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Spectrophotometric Determination Of Fenvalerate In Environmental Samples

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ABSTRACT

A facile simple, sensitive, rapid and non-extractive spectrophotometric method was described for the determination of fenvalerate in its formulations, water and grain samples. The methods are based on the hydrolysis of fenvelarate with methanolic NaOH to form a 3-phenoxy benzaldehyde. The resultant aldehyde group was condensed with 4-chloro aniline in basic medium to give yellowish orange coloured product having λ_{max} 482 nm. The formation of color derivative with the coupling agent is instantaneous and stable for 42 h Beer's law was obeyed in the concentration range of 0.3-15.0 $\mu g\ ml^{-1}$. The experimental results indicate that the procedure can eliminate the fundamental interferences caused by other pesticides and non-target ions, which made these methods more sensitive and selective. The method was applicable to the determination of fenvalerate residue in water and food grain samples up to ng level.

KEYWORDS

Fenvalerate;
Spectrophotometry;
Formulation;
Water and food grain samples.

INTRODUCTION

Fenvalerate belongs to the group of synthetic pyrethroids and is exceptionally active as a contact and stomach poison against lepidopterous larvae. Besides high insecticidal activity, it has moderately long persistence in plants[1]. It is also toxic to birds and mammals (LD_{50} = 450 mg/kg). This insecticide is intensively used for a variety of crops and its residue enters into inland water sources from the fields where it has been applied and contaminates the adjacent streams, ponds, lakes, wells, etc. Several analytical techniques have been developed for the determination of synthetic pyrethroids[2-8]. Some techniques suffer from low sensitivity and selectivity. Other methods require a large number of solvents

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for the extraction of color residues. There is thus a need to develop an entirely new method, which would overcome the existing inadequacies in the determination of fenvalerate.

Spectrophotometric methods can be used for the determination of synthetic pyrethroids occurring in many samples. The availability of spectrophotometric apparatus and the simplicity of analytical procedures made the technique very attractive for a wide range of application. A recent literature survey also reveals that there has been no reported literature for effective and sensitive spectrophotometric methods so far. In the present investigation, determination of fenvalerate based on the condensation of hydrolysed result an aldehyde group with 4-chloro aniline to form color derivative and the developed method successfully employed to formulations, water and grain samples.

EXPERIMENTAL

Apparatus

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

All the chemicals and reagents used were of analytical reagent grade and double-distilled water was used through out experiments. The reagents like sodium hydroxide, sodium nitrate, potassium carbonate, anhydrous sodium sulphate and HCl were purchased from S.D. fine chemicals, Mumbai, India. 4-chloro aniline, methanol, chloroform were purchased from Merck Chemicals, Mumbai, India. The technical grade samples of fenvalerate pesticide in the form of 1% spray, 10% and 20 % EC were obtained from Bayer India Ltd., Mumbai, India. The reagents like sodium hydroxide (2%), sodium nitrate (0.3%), 1N HCl were prepared. The solvents like methanol, chloroform, acetone were purified and employed for the present investigation.

Preparation of stock solution of fenvelarate

3 ml of 2% sodium hydroxide was added to 50mg of the fenvalerate, after 5min, the solution was made up to the mark in a 100ml standard flask with doubly distilled water.

General procedure

0.6-2.6 ml portions of standard fenvelarate solutions were taken into a clean dry 50 ml beakers. 3 ml of 2% methanolic NaOH solution were added to fenvelarate pesticide solution and allowed to stand for 5 min for complete hydrolysis, heated at 40-45°C for 30 min, and neutralised with 0.1 N HCl. 1.5 ml of 0.2% 4-chloro aniline was added, followed by one drop of con HCl, and the solution was heated at 50-55°C for 30 min. for color development The absorbance of the fenvalerate color derivative was measured as 482 nm. The parameters are shown in TABLE 1.

