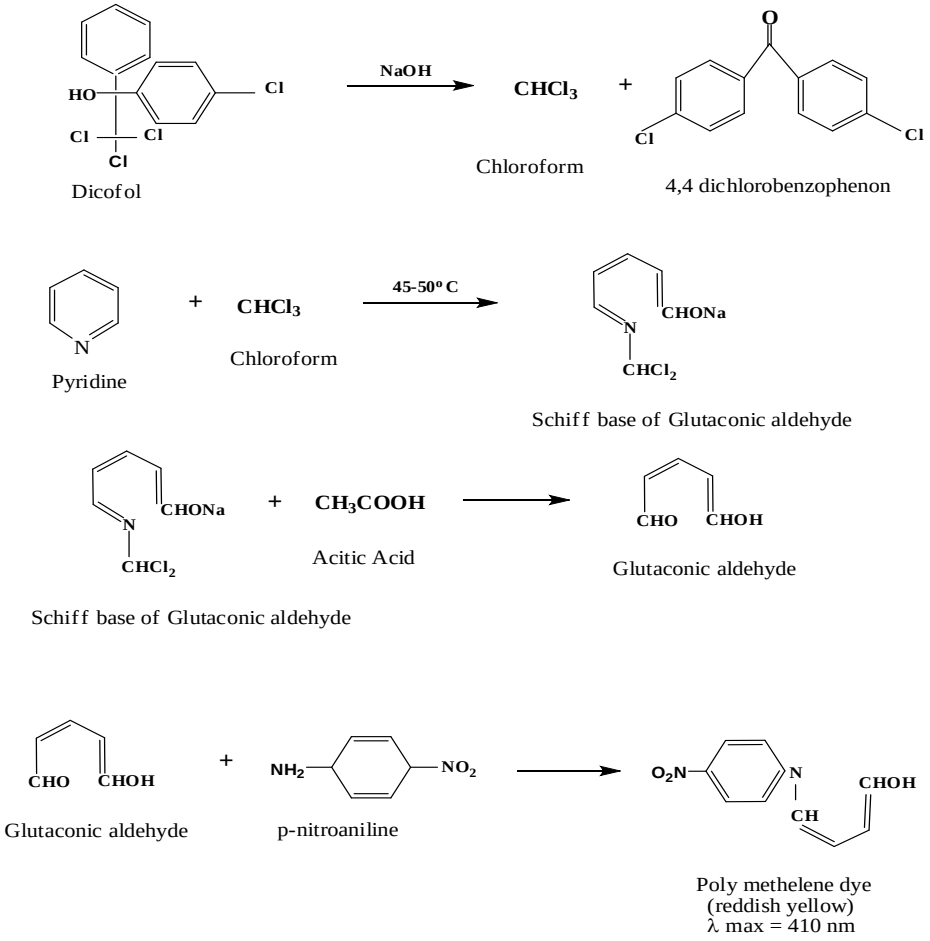
Material and Methods

All spectral measurements were made by a systronic UV-Vis 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 Anala. R. Grade and double distilled water was used during the conduct experiment. A standard stock solution of 1mg/ml solution of dicofol (Nagarjuna Agrichem Limited) is prepared in distilled water. Working standard solution is prepared by proper dilution of the stock solution. A 5.0 mol L^{-1} aqueous solution of sodium hydroxide is prepared. A 0.25 % (W/V) solution of p-nitroaniline reagent in 25% of ethanol is prepared. 10 M aqueous solution of Hydrochloric Acid is also prepared and pyridine and acetic acid is also used.

An aliquot containing 0.2 to 2.0 µg ml^{-1} of dicofol was taken in a 25 ml of calibrated test tube. Solution of test tube was evaporated off up to 0.5 ml on a water bath. To this 1ml of pyridine followed by 2ml of 5 M sodium hydroxide were added and the test tube was kept in a boiling water bath for 2-5 minutes. The pink coloured dye obtained was cooled in ice cold water and then decolourised with few drops of glacial acetic acid. Then 1ml of p-nitroaniline reagent and 10 M HCl was added and the solution was kept for 10 minutes for full colour development. The volume of test tube was made up to 10 ml with distilled water and absorbance of the orange coloured dye was measured at 410 nm against a reagent blank.

