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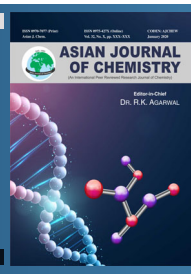

Determination of Fenpyroximate Acaricide in Vegetables, Soil and Water Samples using UV-Visible Spectroscopy

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Modern agriculture makes use of chemical pesticides to increase the crop productivity so as to meet the daily needs of uncontrolled population growth. These increase the productivity neglecting the fertility of soil and food quality, hence risking the health of human beings including animals. Fenpyroximate is a kind of acaricide which attacks and kills mites and decreases the growth of larvae. A method is established for the detection of fenpyroximate and stop excessive use of pesticide. After performing several tests on various wavelengths, the λ_{max} for the detection of fenpyroximate was 435 nm for azo dye. Limit of detection (LOD) and limit of quantification (LOQ) was found to be 0.687 μg mL^{-1} and 2.083 μg mL^{-1}, respectively. Furthermore, molar absorptivity, Sandell′s sensitivity were calculated to be 2.3×10^{-7} mol^{-1} cm^{-1} and 1×10^{-5} μg cm^{-2}, respectively. The azo dye follows Beer′s law in the range 5 μg to 14 μg in 10 mL that can be easily detected by using spectrophotometric analysis. This method is very sensitive, low cost and less time consuming. The present method is applied successfully in various vegetables (*i.e*. apple, cucumber, potato, spinach, *etc*.) soil and water samples.

Keywords: Pesticides, Fenpyroximate, UV-Vis spectrophotometry.

INTRODUCTION

Pesticides such as acaricides, insecticides and herbicides are used to improve the production of crops by killing the pests, mosquitoes, mice and rats [1-6]. Fenpyroximate is pyrazole acaricide chemically known as *tert*-butyl 4-[[(1,3-dimethyl-5-phenoxypyrazol-4-yl)methylideneamino]oxymethyl]benzoate [7] and first synthesized in the laboratory by Halvorsen *et al*. [8]. Fenpyroximate is widely used to prevents acaricides and effective against mites and it also inhibits the growth of nymph, larva [9]. Fenpyroximate target site is mitochondrial of mite and stops feeding of mites [10]. It is basically used to control mites in apple, orange, pears, tomato, spinach, cucumber, potato, *etc*. [11,12] and widely used in China [13]. The toxic effect of fenpyroximate in the human body is very low by dermal but it effects moderately by inhalation [14,15] and causes irritation of eyes and skin [16,17].

Due to the adverse effect of pesticides many techniques were developed to determine the presence of pesticides in different environmental samples. The techniques such as nuclear magnetic resonance (NMR) [18], gas chromatography (GC) [19], high-performance liquid chromatography (HPLC), Fourier transforms infrared spectroscopy (FTIR) [20,21], *etc*. which are time-consuming and very expensive. Al-Rahman *et al*. [22] determined fenpyroximate acaricide in citrus fruits, grapes and apples by HPLC techniques. Hammad [23] determined fenpyroximate residue in grapes using HPLC and photodiode array. Kim and Myung [24] performed an experiment in different types of honey by tandem mass spectroscopy and liquid chromatography and used solid-phase extraction. Ma *et al*. [25] have reported the determination of pyrazole fenpyroximate by SPE using HPLC in different environmental water samples. In the present work, low cost, highly sensitive, simple and selective method was developed. In this method, a coupling reaction with fenpyroximate is performed by using *p*-dimethylamino benzaldehyde reagent as a coupling agent with sodium nitrate and hydrochloric acid. The present method is applied

to determine fenpyroximate in various vegetable samples collected from the different agricultural fields.

EXPERIMENTAL

Analytical grade reagent was used for analysis and double distilled water used for the experiments. Fenpyroximate (purity > 97%) and *p*-dimethylamino benzaldehyde were procured from from Sigma-Aldrich Pvt. Ltd. while sodium nitrate and hydrochloric acid were purchased from Merck, Mumbai, India. All the solutions were prepared in Millipore water.

Absorption spectrum was performed on double beam spectrophotometer made by cary-60 UV-visible spectrophotometer (Agilent Technologies) with accuracy and Quartz Glasses used for analysis. pH measurement was performed with basic pH meter pH700 EUTECH instruments and centrifuge was used of REMI R- 4C.

