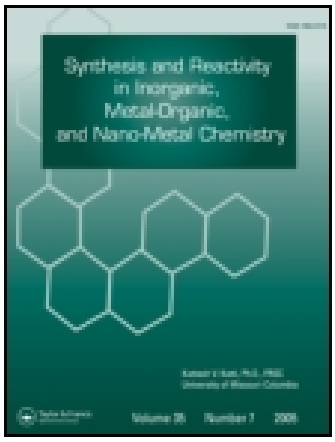

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Determination of Dicofol in Various Environmental Samples by Spectrophotometric Method Using Chromogenic Reagent

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A sensitive spectrophotometric method for determination of dicofol in subparts per million levels is described, which is based on Fujiwara reaction. Dicofol on alkaline hydrolysis gives chloroform, which reacts with pyridine to produce red color. The color is discharged by addition of glacial acetic acid. The glutaconic aldehyde formed reacts with 4-aminoacetanilide to gave an orange-red dye which is extractable in 3-methyl-1-butanol. The extracted dye shows absorption maximum at 525 nm. Beer's law is obeyed in the range of 0.025–0.25 μg mL^{-1}. Important analytical parameters such as time, temperature, reagent concentration, acidity etc. have been optimized for complete color reaction. Sandell's sensitivity and molar absorptivity for the system were found to be 0.000343 μg cm^{-2} and 1.077 $\times$ 10^6 L mol^{-1}cm^{-1}, respectively. The proposed method is satisfactorily applied to microlevel determination of dicofol in various environmental samples.

Keywords: spectrophotometry, dicofol, 4-aminoacetanilide, 3-methyl-1-butanol

Introduction

The tropical environment is contributing to the rapid growth of pests and diseases and has led to extensive and intensive use of pesticides on vegetables. Also, absence of fallow periods in cultivable lands and continuous planting throughout the year leads to higher risks for proliferation of pests and diseases. Several types of pesticides are applied on vegetables depending on the crop type, the particular target pest and disease, the time interval between pathogenic attack and crop harvest, and the preharvest interval prescribed for the pesticide. The intensive use of pesticides may result in high levels of pesticide residues in vegetables. Due to the growing consumer demand for safe food, the regulatory agencies need to analyze a large number of samples within the shortest possible time. Thus, simple, rapid, and robust methods are always preferred. Also, a method that is economical without compromising on the accuracy and precision is preferred due to limited resources and funding provided to the laboratory especially in developing countries. The major drawbacks of the current analysis methods today is that much labor is required and is time consuming also, using high volumes of hazardous solvents causes exposure of workers to hazardous solvents and they result in problems with large amounts of waste. One more drawback is that many types of vegetables and fruits with different matrix interferences are required to be analyzed in the laboratories separately.

Dicofol is a pesticide synthesized by dichlorodiphenyltrichloroethane (DDT).[1] Its toxicity, capacity for endocrine disturbance, and carcinogenicity had a strong influence on the environment and human health.[2–4] Dicofol appears to be effective against a wide range of mite species and is a well known miticide. It is also effective against tetrachid, mites, cydamen, broad, mites, european red spider, apple-rust, cherry-rust, tomato-rust, and various other fruits and vegetable rusts.[5] Dicofol (DCF), trade name Kelthane, is a nonsystemic acaricide extensively used for controlling mites that damage cotton, fruit trees, and vegetables.[6] If released to soil, it is expected to bind with the soil strongly and may reach groundwater and pose a threat to human health. It is classified as slightly toxic compound having acute oral LD 50 for rat of 595 mg kg^{-1}[7] and environmental endocrine-disrupting chemicals.[8] The tolerance level of dicofol in vegetable is 1 mg kg^{-1}.[9] Several instrumental techniques (i.e., gas chromatography electron capture detector [GCECD]),[10] microwave-assisted extraction,[11] gel permeation chromatography,[12] GCMS analysis,[13] multiwall carbon nanotubes modified GCE (MWCNTs/GCE),[14] reversed-phase high performance liquid chromatography (RP-HPLC),[15] and spectrophotometry[16–19] are available in literature, but most of these techniques are costly and require trained operators. Spectrophotometry is a simple, sensitive, rapid and versatile technique for quick determination of analyte. A few spectrophotometric methods based on the hydrolysis of dicofol to

