

A Simple Spectrophotometric Method for Determination of Propoxur

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A new spectrophotometric method for the determination of propoxur is described, based on coupling the hydrolysis product with diazotized *p*-chloroaniline to give an orange coloured compound having an absorption maximum at 459 nm. Beer's law is obeyed over the concentration range 0.5–10 ppm.

INTRODUCTION

Propoxur, 2-(1-methyl ethoxy) phenyl methyl carbamate belongs to carbamate class of pesticides. It is used on a large scale against cockroaches, flies, mosquitoes and other household pests. It has also been used very widely in the control of aphids, lygus bugs, grasshoppers and other insects on various crops. Its insecticidal properties were described by Unterstenhofer¹.

Many methods are reported in literature for the detection and determination of propoxur. Appaiah *et al.*² reported colorimetric method for the determination of propoxur and its residues in vegetables using 4,4-diaminodiphenylsulfone. Naidu and Naidu³ described a new spectrophotometric method for the determination of propoxur using 2-aminobenzophenone as coupling agent. Raju and Abraham⁴ developed a rapid and sensitive spectrophotometric method for the determination of propoxur using *p*-aminoacetophenone. Kahalf *et al.*⁵ adopted flow injection spectrophotometric technique for the determination of propoxur with *p*-aminophenol. Garcia *et al.*⁶ applied partial least-square calibration method to the simultaneous kinetic determination of propoxur, carbaryl, ethiofencarb and formetanate. Deleguradia *et al.*⁷ described a clean analytical technique for the determination of propoxur using *p*-aminophenol. Venkateswarlu *et al.*^{8,9} described spectrophotometric methods for the determination of propoxur with 4-aminoantipyrine. Agrawal and Gupta¹⁰ developed a highly selective sensitive and new spectrophotometric method for the determination of propoxur in grains and vegetable samples. Raju *et al.*¹¹ used *p*-nitroaniline for the determination of propoxur and carbaryl by a new spectrophotometric method. Some other spectrophotometric methods, GC, HPLC and TLC, have also been reported.

We report here a new spectrophotometric method employing diazotized *p*-chloroaniline as a coupling agent in alkaline medium.

EXPERIMENTAL

Reagents: All chemicals used were of analytical grade only.

***p*-chloroaniline (0.1%):** 100 mg of *p*-chloroaniline was dissolved in 1 N hydrochloric acid and diluted to 100 mL.

Standard solution of propoxur (50 µg/mL): A standard solution was prepared by dissolving 50 mg of insecticide in 100 mL of methanol in a volumetric flask. 10 mL of this solution was subsequently diluted to 100 mL.

Sodium nitrite (0.5%): 0.5 g of sodium nitrite was dissolved in distilled water and diluted to 100 mL.

Sodium hydroxide (2%): 2 g of sodium hydroxide was dissolved in 100 mL of distilled water.

Preparation of diazotized reagent: Diazonium salt of *p*-chloroaniline was prepared by adding 30 mL of 0.5% sodium nitrite solution to 18 mL of 0.1% of *p*-chloroaniline.

Preparation of Samples

Formulations: Propoxur 70% wettable powder: Shake a known amount of well mixed formulation (equivalent to about 50 mg of the insecticide) with 50 mL of methanol in a 50 mL volumetric flask for 5 min. 5 mL aliquot of the solution was subsequently diluted to 100 mL with methanol.

Water samples: Adjust the pH of each water sample to 3–4 with 20% sulphuric acid. Take one litre samples of distilled water and tap water fortified with different concentrations of insecticide dissolved in methanol. Transfer the fortified water samples to a 250 mL separating funnel and extract with 100 mL of chloroform. Transfer the chloroform extract into another separating funnel and extract the aqueous phase with 50 mL of chloroform. Wash the combined extracts with 10 mL of 0.1 M potassium carbonate solution to break any emulsion formed during the extraction. Dry the chloroform solution by passing it through 15–20 g of anhydrous sodium sulphate supported on cotton wool in a filter funnel, collect it in a 250 mL standard flask and dilute to the mark with chloroform. Evaporate the chloroform from known volume of this solution on a steam bath, dissolve the residue in methanol, then develop the colour.

Grains: Take 100 g of grains (rice and wheat) in a conical flask and shake with 200 mL of chloroform for 5 min. Decant the solution into a Whatman No. 1 filter paper and wash the grain with two 10 mL portions of chloroform. Dilute the combined extract and washings accurately to 250 mL with chloroform. Evaporate the chloroform from a known volume of solution, dissolve the residue in methanol and complete the analysis.

Procedure: Transfer 0, 0.25, 0.5, 1.0, ... 5 mL of standard insecticide solution into 25 mL standard flasks. To each flask add 2.5 mL of 2% sodium hydroxide and 2.4 mL of diazotization mixture. Mix and dilute to the mark with distilled water. Measure the absorbance of the orange solution against a reagent blank and construct a calibration plot. Analyse the samples by the same procedure.