Samples collection area: Berla, one of the blocks of Bemetara district in Chhattisgarh state of India, located at geographic position 21.5255º N latitude and 81.4773º E longitude at an elevation of 292 m above mean sea level, covering an area of 11.4 km^2. The sample collections from different farm houses and agricultural fields had been performed. Various environmental samples such as vegetables, soil and water has been collected from these fields.

Preparation of dye sample for UV-visible spectrophotometer: Different vegetable samples (*i.e*. orange, pears, tomato, spinach, cucumber, potato) were collected from different fields from Chhattisgarh state and stored in sealed container. Then they were cut and chopped on the first day of experiment then 1 µg of fenpyroximate was added and kept apart for 12 h [26]. The sample was now crushed, filtered and then NaOH was added for hydrolysis. Then $NaNO_2$ and HCl was taken in other graduated tube at > 5 ºC and *p*-dimethylamino benzaldehyde was added. Now, this mixture was added in obtained by hydrolyzed maintaining the temperature below 5 ºC. It was maked up with 10 mL of double-distilled water. Finally, 3 mL of mixture was taken for the UV-visible analysis.

Determination of fenpyroximate in vegetables, fruits and soil samples: For the determination of fenpyroximate sprayed samples of vegetables and fruits were collected. About 10 g of the sample was chopped, crushed and then washed with Millipore water twice. Now the samples were centrifuged, filtered and then 10 mL of unknown fenpyroximate was added. The mixture was kept apart for 3-4 h and then aliquot solution of the sample was used for the determination of fenpyroximate by the proposed method.

Determination of fenpyroximate in water samples: Analysis of fenpyroximate in water samples from different water sources like rives, ponds, *etc*. were collected and kept in an air tight container. Then fenpyroximate was added and allowed to stand for 3-4 h. The solution was now filtered and 1 mL of EDTA was added in order to remove the metal ions present in the samples. An aliquot amount of the solution was taken for determination of fenpyroximate by proposed method.

RESULTS AND DISCUSSION

Reaction mechanism: When fenpyroximate was hydrolyzed by NaOH, it is dissociated into 1,3-dimethyl-5-phenoxy-pyrazole-4-carbonitrile. Resulting compound reacted with the mixture containing *p*-dimethylamino benzaldehyde, $NaNO_2$ and HCl at > 5 ºC. After adding both the mixture, a yellow coloured azo dye was obtained. All the mechanism is shown in **Scheme-I**.

UV-visible analysis: In the present study, fenpyroximate reacted with *p*-dimethylamino benzaldehyde and forms yellow colour azo dye. The absorption spectra of azo dye was recorded at 435 nm maximum absorbance by UV-visible spectrophotometer (Fig. 1a). The calibration curve of fenpyroximate between concentration and absorbance shows strong correlation coefficient which obeys Beer′s law in 10 mL of final solution at 435 nm wavelength (Fig. 1b). The Sandall′s sensitivity and molar absorptivity were calculated and found to be 1×10^{-5} µg cm^{-2} and 2.3×10^{-7} mol^{-1} cm^{-1}, respectively. The limit of detection (LOD) and limit of quantification (LOQ) were found to be

