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## Spectrophotometric Determination of Fenpropathrin in its Formulations and Water Samples

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**Abstract:** Novel spectrophotometric methods were developed for the determination of fenpropathrin in insecticidal formulations and water samples. The methods were based on the hydrolysis of fenpropathrin with ethanolic KOH to form 3-phenoxy benzaldehyde. The resultant aldehyde group was condensed with anthranilic acid in presence of basic medium to form yellowish red color product having  $\lambda_{\max}$  of 485 nm or condensed with 2-chloro phenyl hydrazine to form pink color product having  $\lambda_{\max}$  of 557 nm. The color derivatives were correspondingly stable for 5 and 8 days. The Beer's law was obeyed over the range from 0.03-10.0  $\mu\text{g mL}^{-1}$  and molar absorptivity  $2.586 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  for anthranilic acid and from 0.02-8.0  $\mu\text{g mL}^{-1}$  and molar absorptivity  $3.924 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  for 2-chloro phenyl hydrazine were observed. The optimum reaction conditions and other analytical parameters were established. The proposed methods have been applied for the analysis of water samples.

**Keywords:** Fenpropathrin, Anthranilic acid, 2-Chloro phenyl hydrazine, Spectrophotometry, Water Samples

### Introduction

Fenpropathrin is a synthetic pyrethroid and possess high insecticidal activity. It is used to control many species of mites and insects like whiteflies, cotton field crops, glass house crops, vegetables. Appreciable levels of pyrethroid residues can occur in food commodities from crops, food of animal origin (eg. milk, eggs and meat), soils, sediments, and surface, ground and drinking water<sup>1</sup>. Pyrethroids are now employed worldwide as insecticides,

agriculture, forestry, public health and domestic activity due to their insectidal activity, bio transformation and most importantly non-persistence in their environment. Their non-persistence is essentially due to photodegradation which occurs via decarbonylation, ester bond cleavage and hydration of cyano group to carbamate<sup>2</sup>. However, high toxicity to fish, aquatic species, and honeybees was observed for more pyrethroids<sup>3</sup>. Contamination of fresh-water ecosystems occurs either because of the direct discharge of industrial and agricultural effluents or as a result of effluents from sewage treatment works, residues can thus accumulate in the surrounding biosphere<sup>4</sup>.

Several analytical techniques have been reported for the determination of fenpropathrin which includes GC-ECD<sup>5</sup>, Electron capture method<sup>6</sup>, HPLC<sup>7</sup>, coupled column liquid chromatography<sup>8</sup>, capillary GC-MS<sup>9</sup> and FT-IR<sup>10</sup>. These techniques required large number of solvents for the extractions and also some limitations in terms of high cost of instruments used in routine analysis and matrix effects. Spectrophotometric method is still one of the important techniques for the determination of pesticides because it is less expensive and easy to use.

The present investigation is to provide a simple spectrophotometric technique for the determination of fenpropathrin based on condensation of resultant aldehyde group with anthranilic acid, 2-chloro phenyl hydrazine. The developed methods have been successfully employed for the determination of fenpropathrin in its formulations, water samples.

## Experimental

### *Instrumentation*

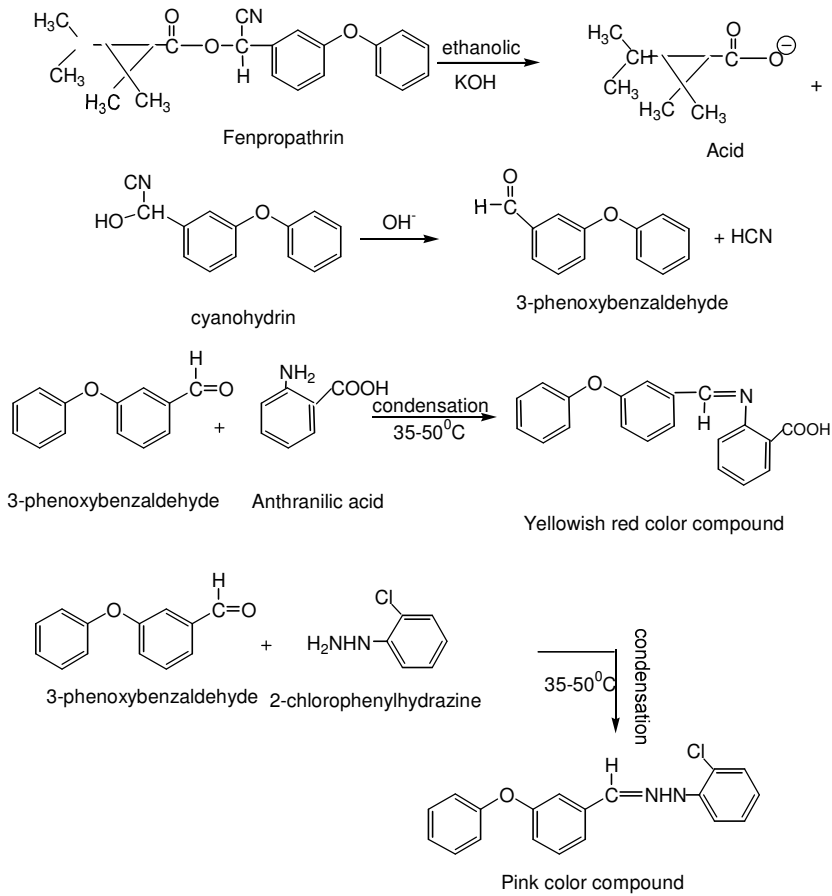
A HITACHI U 2001 spectrophotometric with 1.0 cm matched quartz cells were used for all absorbance measurement. An Elico Li-29 model pH metre with combined glass electrode was used for pH measurements.