Determination of fenvalerate in its formulations

2ml of fenvalerate insecticide formulation was placed in a porcelain dish, and 30 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 fenvalerate was determined by the above procedure. The results are

TABLE 1: Optical characteristics, precision and accuracy of 4-chloro aniline

Compound	Fenvalerate
Color	Yellowish orange
Stability of color(h)	42
Beer's law range ($\mu g\ ml^{-1}$)	0.3-15.0
λ_{max} (nm)	482
Molar absorptivity($1\ mol^{-1}\ cm^{-1}$)	3.574×10^4
Limit of detection ($\mu g\ ml^{-1}$)	0.196
Limit of quantification($\mu g\ ml^{-1}$)	0.876
Sandell's sensitivity ($\mu g\ cm^{-1}$)	0.0878
Regression equation (Y=bx+a)	
Slope (b)	0.134
Intercept (a)	0.9981
Correlation coefficient (r)[c]	0.9999
RSD (%)	0.38
Error, %	0.05

Where x is the concentration in $\mu g\ ml^{-1}$, [b] n= 5, [c] five replicates

TABLE 2: Determination of fenvalerate insecticide in formulations (%)

Technical grade sample fenvalerate	Indicated on label	Found[a]	Reference method[7]
Spray	1%	0.97	0.93
E.C.	10%	9.8	9.6
E.C.	20%	19.8	19.6

[a]Mean of five determinations

shown in TABLE 2 .

Determination of fenvalerate in fortified water samples.

The distilled and tap water samples were fortified with concentrations in the ranges from 0.6-2.6 ml in methanol, under study which are presented in the TABLE 3 respectively. The fortified water samples was extracted with chloroform. The combined extracts were washed with 0.1 M potassium carbonate solution to break any emulsion formed during the extraction and dried over anhydrous sodium sulphate. Finally, extracts were evaporated to dryness on a steam bath and the residue was dissolved in methanol and the amount was determined using the procedures described earlier.

Determination of in grain samples(rice and wheat)

A 50 g sample of grains (rice and wheat) was uniformly mixed with 10 ml of methanol containing various amounts of the insecticide, and left for one day to give acclimatise the environmental conditions of the samples. The insecticidal residues were extracted according to the procedure of Deshmukh and Sidhu[6]. The extracts were treated in the manner given for standard solution preparation and determination. The method indicates the determination of fenvalerate in grain samples was shown in TABLE 3.

RESULTS AND DISCUSSIONS

The method involved alcohol alkaline hydrolysis of fenvalerate to form 3-phenoxy benzaldehyde followed by condensation with 4-chloro aniline. The hydrolyzed fenvalerate that forms a yellowish orange derivative with 4-chloro aniline in basic medium having λ_{max} 482 nm. The corresponding reagent blanks have practically negligible absorbance at these wavelengths.

Effect of reagent concentration

Various concentrations and volume ranges of fenvalerate were studied. However, the following optimum concentrations and volume ranges were needed for color development. For the proposed method, it was found that 3.0 ml of 2% ethanolic KOH and 1.5 ml of 0.2% 4-chloro aniline, was necessary to achieve the maximum color intensity.

Analytical data

The optical characteristics, precision and accuracy data was shown in TABLE 1. Limit of quantification (LOQ) is given by the relation 3 σ/s and limit of

TABLE 3: Recovery of fenvalerate from fortified water and grain samples with 4-chloro aniline

Sample number	Fortification level (ppm)	Water samples				Grain samples			
		Tap water[a]		Distilled water		Rice[b]		Wheat[b]	
		Amount (ppm)	Recovery (%)	Amount (ppm)	Recovery (%)	Amount (ppm)	Recovery (%)	Amount (ppm)	Recovery (%)
1	0.6	0.57	98.33	0.583	97.16	0.575	95.83	0.57	95.00
2	1.0	0.99	99.00	0.989	98.90	0.982	98.20	0.978	97.80
3	1.4	1.38	98.92	1.37	97.92	1.37	97.15	1.37	98.00
4	1.8	1.75	97.22	1.77	98.33	1.74	96.66	1.73	96.11
5	2.2	2.15	97.72	2.16	98.18	2.17	98.86	2.14	97.27
6	2.6	2.56	98.46	2.45	94.20	2.52	96.92	2.52	96.92
Average			98.27		97.44		97.38		96.85
SD			0.6928		1.6898		1.0932		1.1307

