



A simple spectrophotometric method for determination of propoxur using 4-aminopyridine

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ABSTRACT

A facile, rapid, sensitive and inexpensive spectrophotometric method for the determination of propoxur in insecticidal formulations (samples dissolution in methanol) and fortified water, grains (extraction with CHCl_3). Propoxur, also known as undeen or arprocarb contains the active ingredient 2-isopropoxyphenyl-N-methylcarbamate. Alkaline hydrolysis yields 2-isopropoxyphenol, which couples directly with diazotized 4-aminopyridine, in a weakly alkaline medium, to give a yellow coloured phenol derivative (λ_{max} 469nm). Beer's law was obeyed over concentration range of $0.5\text{-}12\mu\text{g ml}^{-1}$. Molar absorptivity and sandell's sensitivity were found to be $3.268 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.007 \mu\text{g cm}^{-2}$. Method has been satisfactory applied for propoxur in various environmental samples.

Keywords: Propoxur, 4-Aminopyridine, spectrophotometer.

INTRODUCTION

Pesticides have been used in the public health sector for disease vector control and in agriculture to control and eradicate crop pests for the past several decades[1]. The application of insecticide a group of pesticides, in crop fields for selective control of pests in the modern age has led to serious environmental contamination resulting in greater loss of crop productivity and growth of many beneficial microorganisms, phytoplankton's etc. [2].

Carbamate pesticides are essential to agricultural communities; their use has been increased substantially in recent years as a consequence of their selective insecticidal properties and low mammalian toxicity. Hence, the number and quantities of carbamate pesticides used in agriculture continue to increase, replacing other types of pesticides such as organochlorine and organophosphorous pesticides[3-4]. One of the most important carbamates, which is widely used in agriculture, is propoxur [2-(1-methylethoxy)phenylmethyl carbamate]. In view of its wide application there is a need for the development of sensitive and reliable methods for the assessment of the quality of insecticidal formulations and for the quantification of the insecticidal residues in environmental samples.

Many methods have been developed for the determination of propoxur and its metabolites in different matrices. Most methods employ chromatographic techniques: thin-layer chromatography (TLC)[5-7], gas chromatography (GC)[8-11], liquid chromatography[12-16] and HPLC[17].

Many spectrophotometric methods have also been developed for the determination of propoxur, most of them based on the previous alkaline hydrolysis of propoxur to yield 2-isopropoxy phenol followed by coupling with different chemical reagents (such as 3-nitroaniline-4-sulfonic acid[18-19], sulfanilic acid[20], 3,5-dibromo-p-benzoquinochloramines [21], 4,4-diaminophenolsulfone[22-23], 2-aminobenzophenone[24], p-dimethylphenylene diaminedihydrochloride[25], 4-aminoantipyrine[26], p-nitroaniline[27] and 2,4-dichloroaniline [28]) to produce colored compounds.

In this paper, a simple and sensitive spectrophotometric method is proposed for the determination of propoxur using diazotized 4-aminopyridine as a coupling agent. The reaction mechanism is shown in Fig. 1. The developed method is extended to the determination of propoxur in commercial formulations and environmental samples

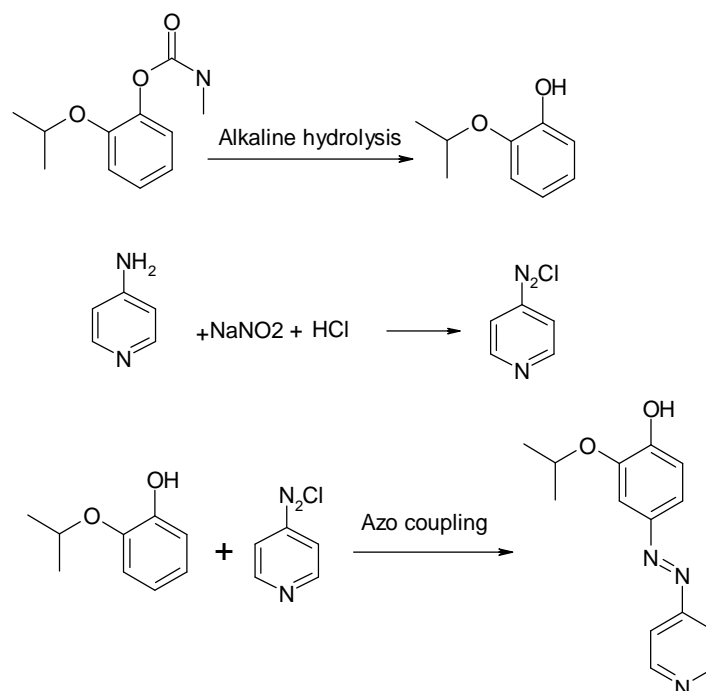


Fig:1 Reaction Mechanism

EXPERIMENTAL SECTION

Reagents

All reagents used were of AnalaR grade and doubly distilled water was used throughout the experiment.

Preparation of Standard solutions

A stock solution containing 1 mg/ml propoxur (Bayer, India) was prepared in 20% methanol and working standards were prepared by appropriate dilution of the stock solution. Sodium nitrite: 0.5% aqueous solution. Sodium hydroxide: 2% aqueous solution. Hydrochloric acid: 1N aqueous solution. 4-Aminopyridine: 0.2% solution prepared in 1N hydrochloric acid. Diazotized 4-aminopyridine: 0.1% 4-aminopyridine, 0.5% sodium nitrite and 1N hydrochloric acid were added with continuous shaking. The solution was stable for 48 h.

