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Technical Note

Sensitive Spectrophotometric Determinations of Carbaryl and Propoxur in Formulations, Water, Grains and Pulses

ABSTRACT

New spectrophotometric methods for the assay of carbaryl and propoxur, based on the reaction with p-dimethylaminobenzaldehyde (pDAB) and p-dimethylaminocinnamaldehyde (pDAC) under acidic conditions, have been developed. The absorption maxima of the coloured species so formed are measured at 480 nm for pDAB and 560 nm for pDAC, respectively. The methods are simple, sensitive, reproducible and accurate within ± 1% and applicable to the assay of carbaryl and propoxur in insecticidal formulations, water samples, grains and pulses.

INTRODUCTION

Carbaryl (1-naphthyl-*N*-methyl carbamate) and propoxur (2-isopropoxyphenylmethyl carbamate) are used in pest control in many countries and thus their determination in formulations and residues has become imperative. Spectrophotometric methods reported earlier for their determination include chromogenic reagents such as 4-aminophenazone (Appaiah *et al.*, 1982), diazotised 3-nitroaniline (Bracha, 1964), vanillin (Handa & Dikshit, 1979), *p*-nitrobenzenediazoniumfluoroborate (McDermatt & Duvall, 1970), diazotised sulphanilic acid (Mukherjee *et al.*, 1975; Yuen, 1965), diazotised *o*-toluidine (Rangaswamy & Majundar, 1974), 4-amino-2-nitrobenzenesulphonic acid (Ramaswamy, 1974), 3,5-dibromo-*p*-benzoquinonechloroimine (Vangils, 1970; Syoyama *et al.*, 1975) and diazotised 2,5-dichloroaniline (Vonesch & Riveros, 1971). We

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have now developed simple, rapid and sensitive methods of determination of carbaryl and propoxur at the microgram level with *p*DAB and *p*DAC in the presence of acid.

MATERIALS AND METHODS

Spectral absorbance measurements were made with an Elico model 24 (CL) spectrophotometer.

All the chemicals used were of CP or AR grade. Methanolic solutions of *p*-dimethylaminobenzaldehyde, *p*-DAB (0·5%), *p*-dimethylaminocinnamaldehyde, *p*-DAC (0·1%), sulphuric acid (14 M), hydrochloric acid (8 M), sodium hydroxide (0·5 N), carbaryl and propoxur (20 μg ml) were prepared.

Preparation of standard curve

To a series of 10-ml graduated test tubes, aliquots of 0·6–5·0 ml (for the *p*-DAB method) or 0·3–3·0 ml (for the *p*DAC method) of carbaryl solution or 1·0–6·0 ml of propoxur (for the *p*DAC method) were delivered, the volume made up to 6 ml with methanol and the solvent evaporated under a current of dry air. 0·5 ml of methanolic sodium hydroxide was then pipetted into each of the tubes and was allowed to stand for 3 min for complete hydrolysis. The solvent was evaporated from each test tube and appropriate volumes of aldehyde and mineral acid (*p*DAB, 1 ml and HCl, 5 ml; *p*DAC, 1·5 ml and H_2SO_4, 2 ml) were added and kept in a water bath at 60 °C (for the *p*DAB method) or 90 °C (for the *p*DAC method) for 20 min. The test tubes were removed from the bath, cooled and diluted to 10 ml with methanol and the absorbance read against a corresponding reagent blank at 480 nm (for the *p*DAB method) or 560 nm (for the *p*DAC method) within the stability period 20 min to 1 h. The amounts of carbaryl and propoxur were deduced from their respective standard calibration curves.

Procedure of formulation–analysis

Fifty milligrams of well-mixed formulation were dissolved in 25 ml anhydrous methanol and centrifuged for 5 min. The supernatant was decanted and filtered into a 50 ml volumetric flask. The residue was washed with methanol and the volume made up to the mark. The above

solution was further diluted with methanol so as to contain 20 μg ml of pesticide and a suitable aliquot was taken for the spectrophotometric determination as indicated for the calibration curve.