[a] Collected from Teluguganga municipal water
[b] Collected from Local Market

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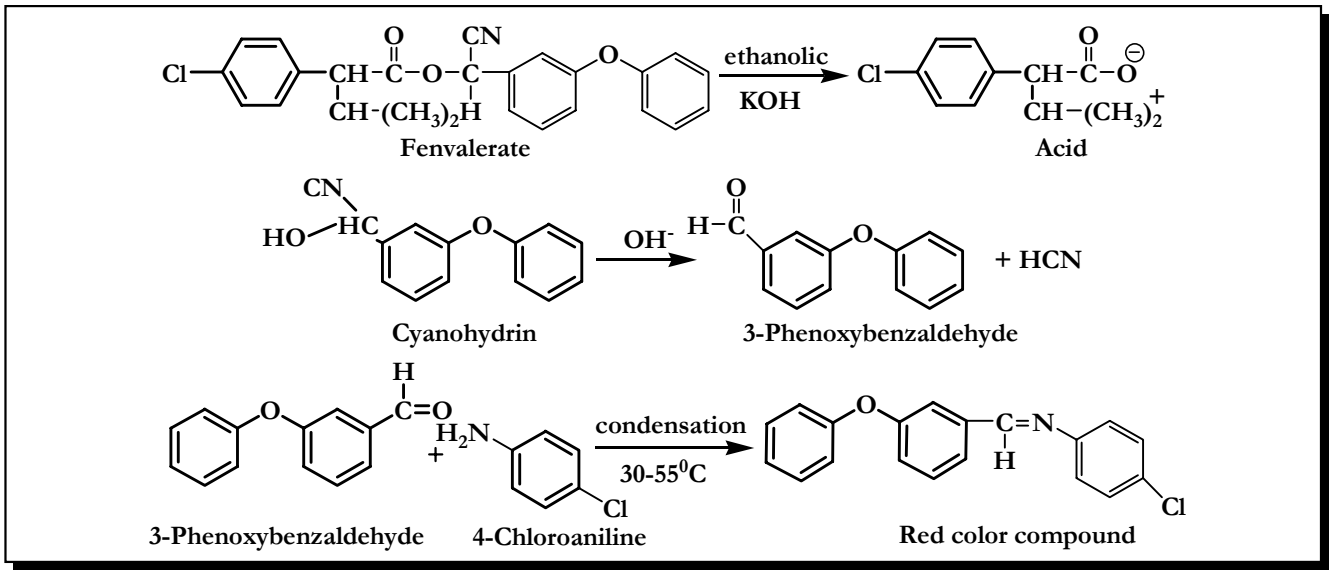

TABLE 4: Comparison of fenvalerate in its environmental samples (in percentage)

Sample	Proposed method of fenvalerate	t-test	f-test	Reported method[9]
Tap water	98.27	0.28	0.10	96.83
Distilled water	97.44	0.19	0.49	98.50
Rice	97.38	0.31	0.07	94.55
Wheat	96.85	0.12	0.44	95.65

detection is 3s/s, where s 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 λ_{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.

Effect of non target species

The water samples(1 lit) were fortified with known amounts of fenvalerate 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 3 and 4 with 50% sulphuric acid. 10 g of sodium sulphate was dissolved in each sample and the fenvalerate 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 sodium carbonate solution per wash to remove the acid and unreacted m-chloroperbenzoic acid. Finally, washed 3 to 4 times with distilled water suing 50 ml for each 5 washing to remove excess carbonate. The chloroform solution was then dried over 10 g of anhydrous sodium sulphate and the solvent was evaporated by exposure to air. The residue obtained was dissolved in methanol 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 fenvalerate was carried out with the 4-chloro aniline.

CONCLUSION

The color of derivatives of fenvalerate with 4-chloro aniline is stable at room temperature of 42 h. The proposed method is simple, rapid and sensitive and can be used for the determination of fenvalerate in trace amounts. 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 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 required by other methods[7,9] and can be suitably adopted for routine check-up of the purity of fenvalerate in their formulations, environmental 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 methods[7,9].

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