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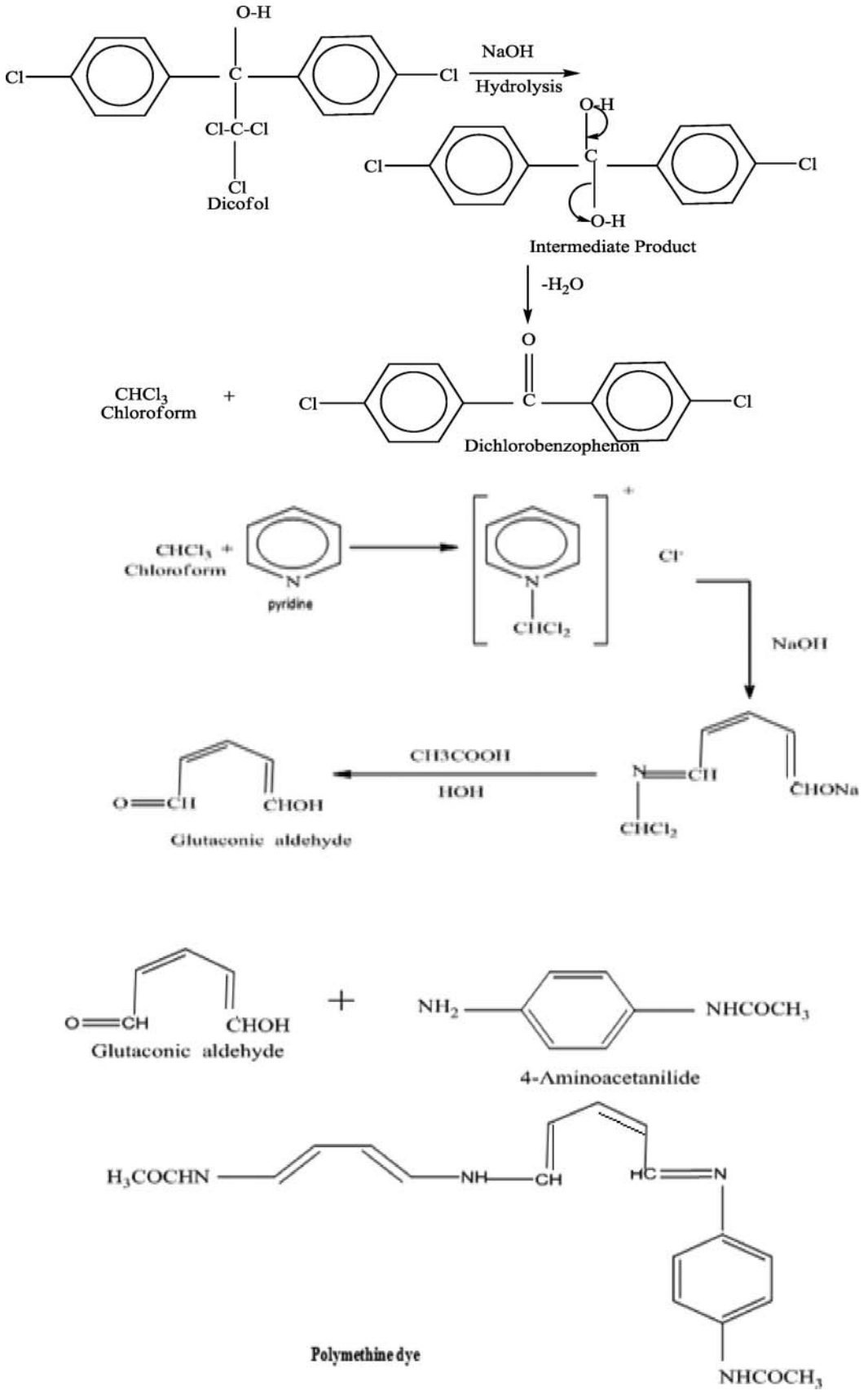

Sch. 1. Color reaction of dicofol.

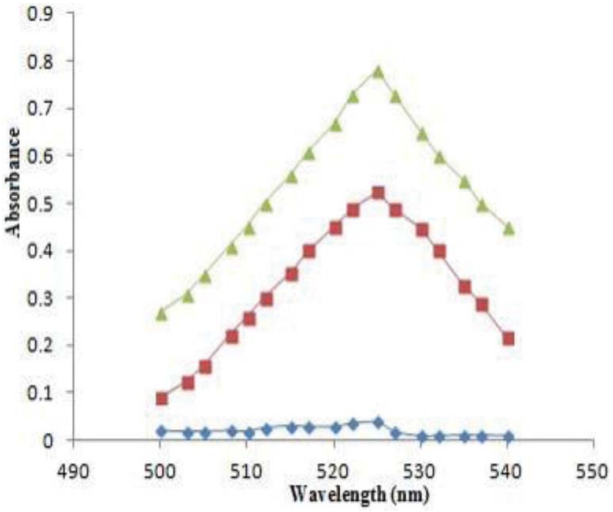

Fig. 1. Absorption spectra of colored product and reagent blank.