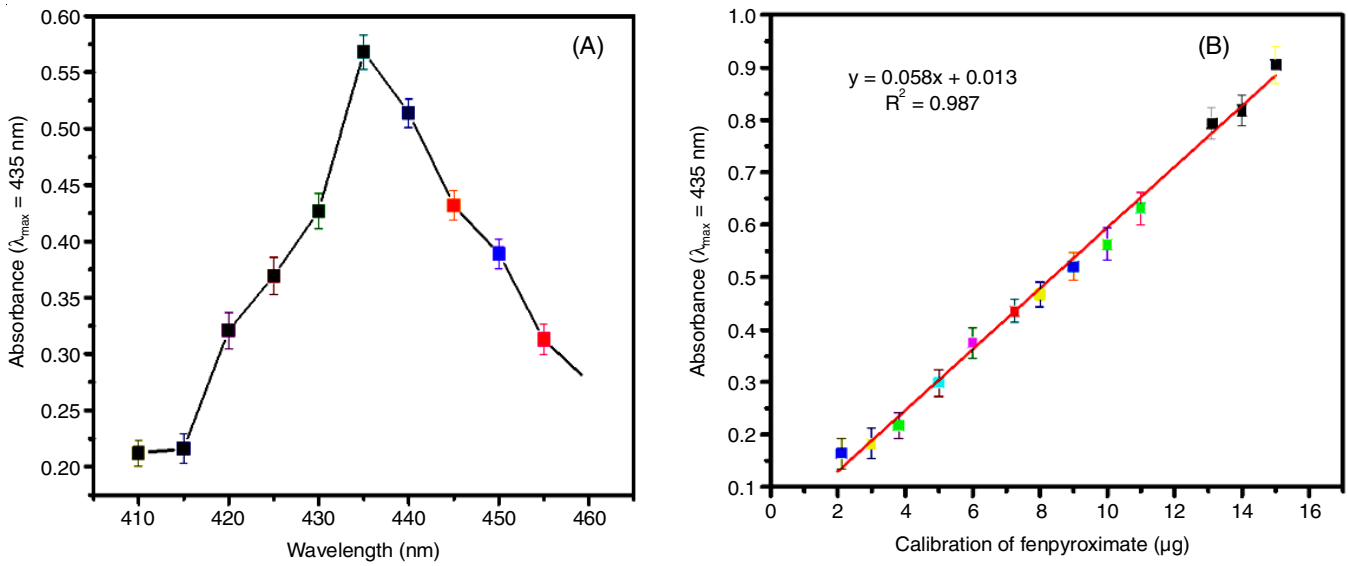
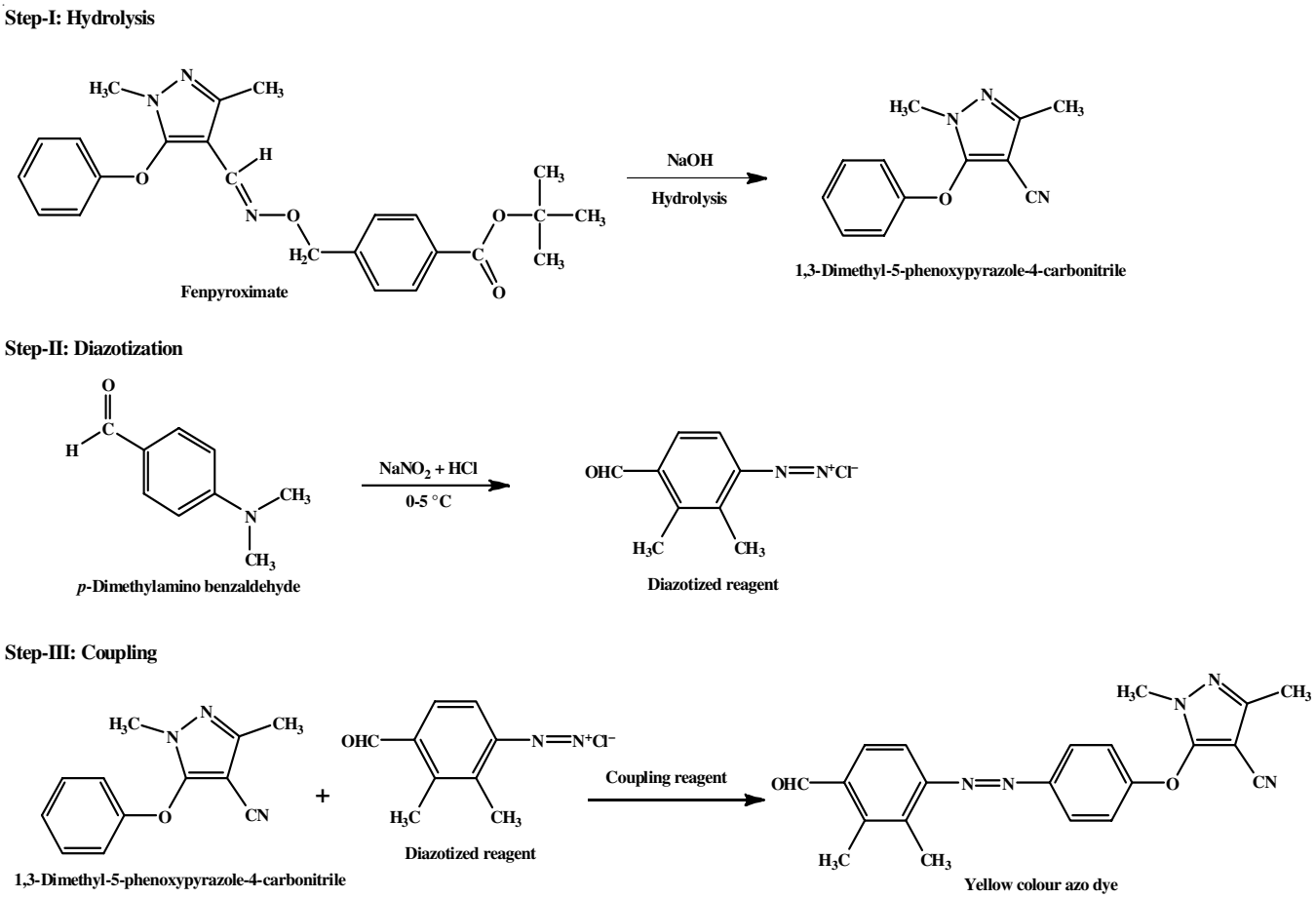