### *Reagents and materials*

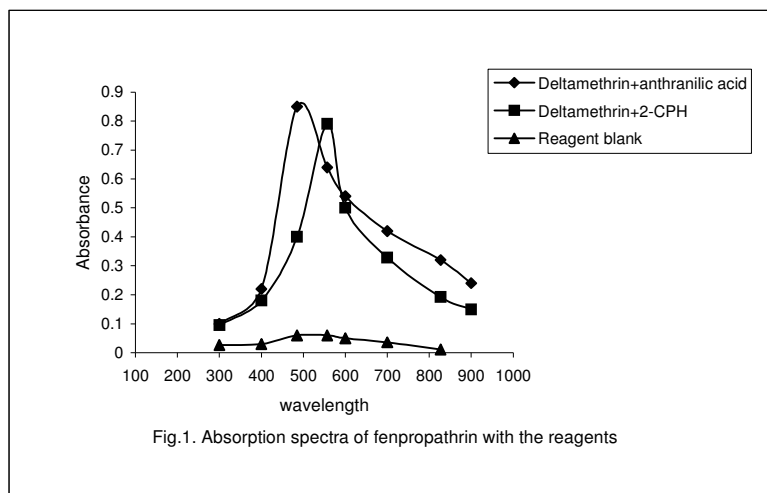
Technical grade samples of fenpropathrin were obtained from Bayer India limited, India. 0.25% of anthranilic acid, 2-chloro phenyl hydrazine was prepared by dissolving 0.25g, in 100 mL methanol. Fenpropathrin stock solution was prepared by dissolving appropriate amount of fenpropathrin in 100 mL acetonitrile. 10 mL of this solution was subsequently diluted to 100 mL acetonitrile. Fenpropathrin stock solution was preserved at 4 °C in a refrigerator and desired concentrations were prepared freshly. An amount of 3.4 mL concentrated sulphuric acid is added to 250 mL distilled water in a 500 mL flask. 25 g of monopotassium di hydrogen phosphate is added to this, shaken until dissolution is complete and diluted to 500 mL for pH 8.0.

### *General procedure*

Transfer 0.5-3.5 mL portions of fenpropathrin (10 µg/mL) solution of insecticide solutions into a clean dry 50 mL beaker. 4 mL of 2% ethanolic potassium hydroxide solution was added and allowed to stand for 7 min for complete hydrolysis, heated 40–45 °C for 45 min and neutralised with 0.1 N HCl, 2 mL of 0.25 % of anthranilic acid was added followed by one drop of concentrated HCl and heated to 50-55°C for 30 min for color development. The same procedure was carried out for 2-chloro phenyl hydrazine. The absorbance of the color derivatives were measured at  $\lambda_{\max}$  485 nm for anthranilic acid, 557 nm for 2-chloro phenyl hydrazine against reagent blank as shown in Figure 1. The formation of color derivatives was shown in Scheme.1.