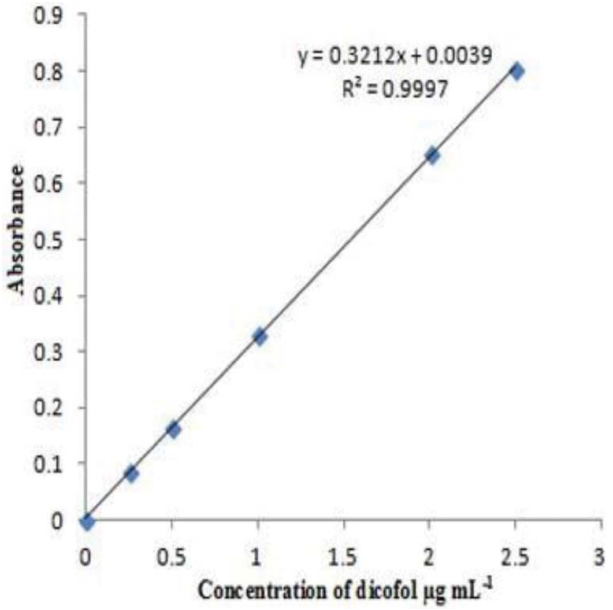

Fig. 2. Calibration data for the determination of dicofol (aqueous medium).

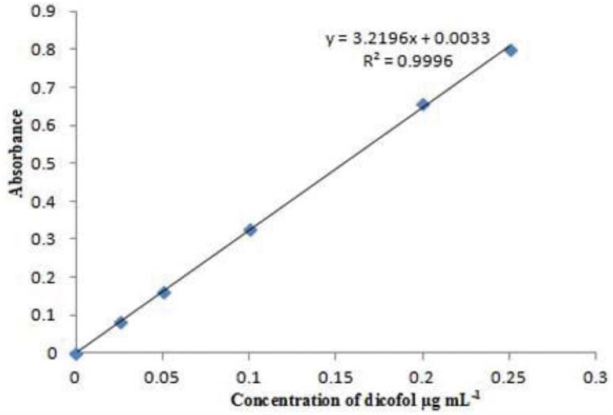

Fig. 3. Calibration data for the determination of dicofol (extracted medium).

Table 1. Analytical and method validation parameters

Parameter	Results
λ_{max} (nm)	525
Range of Beer's law / (μg mL−1)	0.025–0.25 (extracted medium)
	0.25–2.5 (aqueous medium)
Stability of color / h	24
Molar absorptivity / (L mol−1 cm−1)	1.077×10^6
Sandell's sensitivity / (μg cm−2)	0.000343
Relative standard deviation /%	
Intra day	0.609–4.3
Inter day	0.46–1.25
Limit of detection	0.0045
Limit of quantification	0.014
Regression equation (y = bx+a)*	
Correlation coefficient	0.9997
Slope (b)	0.3212
Intercept (a)	0.0039

*Concentration in μg mL^{-1}.

chloroform and determination of chloroform by Fujiwara method[16–19] are available, but all these methods require specially constructed apparatus and have poor sensitivity than the present method.

In the present study, a simple and more sensitive method is developed for the determination of dicofol. The reagent used in the present method is 4-aminoacetanilide, which increases sensitivity of the Fujiwara reaction. The method has been successfully applied for the determination of dicofol in environmental samples.

Experimental

Apparatus

To record the UV-visible spectra, a Varian Cary 50 Bio UV-visible spectrophotometer with 1.0 cm quartz cell was used. A thermostatic water bath (MAC Macro Scientific Works Pvt. Ltd. Model no. MSW-273) was used to control the reaction temperature. The pH measurements were made with Systronics digital pH meter 335.