Fig. 1. (A) UV-Vis absorbance spectra of azo dye colour complex and (B) Calibration curve of fenpyroximate



Scheme-I: Chemical reaction for the determination of fenpyroximate (Steps I-III)

0.687 μg mL^{-1} and 2.083 μg mL^{-1}, respectively which were sufficiently low. In all cases, these limits were below the maximum residue limits (MRLs) and average recovery ranges from 85% to 96% and RSD value was lower than 2 %. Present method also showed a very good repeatability by RSD value.

Effect of temperature, pH, time and reagent: It was found that 15 min was required for full colour development and the colour was stable for several days at > 5 ºC. Absorbance value was obtained at the pH 6 and found suitable for complete colour development of pesticide at lower and at higher pH the absorbance value decreases (Fig. 2a).

When 1 mL mixture (3 mL HCl and 3 mL $NaNO_2$) was added to 1 mL of *p*-dimethylamino benzaldehyde, the reaction was completed. When amount of *p*-dimethylamino benzaldehyde was increased or decreased the absorbance value also changed. When the concentration of *p*-dimethylamino benzaldehyde was altered, firstly absorbance value was increased by increasing the concentration of *p*-dimethylamino benzaldehyde and then absorbance values decreases (Fig. 2b).

Effect of interference and reproductivity: It is found that different types of compounds were present in the vegetables, soil and water samples, foreign species and different types of pesticides were added to the solution containing 10 μg of 10 mL fenpyroximate. It is found that no interference of the studied foreign species occured in the proposed method (Table-1).

TABLE-1
TOLERANCE LIMIT OF INTERFERING IONS AND FOREIGN SPECIES ON DETERMINATION OF FENPYROXIMATE USING SPECTROPHOTOMETRIC METHOD

Foreign species	Tolerance limit (μg mL^{-1})	Foreign species	Tolerance limit (μg mL^{-1})
Butachlor	400	Ca^{2+}	150
Bifenthrin	350	Zn^{2+}	520
Ethion	250	SO_4^{2-}	470
Dicofol	300	Mn^{2+}	300
Pyridine	300	Al^{3+}	600
Thiacloprid	250	Ba^{2+}	600
Fenvalerate	250	Cu^{2+}	200

Method validation

Linearity, accuracy and precision: In this experiment, a linear graph between concentration of fenpyroximate *versus* absorbance and plotted a graph between intercept and slope and found correlation coefficient of regression constant. Accuracy and precision was also investigated for the proposed method and fenpyroximate was analyzed three times. The recovery range found 85% to 96%. In this method, the RSD values do not exceed ± 2% (Table-2).

Robustness and ruggedness: Robustness and ruggedness were also evaluated. Parameters like temperature, pH and time changes sometimes but the values observed has not changed for this method.