**Scheme.1** Color product of the fenpropathrin with anthranilic acid and 2-chlorophenyl hydrazine



*Determination of fenpropathrin in their formulations*

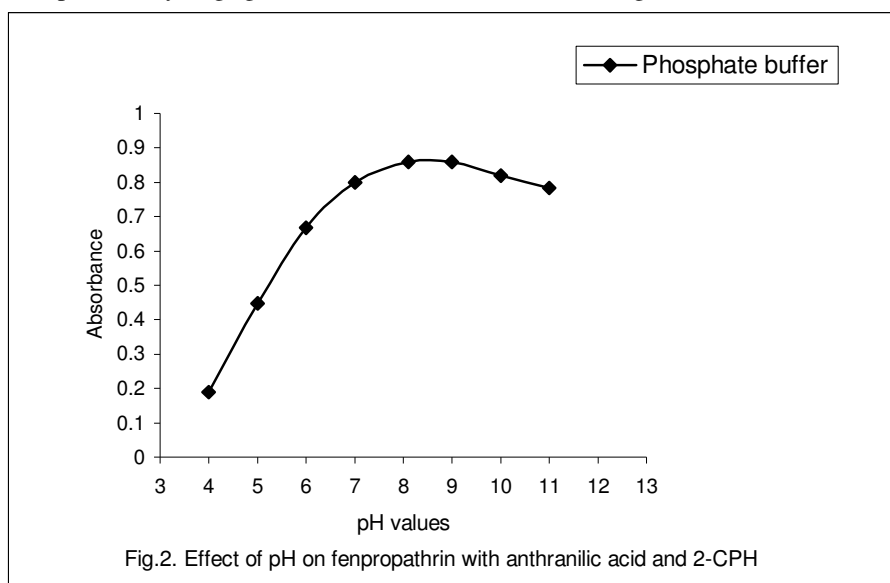
3 mL (50 mg) of fenpropathrin insecticide formulation was placed in a porcelain dish, and 20 mL of methanol was added. This mixture was stirred well and heated the samples on a hot water bath then evaporated the solvent. The procedure was repeated five times, and the resulting solution was diluted to 50 mL with methanol in a calibrated flask. The fenpropathrin was determined by the above procedure. The results were shown in Table 2.

*Determination of fenpropathrin in water samples*

The tap and river water samples were fortified with concentrations in the ranges from 0.5 – 3.0 and 0.7- 4.2 ppm in methanol for two methods, under study which are presented in the Table 3 and 4 respectively. Apart from the synthetic pesticide standards in n-hexane, aqueous samples were analysed with liquid-liquid extraction. Fresh water samples of river and tap water collected in amber glass bottles. A volume of 1 mL of 0.1M  $\text{Na}_2\text{S}_2\text{O}_3$  per litre of water sample was added on site to suppress the interferences of chloride, humic acid, fulvic acids. All samples were filtered through a micro separations in 0.45  $\mu\text{m}$  nylon filter to remove particulate matter. In order to avoid degradation of some of the pesticides under alkaline conditions<sup>11</sup>, the pH of the all water samples was adjusted to 5-6. Finally, extracts were evaporated to dryness on a steam bath and the residue was dissolved in MeOH. The amount was determined according to aforesaid procedure.

**Results and Discussion**

The method involved in alcohol alkaline hydrolysis of fenpropathrin to form 3-phenoxy benzaldehyde followed by condensation with anthranilic acid and 2-chloro phenyl hydrazine. The hydrolyzed fenpropathrin forms yellowish red and pink derivative with anthranilic acid, 2-chloro phenyl hydrazine in basic medium of pH 8-9 (as shown in Figure 2.) having  $\lambda_{\text{max}}$  485 and 557 nm. The corresponding reagent blanks have practically negligible absorbance at these wavelengths.



*Analytical data*

The optical characteristics, precision and accuracy data was shown in Table 1. Limit of quantification (LOQ) is given by the relation  $3\sigma/s$  and limit of detection is  $3\sigma/s$ , where  $\sigma$  is the standard deviation of the blank with respect to water and  $s$  is the slope of the calibration curve. Naturally, the limit of quantification slightly crosses the lower limit of Beer's law range. But, limit of detection is well below the lower limit of Beer's law range. The upper limit of the Beer-Lambert range is determined by a plot of absorbance against concentration at the volume of  $\lambda_{\max}$ . The Beer's law limits, molar absorptivity, Sandell's sensitivity, slope, intercept, correlation coefficient and optimum concentration range by photometric determinations are summarised in Table 1.

**Table 1.** Optical characteristics, precision and accuracy of the present method

Optical characteristics	Anthranilic acid	2-Chloro phenyl hydrazine
Concentration range, $\mu\text{g mL}^{-1}$	0.03 – 10.0	0.02-8.0
$\lambda_{\max}$ , nm	485	557
Color	Yellowish red	Pink
Limit of Detection, $\mu\text{g mL}^{-1}$	0.039	0.046
Limit of Quantification, $\mu\text{g mL}^{-1}$	4.163	4.349
Stability of the color, days	5	8
Molar absorptivity, $\text{L mol}^{-1} \text{cm}^{-1}$	$2.586 \times 10^4$	$3.924 \times 10^4$
Sandell's sensitivity, $\mu\text{g cm}^{-2}$	0.0205	0.0236
Regression equation, $Y=bx+a$ )	0.1057	
Slope (b)	0.0386	0.1282
Intercept (a)		0.0409
Standard deviation (S.D.) <sup>a</sup>	0.587	0.662
Correlation coefficient	0.9994	0.9986
Relative error, %	0.12	0.27

<sup>a</sup> Calculation for five samples containing same amount of fenpropathrin, Where  $x$  is the concentration in  $\mu\text{g mL}^{-1}$ .