Reagents

All reagents used were of analytical grade and all the solutions were made with deionized water. Dicofol (Aldrich) stock: 1 mg mL^{-1} solution of dicofol was prepared in alcohol. Working standard was prepared by appropriate dilution of the stock with water. Pyridine, p-aminoacetanilide reagent (Merck, Mumbai, India): pyridine reagent was prepared by mixing 3 mL of concentrated hydrochloric acid with 18 mL of pyridine (Merck, Mumbai, India) and volume was made up to 30 mL with distilled water. The new reagent system

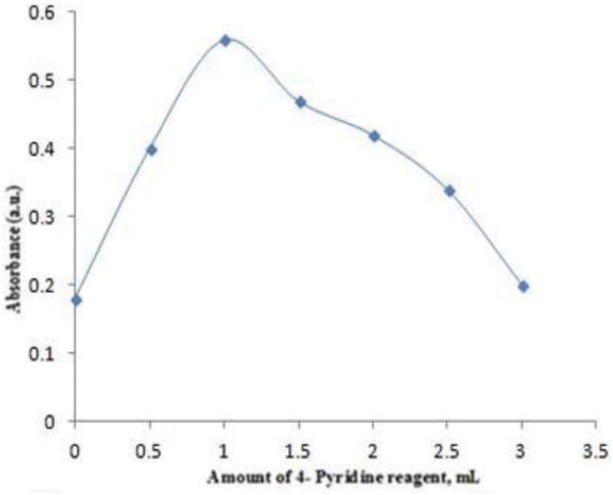

Fig. 4. Effect of pyridine reagent on sensitivity of reaction.

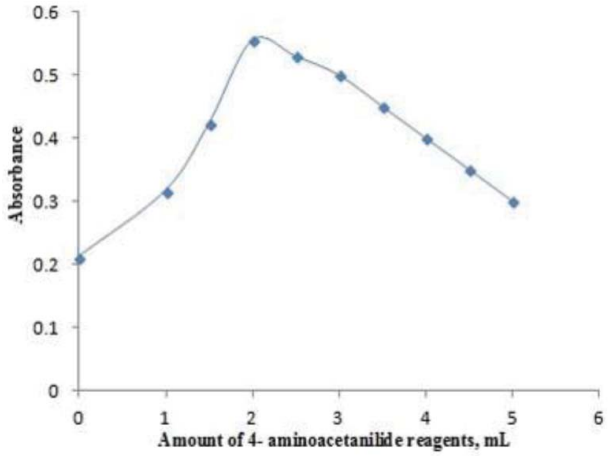

Fig. 5. Effect of 4-aminoacetanilide reagent on sensitivity of reaction.

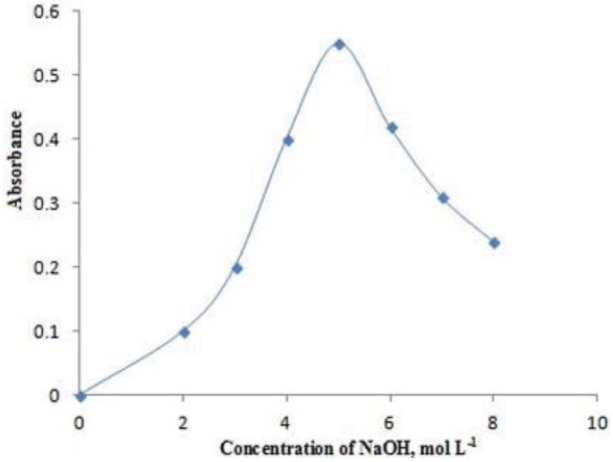

Fig. 6. Effect of NaOH on sensitivity of reaction.

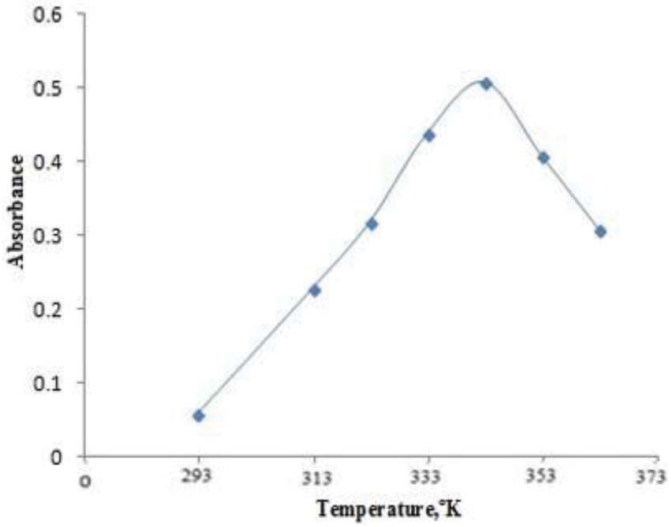

Fig. 7. Effect of temperature on sensitivity of reaction.

was prepared by mixing equal volume of pyridine reagent and 1% aqueous p-aminoacetanilide. 5 M aqueous solution of Sodium hydroxide solution (Merck, Mumbai, India) and 10 M aqueous solution of hydrochloric acid (Merck, Mumbai, India) was prepared in deionised water. Glacial acetic acid (Aldrich) was used for the present study.