Recovery of carbaryl and propoxur added to grains, pulses and water samples

To obtain an indication of the efficiency of the procedures, grains, pulses and field water samples were spiked with the carbamate and analysed. The preliminary extraction procedures, as reported by Handa & Dikshit (1979) and Appaiah *et al.* (1982) were adopted so as to obtain the carbamate of desired concentration from the spiked samples.

RESULTS AND DISCUSSION

The optimum conditions incorporated in the procedure for the determination of carbamate after hydrolysis were established through control experiments based on the maximum colour development and its stability.

The Beer's law ranges, molar absorptivity and Sandell's sensitivity values of the pesticides studied are given in Table 1. The precision and accuracy of the two methods were found by analysis of six separate samples containing known amounts of pesticide and the results are summarised in Table 1.

TABLE 1
Optical Characteristics, Precision and Accuracy

	Carbaryl		*Propoxur*
	pDAB method	*pDAC method*	*pDAC method*
Beer's law limits (μg/ml)	1·2–10	0·65–6	2–12
Molar absorptivity (litres/mol/cm)	$7{\cdot}85 \times 10^3$	$1{\cdot}51 \times 10^4$	$4{\cdot}18 \times 10^3$
Sandell's sensitivity (μg/cm^2/0·001 absorbance unit)	0·025 5	0·013 3	0·05
Per cent relative standard deviation	1·21	0·85	1·07
Per cent range of error (95% confidence limit)	1·27	0·89	1·12

TABLE 2
Determination of Carbaryl and Propoxur in Wettable Insecticidal Formulations

Technical grade sample	*Labelled amount* (%)	*Carbaryl or propoxur found* (%)[a]		
		pDAB method	*pDAC method*	*Reported method*[b]
Carbaryl				
I (dust)	—	97·2	98·2	97·9
II	85	83·8	84·0	83·6
III (dust)	5	4·16	4·18	4·14
Propoxur				
I				
(Baygon spray)	1		0·95	0·89
II				
(Baygon dust)	4		3·94	3·90

[a] Each value is an average of three determinations.
[b] Handa & Dikshit (1979).

TABLE 3
Recovery of Carbaryl and Propoxur Added to Water, Grains and Pulses

Sample	*Carbaryl*[a] *or propoxur*[b] *added* (*mg*)	*Amount found* (*mg*)[c]			*Per cent recovery*		
		pDAB method	*pDAC method*	*Reported method*	*pDAB method*	*pDAC method*	*Reported method*
Water	10[a]	9·81[a]	9·86[a]	9·81	98·1[a]	98·6[a]	98·1
	10[b]		9·79[b]			97·9[b]	
Wheat	10[a]	9·84[a]	9·88[a]	9·83	98·4[a]	98·8[a]	98·3
	10[b]		9·87[b]			98·7[b]	
Rice	10[a]	9·84[a]	9·86[a]	9·82	98·4[a]	98·6[a]	98·2
	10[b]		9·83[b]			98·3[b]	
Gram	10[a]	9·83[a]	9·84[a]	9·81	98·3[a]	98·4[a]	98·1
	10[b]		9·83[b]			98·3[b]	
Corn	10[a]	9·86[a]	9·88[a]	9·84	98·6[a]	98·8[a]	98·4
	10[b]		9·86[b]			98·6[b]	

[a] For carbaryl.
[b] For propoxur.
[c] Each value is an average of three determinations.

Comparison of the values of formulation–analysis of the pesticides with the method proposed by Handa & Dikshit, (1979) reveal good accuracy and the data are given in Table 2.

To check the reproducibility of the methods, a known amount of the pesticide was added to each sample of grains, pulses and water and recovery experiments were performed. The results obtained are in good agreement with those of the reported method which ranged from 97·5% to 99% (Table 3).

Reaction mechanism

Under acidic conditions protons attack the aldehyde group of *p*DAB or *p*DAC to give an electrophilic radical which condenses with the 1-naphthol or 2-isopropoxyphenol, the hydrolysis products of carbaryl and propoxur, to form an intermediate. This intermediate undergoes dehydration to give a coloured compound. The higher λ_{max} with *p*DAC than *p*DAB is due to extended conjugation.

The *p*DAC method is more sensitive and precise for the determination of carbaryl or propoxur in insecticidal formulations, field water samples, grains and pulses than most of the reported methods, including the vanillin method.

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