Chemical Reaction (Colour reaction)

The reaction takes place in four steps. In the first step dicofol is hydrolysed by NaOH to form chloroform (I), which is now further used in the reaction. In the second step chloroform react with pyridine in alkaline medium to form schiff's base of glutaconic aldehyde (II). In the third step on addition of glacial acetic acid, the pink colour of schiff's base of glutaconic aldehyde (II) is converted into glutaconic aldehyde (III), which forms an orange coloured dye (IV) with p-nitroaniline reagent in the fourth step (Scheme 1).



Scheme 1

Results and Discussion

Spectral characteristics

The absorption spectrum of orange colour dye shows maximum absorbance at 410 nm. The reagent blank had negligible absorbance at this wavelength figure 2. All spectral measurements carried out against double distil water as the reagent blank shows negligible absorption at this wavelength. The colour system obeys the Beer's law in the range of 0.2 to 2.0 µg ml^{-1} of dicofol in 10 mL of final solution at 410 nm figure 3. The molar absorptivity and Sandell's sensitivity were found to be 4.2×10^{6} $molL^{-1}$ cm^{-1} 4.131×10^{-5} µg cm^{-2} respectively (Table 1).

Table 1: Analytical parameters and optical characteristics

S. No.	Parameters	Values for the reaction
1.	λ max (nm)	410
2.	Beer's law limit(µgmL^{-1})	0.2 to 2.0
3.	Molar absorptivity $\times10^{6}$ (L mol^{-1} cm^{-1})	4.2
4.	Sandell's sensitivity$\times10^{-5}$ µg cm^{-2}	4.131
5.	Relative standard deviation (%)	0.47

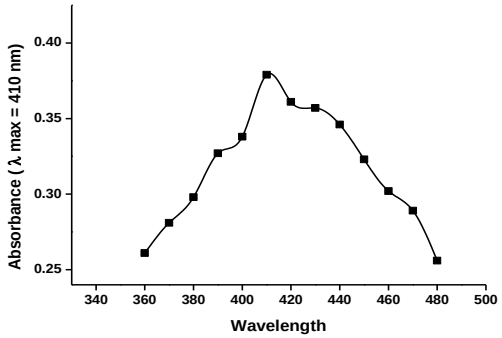


Figure 2: Absorbance spectra of coloured product

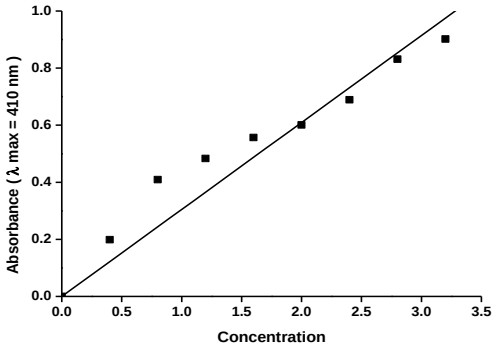


Figure 3: Calibration curve

Optimization of condition

Hydrolysis of dicofol to chloroform and the reaction of chloroform with pyridine to form pink coloured dye was studied at different temperature and alkalinity. The effect of pH on the colour reaction (Figure 5) of dicofol was examined. By the pH range of ~ 6-7 was found for complete the reaction. At lower pH and higher pH absorbance value decreased. It was found that 2-5 minutes in a water bath at temperature range 50^{0}C were sufficient for the complete colour development. It was observed that 1 ml of dye was sufficient for complete colour development figure 4. Precision of the method was checked by the replicate analysis of working standard solution containing 2 µg of dicofol in 10 mL final solution over a period of 7 days. The standard deviation and relative standard deviation for the absorbance value were found to be 2.12×10^{-3} µg ml^{-1} and 0.47% respectively (Table 1).