Procedure

In order to construct calibration curve, 50 mL sample solutions containing dicofol in the range of 0.025–0.25 μg were taken in a conical flask, 1 mL of pyridine was added followed by addition of 2 mL of 5 M NaOH and thoroughly shaken. The contents were kept in water bath at 70°C for 3 min and shaken time to time. A pinkish red ring was obtained which was cooled in ice cold water and the color of ring was discharged by adding 1 mL glacial acetic acid drop wise. To which 2 mL of 1% 4-aminoacetanilide and 1 ml of 10 M HCl solution were added and the content was allowed to stand for 10 min. The orange-red product obtained was extracted in 2.5 × 2 mL of 3-methyl-1-butanol. The extract was dried over anhydrous sodium sulfate and the absorbance was measured at 525 nm against 3-methyl-1-butanol.

Color Reaction of Dicofol

The reaction involves four steps.

1. Dicofol was hydrolyzed by sodium hydroxide to generate chloroform (I) and 4,4-dichlorobenzophenone.
2. Chloroform reacted with pyridine in alkaline medium to form the Schiff base of glutaconic aldehyde (II).
3. By addition of glacial acetic acid, the pink color of Schiff's base of glutaconic aldehyde was converted in to the yellow colored glutaconic aldehyde (III).
4. Yellow colored glutaconic aldehyde reacted with 4-Aminoacetanilide reagent and formed an orange-red colored polymethine dye (IV) (Scheme 1).

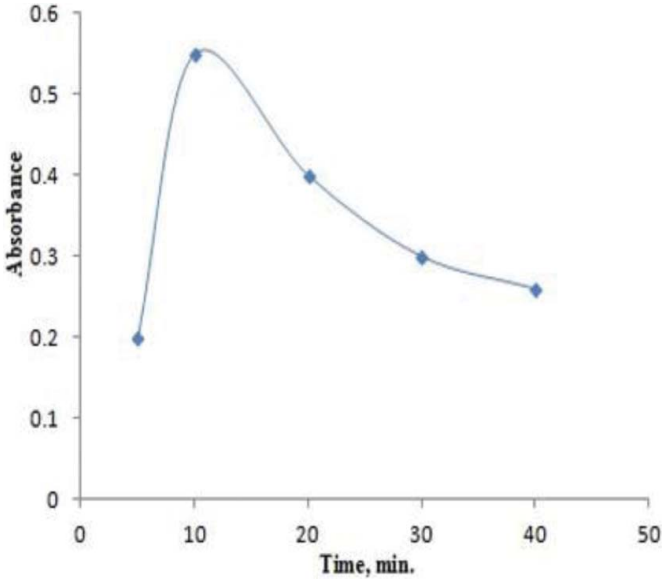

Fig. 8. Effect of time on the sensitivity of reaction.

Results and Discussion

Spectral Characteristics and Method Validation

The absorption spectra of final colored product gave absorption maximum at 525 nm corresponding to the particular band. The reagent blank had negligible absorbance at this wavelength (Figure 1). Beer's law is obeyed over the concentration range of 0.025–0.25 μg mL^{-1} in extracted medium (Figures 2 and 3). The molar absorptivity and Sandell's sensitivity were found to be 1.077 $\times$ 10^6 L mol^{-1}cm^{-1} and 0.000343 μg cm^{-2} respectively. The slope, intercept and the correlation coefficient were evaluated by least squares regression analysis are also included (Table 1).

Precision of the method has been checked by 5 replicate analysis of solution containing 0.15 μg of dicofol in 50 mL final solution. The standard deviation and relative standard deviation have been found to be (±) 0.002 and 0.420%, respectively (Table 1).