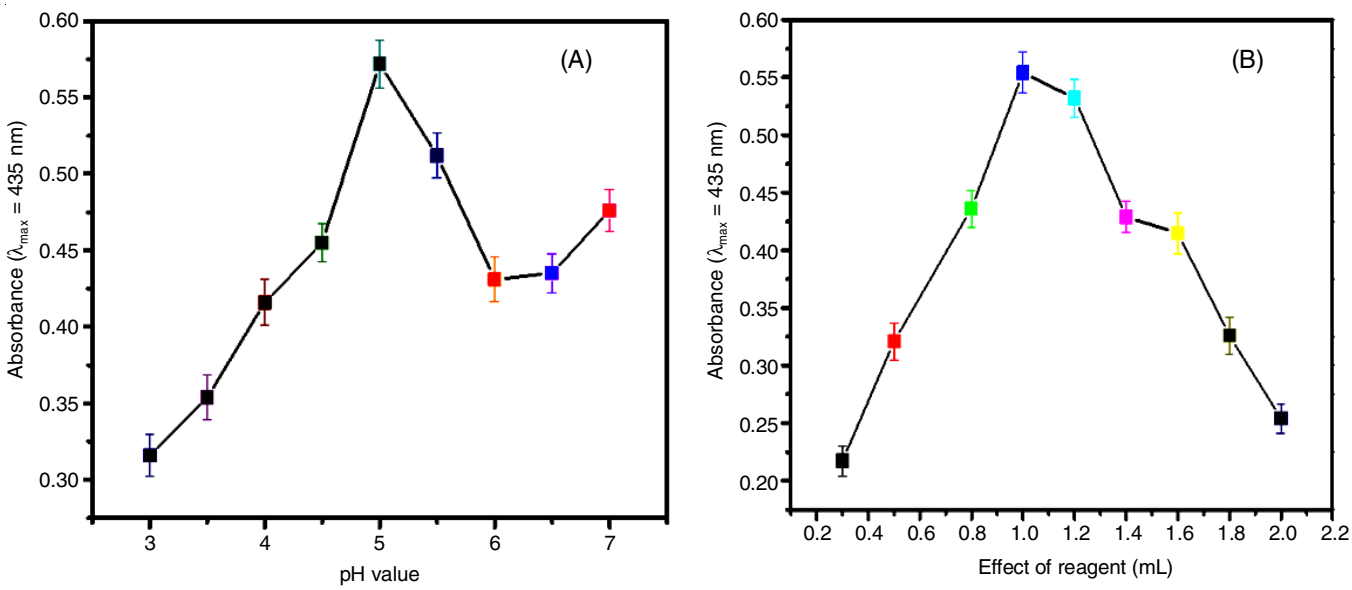


Fig. 2. The graph plotted between (A) pH value *versus* absorbance and (B) effect of *p*-dimethylamino benzaldehyde *versus* absorbance

TABLE-2
OPTICAL CHARACTERIZATION AND STATISTICAL DATA OF THE REGRESSION EQUATION FOR THE REACTION OF FENPYROXIMATE

Parameter	Value for the reaction
λ_{max} (nm)	435
Colour	Yellow coloredazo dye
Beer's law limit (µg mL^{-1})	5 to 14
Molar absorptivity × 10^{8} (L mol^{-1} cm^{-1})	2.3×10^{-7}
Sandell's sensitivity × 10^{-6} (µg cm^{-2})	1×10^{-5}
Detection limit (µg mL^{-1})	0.7
Quantization limit (µg mL^{-1})	2.1
Regression equation:	y = 0.058x + 0.013
Relative standard deviation (%)	2.19
Intercept (a)	0.058
Slope (b)	0.013
Correlation coefficient (r)	0.987

Applications

The proposed method is applied successfully in the determination of fenpyroximate in the environmental samples *viz.* vegetables, soil and water samples. The recovery and RSD data shown in Table-3 implies the validation of the proposed method.

Conclusion

A new method is proposed for the determination of fenpyroximate. This method is sensitive and cost effective for the determination of environmental samples *i.e.* vegetables, soil and water samples and found to be the best in comparison with other methods. The interference of foreign species is negligible and LOD and LOQ were very low as compared to other expansive methods. This method is found to be very adaptable and cost effective.

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TABLE-3
RESULT OBTAINED FROM THE APPLICATION OF THE PROPOSED METHOD FOR THE DETERMINATION OF FENPYROXIMATE IN VARIOUS ENVIRONMENTAL SAMPLES

Sample	Fenpyroximate originally found* (µg mL^{-1})	Fenpyroximate added (µg mL^{-1})	Total fenpyroximate found (µg mL^{-1})	Recovery (% ± RSD)
Water**	3.19	1	4.10	91.0 ± 0.21
Soil***	5.61	1	5.61	92.0 ± 0.42
Apple***	3.14	1	4.02	88.2 ± 0.53
Orange***	4.15	1	5.11	96.0 ± 0.97
Pears***	4.25	1	5.19	94.4 ± 0.50
Tomato***	3.87	1	4.72	85.0 ± 0.01
Spinach***	3.20	1	5.10	92.6 ± 0.12
Cucumber***	4.28	1	5.18	90.4 ± 0.52
Potato***	4.06	1	5.01	94.2 ± 0.50

*Mean of three replicate analyses; ** Water sample taken 50 mL; ***Sample taken 10 g, Value are Mean ± RSD, for three determinations. Recovery calculation as the amount added found/amount added × 100.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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