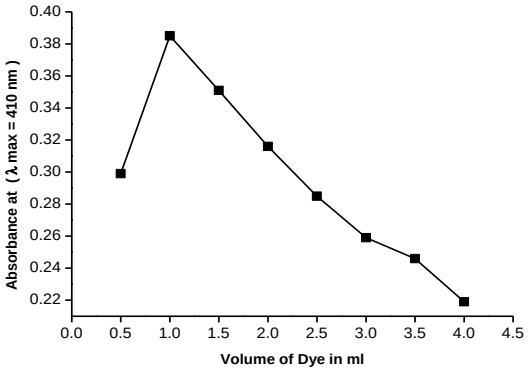


Figure 4: Effect of Dye

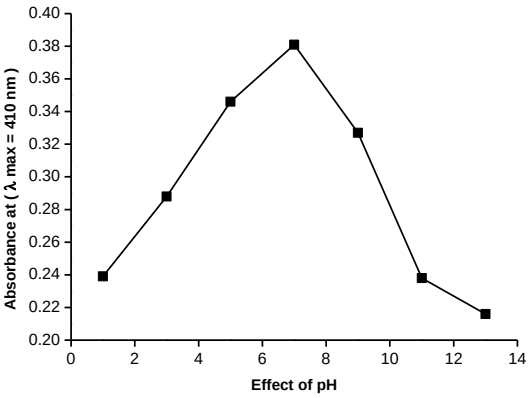


Figure 5: Effect of pH

Effect of interferents

To assess the validity of the proposed method, the effects of various common foreign species and other pesticides were added to the standard solution containing 2µg of dicofol prior to hydrolysis and analyzed by the proposed method. The method was free from interference of various foreign species and

pesticides. An error of ±2% in the absorbance reading was considered tolerable (Table 2).

Table 2: Effect of Interferents on the determination of dicofol

Foreign Species	Tolerance Limit* µg mL^{-1}	Foreign Species	Tolerance Limit* µg mL^{-1}
Dicholorovos	250	SO_4^{2-}	600
Thiochloprid	300	Fe^{++}	50
Monocrotophos	450	Zn^{++}	800
Cypermethrin	500	Ca^{++}	100
Acetamethrin	550	Bifenthrin	150
Tolerance limit is the amount of foreign species that causes an error of ±2% in absorbance value.			

Table 3: Determination of dicofol in various agricultural samples

Sample	Dicofol originally found	Dicofol added (µg/mL)	Total dicofol found by proposed method (µg/mL)	Recovery (% ± R.S.D)*
	Proposed method (µg/mL)			
Soil	0.98	2.5	3.38	97.26 ± 0.39
	2.60	5	7.42	96.99 ± 0.20
Rice	1.20	2.5	3.59	97.62 ± 0.25
	2.16	5	7.06	98.11 ± 0.16
Beans	1.58	2.5	3.98	98.14 ± 0.12
	2.69	5	7.51	96.16 ± 0.11
Potato	1.61	2.5	4.01	98.55 ± 0.22
	2.81	5	7.79	97.33 ± 0.14
Sugarcane	1.16	2.5	3.59	98.19 ± 0.21
	1.98	5	6.71	96.42 ± 0.44
*Recovery was calculated as the amount found / amount added × 100. Values are mean ± R.S.D. for three determinations				

Application

Determination of dicofol in different vegetables, fruits, grains and soil: Various samples of vegetables, fruits and soil each 5g were collected from agricultural field, where dicofol had been sprayed as a pesticide. The samples were macerated with 20mL portions of ethanol: double distilled water (1:1) filtered through a whatman filter paper No. 40 and the filtrate was centrifuged at 1850 rpm for 10 minutes. In case of vegetables, grains and fruits, the filtrate was quantitatively transferred into 50mL calibrated flask and made up to the mark with distilled water. 5ml aliquot were taken in a 10ml volumetric flask, and analysed as described above. Synthetic sample were prepared by adding known amount of dicofol and kept for 3-4 h and analysed as described above. The recoveries range from 97-98% and the results are summarized in Table 3.

Conclusion

The proposed method is simple, sensitive, rapid and can be used for the determination of dicofol in trace amounts in different environmental samples. This method is good alternative to some reported costly instrumental method. The technique also been statistically evaluated and free from the interferences by excipients and the results obtained are accurate and precise as indicated by good recoveries of the pesticide and low RSD values.

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