*Effect of foreign ions*

The water samples (500 mL) were fortified with known amounts of fenpropathrin dissolved in 5 mL methanol. Known amounts of benzaldehyde dissolved in 10 mL of methanol were added, and the pH of each solution was adjusted to between 4 and 6 with 50% sulphuric acid. 10 g of  $\text{Na}_2 \text{SO}_4$  was dissolved in each sample and the fenpropathrin along with the aldehyde was extracted three times using 50 mL of chloroform for each extraction. The extracts were combined and placed in a 500 mL round bottom flask into which 100 mg *m*-chloroperbenzoic acid was dissolved. The resulting solution was refluxed on a hot water bath for a 15 min to convert the aldehyde into an acid. Thereafter, the solution was cooled, washed three times with 25 mL of 0.2 M  $\text{Na}_2 \text{CO}_3$  solution per wash to remove the acid and unreacted *m*-chloroperbenzoic acid. Finally, washed 3 to 5 times with distilled water using 50 mL for each 5 washing to remove excess carbonate. The chloroform solution was then dried over 10 g of anhydrous  $\text{Na}_2 \text{SO}_4$  and the solvent was evaporated by exposure to air. The residue obtained was dissolved in MeOH and then diluted to 250 mL with methanol in a calibration flask. Known amounts of this solution were placed in 25 mL conical flask. The determination of fenpropathrin was carried out with the anthranilic acid, 2-chloro phenylhydrazine .

**Table 2.** Determination of fenpropathrin insecticide in formulations.

Technical Grade Fenpropathrin	Anthranilic acid		2- Chlorophenyl hydrazine	
	Indicated label %	Found %	Indicated label %	Found %
Oil Spray	1	0.96	1	0.95
EC	10	9.82	10	9.85
EC	20	19.79	20	19.83

**Table 3.** Estimation of fenpropathrin in fortified water samples using anthranilic acid

Sample number	Fortifica- tion level ppm	Water samples			
		Tap water		River water	
		Amount ppm	Recovery %	Amount ppm	Recovery %
1	0.7	0.69	98.57	0.68	97.17
2	1.4	1.37	97.85	1.38	98.60
3	2.1	2.07	98.57	2.05	97.61
4	2.8	2.77	98.92	2.74	97.85
5	3.5	3.46	98.85	3.49	99.71
6	4.2	4.12	98.09	4.16	99.04
Average			98.47		98.33

**Table 4 .** Estimation of fenpropathrin in fortified water samples using 2-chloro phenyl hydrazine

Sample number	Fortifica- tion level ppm	Water samples			
		Tap water		River water	
		Amount ppm	Recovery %	Amount ppm	Recovery %
1	0.5	0.48	96.00	0.49	98.00
2	1.0	0.98	98.00	0.96	96.00
3	1.5	1.47	98.00	1.48	98.66
4	2.0	1.97	98.50	1.95	97.50
5	2.5	2.48	99.20	2.47	98.80
6	3.0	2.97	99.00	2.98	99.33
Average			98.20		98.05

## Conclusions

The color of derivatives of fenpropathrin with anthranilic acid and 2-chloro phenylhydrazine is stable at room temperature of 5 and 8 days . The proposed method is simple, rapid and can be used for the determination of fenpropathrin in trace amounts. When compared with the literature method as summarized in Table 5. Interference from many substances other than aldehyde is eliminated by the selective extraction procedure used and also by measuring the absorbance of the sample against that of a corresponding crop control (blank). Additional advantages of these methods are that color develop instantaneously and are stable for long

**Table 5.** Comparison of present method with the reported methods

Sample	Fenpropathrin Added $\mu\text{g mL}^{-1}$	Anthranilic acid			2-Chloro phenyl hydrazine			Reference method <sup>10</sup>		
		Found $\mu\text{g mL}^{-1}$	Recovery %	f-test	t-test	Found $\mu\text{g mL}^{-1}$	Recovery %		f-test	t-test
Tap water	5	5.09	101.8	0.68	0.41	5.04	100.8	0.98	0.27	$102 \pm 7$
River water	10	9.97	99.7	0.52	0.26	9.95	99.5	0.61	0.34	$89 \pm 3$

period of time. Thus excess reagent has no effect on the absorbance of the colored derivatives. Moreover, this method do not involve the elaborate cleanup procedures and can be suitably adopted for routine check-up of the purity of fenpropathrin in their formulations, water samples. The performance of the proposed method was compared statistically in terms of student's 't' test and the variance ratio of 'f'-test. The 'f' and 't' test indicates the significance of the proposed method with the reference method<sup>10</sup>.

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