Apparatus

A Hitachi U-3400 spectrophotometer with 10 mm glass cells was used for all spectral measurements; pH measurements were made with an Elico pH meter Model CL-110.

Procedure

Preparation of calibration curve

An aliquot containing 0.5 – 10 $\mu\text{g/ml}$ of propoxur was taken in a 25 ml standard flask and diazotized 4-aminopyridine has been added, followed by 2% sodium hydroxide solution, with continuous shaking in an ice bath. A yellow dye formed. The solution was made up to the mark and kept for 15 min for full color development. The absorbance of the colored solution was measured at 469 nm against the reagent blank.

Formulations

Amount equivalent to 50 mg of insecticide dissolved in 100 ml of methanol in volumetric flask. Aliquots (10 ml) of solution was diluted to 100 ml with methanol.

Determination of propoxur in water samples

pH of each water samples was adjusted to 3-4 with 20% sulphuric acid, one liter samples of distilled water and tap water was fortified with different concentrations of insecticide dissolved in methanol. Each sample was extracted with chloroform (2×100 ml). The extracts were combined and washed with 20 ml of 0.1 M K_2CO_3 solution to

break any emulsions. The chloroform extracts were dried over anhydrous sodium sulfate in a filter funnel and the filtrate was collected in a 250 ml calibrated flask. The filter funnel was washed with 20 ml of chloroform and the volume of the filtrate was made up to the mark, known aliquots of chloroform extracts were taken and evaporated on a water bath at about 50°C. The residue was dissolved in 10 ml methanol. The solution was then transferred into a separating funnel with 25 ml of water. To this, diazotized 4-aminopyridine and 2% sodium hydroxide were added, then the yellow color developed spontaneously.

Determination of propoxur in food samples

Different samples of plant materials like grains (rice and wheat) 25 g of each were collected from the fields where propoxur had been sprayed. The samples were weighed, macerated and blended in a mixer. It was extracted using 25 ml of chloroform blended sample and it was extracted using 25 ml of chloroform. After extraction, the samples were spiked with different concentrations of propoxur in 5 ml of methanol. The spiked samples were blended for a further 2 min. The chloroform solution was then decanted into a 250 ml calibrated flask through Whatman No. 1 filter paper. Blending and decanting was repeated twice with 10 ml portions of chloroform. The extracts were combined and diluted to the mark. The chloroform extract was evaporated off, under reduced pressure using a water bath at about 50°C. The residue was dissolved in 10 ml of methanol and the color developed as described before

RESULTS AND DISCUSSION

The optimum conditions were established by alternating one variable at a time. The yellow colour species formed by propoxur derivative shows maximum absorbance at 469 nm. The reagent blank has negligible absorbance at this wavelength. Beer's law was obeyed in the range of 0.5 – 10 µg ml⁻¹. Molar absorptivity and Sandell's sensitivity were found to be 3.268×10^4 l mol⁻¹ cm⁻¹ and 0.007 µg cm⁻² respectively. The colour of the dye formed was found to be stable for 48h. This is an additional advantage of the method than reported by Harikrishna and Naidu²⁶.

The suitability of the proposed method was studied by analysis of six replicate samples containing 5 ppm of propoxur. The relative standard deviation values are given in Table-1.

Table 1 Characteristics of the method

Compound	Propoxur	
	Present work	Harikrishna and Naidu[28]
Concentration range, µg/ml	0.5-12	0.5-12
Stability of coloured species, h	48	48
Relative standard deviation, %	1.44	1.26
Molar absorptivity, l mol ⁻¹ cm ⁻¹	3.268×10^4	2.448×10^4
Sandell's sensitivity, µg cm ⁻²	0.007	0.085

Formulations containing propoxur were analysed. For 1% propoxur spray and 4% dust, the mean ± standard deviation was 0.96±0.009% and 3.86±0.051% respectively.

Table-2 Recovery of propoxur from grains and spiked water samples

Sample	Propoxur(Recovery, % [*])		
	Added ppm	Present work	Harikrishna and Naidu[28]
Rice	1.0	98.10±1.0	97.78±1.0
	3.0	97.81±0.8	97.49±0.7
	5.0	97.32±0.6	96.67±0.6
	7.0	96.95±0.5	97.22±0.5
wheat	1.0	98.85±1.0	98.89±1.0
	3.0	98.75±0.8	98.83±0.9
	5.0	98.38±0.5	97.04±0.5
	7.0	96.62±0.5	97.85±0.2
water	1.0	99.23±1.0	98.67±1.0
	3.0	98.36±0.7	98.22±0.7
	5.0	97.37±0.6	96.80±0.6
	7.0	96.62±0.4	96.94±0.5

**each value is average ± standard deviation of six determinations*

Recovery experiment was performed with known amounts of the compounds added to different samples of grains and water. Grains samples were spiked by adding a methanol solution of the insecticides to the dry grains and evaporating the solvent.

The results presented in Table-2 show that recovery was in the range 96-99%. The results in Table-3 suggest that the method is applicable for the analysis of field water samples.

Table 3 Determination of propoxur in field water samples found, ppm

Sample volume, ml	Preset work	Harikrishna and Naidu[28]
250	0.19	0.18
250	0.30	0.29

CONCLUSION

The proposed method was compared with the other spectrophotometric methods reported for the determination of propoxur was found to be simpler and sensitive the earlier methods. Hence the proposed method can easily be used as rapid screening method for the determination of propoxur.

Acknowledgements

The authors are thankful to M/s. Bayer India Ltd., Mumbai, for supplying analytical and technical grade samples of the insecticide.

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