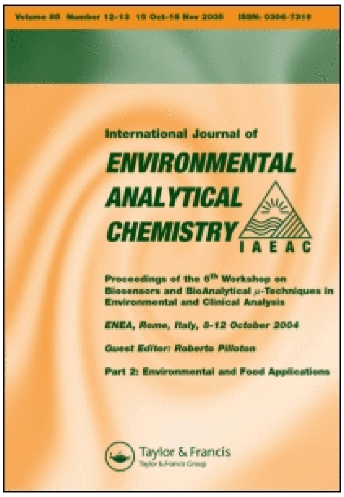

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RAPID AND SENSITIVE SCREENING METHOD FOR THE DETERMINATION OF CARBARYL AND PROPOXUR USING p-NITROANILINE

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A rapid screening method for the determination of carbaryl and propoxur using p-nitroaniline is described. Carbaryl and propoxur are determined spectrophotometrically: carbaryl forms a stable blue coloured species with diazotized p-nitroaniline in a fairly alkaline medium while propoxur forms a purple coloured species with the same reagent under similar conditions. The blue and purple coloured species are extracted into 3-methyl-1-butanol showing absorbance maxima at 605 and 540 nm, respectively. The relationship between absorbance and concentration is linear in the range of 0.12 - 0.96 ppm and 0.19 -1.5 ppm, respectively for carbaryl and propoxur. The method can successfully be applied for the determination of carbaryl and propoxur to levels as low as 0.04 and 0.06 and 0.12 and 0.19 ppm in water and grain samples, respectively.

KEY WORDS: Carbaryl, propoxur, water, grain, spectrophotometry.

INTRODUCTION

Carbaryl (1-naphthyl methyl carbamate) and propoxur (o-isopropoxy phenyl methyl carbamet) are amongst the most widely used carbamet insecticides. The tolerance residue limit of these pesticides in grain is 2.5 ppm[1]. Various methods for their detection[2] and determination have been reported, e.g. spectrophotometry[3-10], GC[11], HPLC[12, 13] and TLC[14].

In spectrophotometry carbamates are generally determined by coupling their hydrolysis products with various reagents[3-6, 8]. Other methods are based on the reaction of carbamates with diazotized 2, 5 dichloroaniline[7], o-toludine[9] or sulphanilamide[10]. These methods do not require preliminary hydrolysis but suffer from poor dye stability and low sensitivity.

In the present communication a new screening method is proposed where diazotized p-nitroaniline has been used for the determination of carbaryl and propoxur. Though more sensitive HPLC and GC methods are available in the literature, this spectrophotometric method is rapid, simple, and inexpensive, and uses commonly available reagents. The

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method does not require elaborate clean-up or preliminary hydrolysis. It has been compared with other spectrophotometric methods and found to be of comparable sensitivity.

EXPERIMENTAL

Apparatus

EK 1 Carl Zeiss specol spectrophotometer with 1 cm glass cells, a separatory funnel of 250 ml and caliberated glasswares were used.

Reagents

Carbaryl: Supplied by Union Carbide, Bhopal, India: Stock solution of 1 mg/ml in ethanol.
Propoxur: Supplied by Bayer India: Stock solution of 1 mg/ml in ethanol.
p-Nitroaniline (PNA): 0.05% in 1:4 conc. hydrochloric acid.
Sodium nitrite: 0.2% w/v aqueous solution
Sodium hydroxide: 8 M aqueous solution
3 Methyl-1-butanol and all other reagents used were of analytical reagent grade.

Preparation of calibration graph

100 ml of aqueous solutions containing 12-96 μg of standard carbaryl or 19-150 μg of standard propoxur were taken in a 250 ml separatory funnel. To this 2 ml of PNA reagent were added and the acidity was adjusted to Ca 0.5 M by adding hydrochloric acid. After 2 min, 4 ml of sodium nitrite solution were added and the colour was developed with 10 ml of 8 M sodium hydroxide solution, which was added by a fast running pipette. After 5 min the blue or purple coloured species was extracted with 10 ml of 3-methyl-1-butanol. The extracts were dried over anhydrous sodium sulphate and the absorbance was measured at 605 nm for carbaryl and at 540 nm for propoxur. The calibration graph was obtained by plotting absorbance versus concentration.

In water samples: Water samples (500 ml) were collected and each sample was adjusted to pH < 5 with 20% sulphuric acid. To each sample 5 g of sodium sulphate are added and then the sample was fortified with different amounts of carbaryl and propoxur in 5 ml of ethanol. Each sample was extracted in a separatory funnel with two 100 ml portions of chloroform by shaking the funnel for 2-3 min. The extracts were combined and washed with 20 ml of 0.1 M potassium carbonate solution. The chloroform solution was dried over anhydrous sodium sulphate in a filter funnel and extract collected in 250 ml calibrated flask. The filter funnel was washed with 20 ml of chloroform and the volume was made up to the mark. Known aliquots of the chloroform extract were taken and the chloroform was evaporated off under reduced pressure using moderate suction on a water bath at about 50°C. The residue was dissolved in 10 ml of ethanol and solution transferred to a separatory funnel