RESULTS AND DISCUSSION

The optimum conditions were established by altering one variable at a time. The absorbance maximum is 459 nm. Beer's law is obeyed over the range 0.5–10 $\mu\text{g/mL}$ in the final solution for insecticide. The colour develops instantaneously and remains stable for more than 24 h. The coupling reaction can be done at room temperature only. The calibration plot and absorption spectrum shown in Fig. 1 and Fig. 2 respectively.

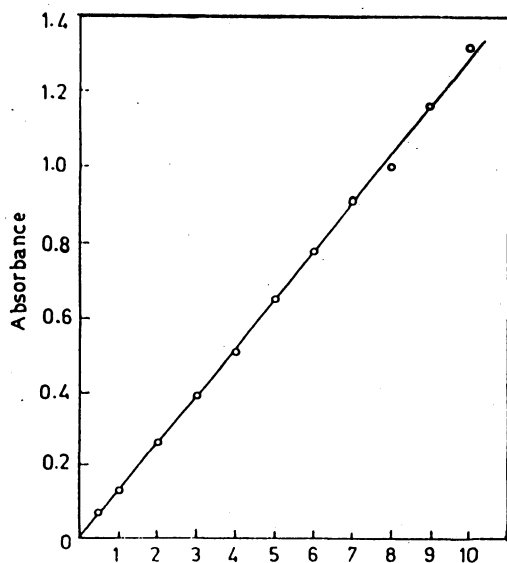


Fig. 1. Calibration plot of propoxur with *p*-chloroaniline.

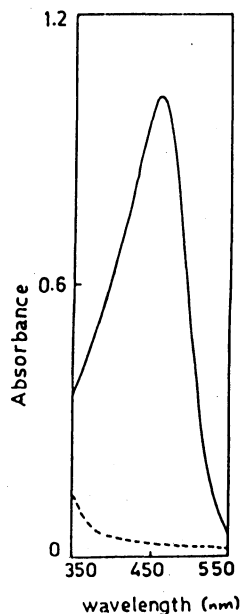


Fig. 2. Absorption spectrum of the complex: —; reagent:

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

TABLE-1
CHARACTERISTICS OF THE METHOD

Compound	Propoxur	
	Present work	Appiah <i>et al.</i> ²
Concentration range, $\mu\text{g/mL}$	0.5–10	0.25–5.0
Stability of the colour, (h)	24	12
Relative standard deviation, (%)	0.5	0.6
Relative error	0.2	0.3
Molar absorptivity, $1 \text{ mol}^{-1} \text{ cm}^{-1}$	2.765×10^4	—
Sandell's sensitivity, $\mu\text{g cm}^{-2}$	0.0076	—

Formulations containing propoxur were analysed. For 1% propoxur spray and 4% dust, the mean \pm standard deviation was $0.96 \pm 0.01\%$ and $3.93 \pm 0.02\%$ respectively.

Recovery experiments were performed with known amounts of the compounds added to different samples of grains and water. Grain samples were spiked by adding a methanol solution of the insecticide to the dry grains and evaporating the solvent.

The results presented in Table-2 show that recovery was in the range 94–98%. The results in Table-3 suggest that the method is applicable for the analysis of field water samples.

TABLE-2
RECOVERY OF PROPOXUR FROM GRAINS AND SPIKED WATER SAMPLES

Sample	Propoxur (Recovery, %*)		
	Added ppm	Present work	Appaiah <i>et al.</i> ²
Rice	1.0	96.80 \pm 1.0	96.0 \pm 1.2
	3.0	96.20 \pm 0.9	96.0 \pm 1.0
	5.0	96.40 \pm 0.8	95.8 \pm 0.8
	7.0	96.20 \pm 0.6	94.7 \pm 0.6
Wheat	1.0	97.60 \pm 1.2	96.0 \pm 1.4
	3.0	96.40 \pm 1.0	95.6 \pm 1.0
	5.0	96.53 \pm 0.8	94.7 \pm 0.9
	7.0	96.30 \pm 0.5	93.0 \pm 0.7
Water	1.0	98.10 \pm 1.0	97.2 \pm 1.0
	3.0	97.70 \pm 1.0	97.0 \pm 1.0
	5.0	97.27 \pm 0.9	96.3 \pm 0.9
	7.0	96.10 \pm 0.2	95.1 \pm 0.7

*Each value is an average \pm standard deviation of six determinations.

TABLE-3
DETERMINATION OF PROPOXUR IN FIELD WATER SAMPLES

Sample volume (mL)	Propoxur found, ppm	
	Present work	Appaiah <i>et al.</i> ²
250	0.17	0.14
250	0.29	0.26

ACKNOWLEDGEMENT

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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(Received: 24 November 2000; Accepted: 2 February 2001)

AJC-2242