Table 2. Effect of diverse ions (concentration of dicofol 0.15 μg 50 mL^{-1})

Foreign species	*Tolerance level (μg mL^{-1})	Foreign species	*Tolerance level (μg mL^{-1})
Al^{+3}, Fe^{+3}	600	DDT	1000
Mn^{+2}, Cu^{+2}	750	Malathion, CCl_4	100
Co^{+2}, Mg^{+2}	1100	Phenol	700
Hg^{+2}	90	Benzene	2000
Pb^{+2}	150	Toluene	700
Ca^{+2}	800	Ethanol	1700
SO_3^{-2}	70	Aniline	200
NO_3^-	100	Nitrobenzene	200
F^-	1000	Carbonate	5000
		Benzaldehyde	800

*Causing (±) 2% variation in absorbance value.

Table 3. Recoveries of dicofol in various environmental samples

		Total dicofol found* (μg)		% of Reported	
Sample volume or mass	Dicofol added (μg)	Present method	Reported method	Present method	Reported method
Water[a]					
(A)	15	14.50	14.25	96.66	95.00
(B)	25	23.90	23.75	95.60	95.00
Milk[a]					
(A)	15	14.15	14.12	94.33	94.13
(B)	25	23.50	23.46	94.00	93.84
Tomato[b]					
(A)	15	14.50	14.42	96.66	96.13
(B)	25	24.50	24.26	98.00	97.44
Beans[b]					
(A)	15	14.20	13.95	94.66	94.33
(B)	25	24.80	24.70	99.20	98.80
Grapes[b]					
(A)	15	14.60	14.23	97.30	94.80
(B)	25	24.50	24.13	98.00	96.52

*Mean of three replicate analysis; [a]Size of sample 100 ml, [b]Size of Sample 50 g.

Table 4. Comparison of the proposed method with other spectrophotometric method

S. No.	Method/reagents medium/ pH	λ_{max} (nm)	Beer's Law (ppm)	Remarks
1.	Fujiwara method pyridine/ NaOH	530	12.40–124.0	Methods require special type of distillation apparatus
2.	Modified Fujiwara method/ pyridine/NaOH	530	200	Poor sensitivity
3.	Sulphanilic acid + Formic acid	505	1.48–11.80	Less sensitive
4.	Benzidine	490	0.13–1.04	Interference of other chlorinated hydrocarbon
5.	Present method (4-Aminoacetanilide)	525	0.025–0.25	Method is simple, more sensitive free from interference of other chlorinated hydrocarbon

Effect of Reagent Concentration

Under the proposed reaction conditions it was found that 1 mL of pyridine (Figure 4) and 2 mL of 1% 4-aminoacetanilide was required for complete color development (Figure 5).

Effect of NaOH

2 mL of 5 M NaOH was required for maximum color intensity. Excess of NaOH made the solution slightly turbid (Figure 6).

Effect of Temperature, Time, and pH

Under the optimum condition the final absorbance was measured at pH 5.0–5.5. It was found that temperature range of 25–35°C had no adverse effect on color development and 10 min time was sufficient for complete color development after addition of the reagent (Figures 7 and 8).

Effect of Foreign Species

The effect of diverse ions expected to coexist with dicofol were studied by adding known amount of different organic pollutants and inorganic ions to 50 mL test solution containing 0.15 μg of dicofol per 50 mL of final volume. The method was found to be free from most of the interferents. Trichloroacetic acid and chloroform gave positive interference since they also give Fujiwara reaction.[20] The tolerance limits shown in Table 2 are the concentration of interfering species that cause (±) 2% error.

Applications

In water sample

100 mL of dicofol free water sample was taken and fortified with known amounts of dicofol and kept for 5 h. Then dicofol was extracted in 3-methyl-1-butanol. 3-methyl-1-butanol was evaporated and dicofol was determined by the present as well the reported method.[21] The recoveries are shown in Table 3.

In milk sample

To assess the applicability of the method for the determination of dicofol in milk samples, known amounts of dicofol were added to the milk sample. Dicofol was extracted in 3-methyl-1-butanol and determined by present as well as reported method.[21] The recoveries are shown in Table 2.

In vegetables and fruits samples

Various vegetable and fruit samples such as tomato, beans and grapes were weighed, crushed and then spiked with known amounts of dicofol and kept for 3–4 h. Dicofol was extracted in 3-methyl-1-butanol. 3-methyl-1-butanol was evaporated and dicofol was determined by the present as well as reported method.[21] The recoveries are shown in Table 2.

Conclusion

The proposed method is simpler, sensitive, and rapid as compared with other methods for dicofol determination shown in Table 4. The rapid color development, reproducibility, stability and easy availability of the reagent and freedom from a large group of interfering species are some advantages of the method. Extraction method lowers the detection limit.

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