Table 1 Analytical data of the method

Parameter	*Carbaryl*	*Propoxur*
Reagent	PNA	PN
A Colour	Blue	Purple
λ max	605	540
Solvent used	3-methyl-1-butanol	3-methyl-1-butanol
Stability of colour	24 h	24 h
Time taken for colour development	immediate	immediate
Limits of Beer's law (ppm)	0.12–.96	0.19–1.5
Molar absorptivity (1/mol/cm)	1.68×10^5	1.09×10^5
Standard deviation*	0.014	0.012
R.S.D%*	2.7	2.8

*4 μg of carbaryl and propoxur in final 100 ml of volume were studied for a period of 7 days.

with 70 ml water. To this 2 ml of PNA reagent were added and the acidity was adjusted to 0.5 M with hydrochloric acid. After 2 min, 4 ml of sodium nitrite solution were added and the colour was developed as described under preparation of caliberation graph. The recovery of carbaryl and propoxur from water was ca. 99%.

In grain samples: 100 g of grain samples were fortified with different amounts of carbaryl or propoxur in 5 ml of ethanol. The fortified samples were blended for 5 min with 200 ml chloroform in a blender. The chloroform solution was then decanted into a 250 ml calibrated flask through Whatman No. 1 filter paper, the residue being retained in the blender. Blending and decanting was repeated twice with 10 ml portions of chloroform. The chloroform extracts were combined and diluted to the mark. The chloroform extract was evaporated off under reduced pressure using moderate suction on a water bath at about 50°C. The residue was dissolved in 10 ml of ethanol and the solution transferred to a separatory funnel with 70 ml water, next the colour was developed as described under preparation of caliberation graph. The recovery of carbaryl and propoxur from grain samples was ca. 98%.

RESULTS AND DISCUSSION

The blue coloured species formed by carbaryl was measured at 605 nm, while the purple coloured species formed by propoxur was measured at 540 nm in 3-methyl-1-butanol.

A temperature change from 15 to 40°C did not cause any adverse effect. Temperatures above 50°C caused changes in the final colour, while the absorbance feadings became irreproducible. Various important analytical data are given in Table 1.

To assess the validity and the selectivity of the method 100 ml of a solution containing 40 μg carbaryl or 40 μg propoxur along with various foreign species (in μg) such as parathion (200), malathion (200), DDT (200), aldrin (300), PO_4^{3-} (300), Pb^{2+} (200), was analysed by the proposed method. The recovery for both pesticides was ca. 99%, which proves the selectivity of the method. It was observed that when 1-naphthol or phenol was added individually to a solution containing carbaryl or propoxur, they did not interfere up to an

Table 2 Comparison with other spectrophotometric methods

No.	*Reagent/compound/ Reference*	*λ max*	*Det.limit (ppm)*	*Remarks*
1.	4-Aminophenazone - Carbaryl (3)	475	0.5–20	Reagentunstable
2.	Ethanolic ammonia -Propoxur (4)	420	0.5–10	Requires heating under reflux for 30 min at 100°C.
3.	4-Dimethyl aminobenzaldehyde - Carbaryl (5)	480	1.2–10	Poor sensitivity
4.	4-Dimethyl amino cinnamaldehyde (5)			
	- Carbaryl	560	0.65–6	Requires60°C temp.
	- Propoxur		2–2	Required 90°C temp.for hydrolysis.
5.	p-Aminophenol (6)			
	- Carbaryl	600	0.8–10	Dye stability 7 min
	- Propoxur	600	0.8–8.0	Dye stability 7min
6.	p-Dimethyl phenoldiamine dihydrochloride (6)			
	- Carbaryl	600	0.7–8.0	Reagent toxic
	- Propoxur	600	1.0–8.8	Reagent toxic
7.	1-Amino 2-naphthol 4-sulphonic acid - Carbaryl(6)	700	3.0 –35.0	Poor sensitivity and reagent unstable
8.	Present method p-Nitroaniline			
	- Carbaryl	605	0.12–60.96	Dye stable for 24 hrs
	- Propoxur	540	0.19–1.5	Sensitive and does not require preliminary hydrolysis.

eight fold excess. However, with ratios higher than this, the chloroform extract should be washed twice with a 0.2 - 0.4 M sodium hydroxide solution and then with water to remove these contaminants before the chloroform is evaporated off and the colour is developed[10].

Application of the method to water and grain samples

To check the validity of the method in real samples, different water samples were collected from nearby stream and grain samples were collected from the fields where the carbaryl and propoxur were sprayed. Carbaryl and propoxur were extracted from these samples using chloroform as described above and determined by proposed method. Carbaryl and propoxur could be detected as low as 0.04 and 0.06 ppm in water and 0.12 and 0.19 ppm in grain samples, respectively. The method was compared with other spectrophotometric method and found to be of comparable sensitivity.

CONCLUSION

p-Nitroaniline can be used as a sensitive reagent for the determination of carbaryl as well as propoxur, forming two differently coloured species with these pesticides. In the absence of large amounts of 1-naphthol, phenols and other similar N-methyl carbamates. The proposed method can easily be used as a rapid screening method for the routine analysis of carbaryl and propoxur.

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