

Spectrophotometric Determination of Carbosulfan in Formulations and Water Samples

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A sensitive spectrophotometric method for the determination of carbosulfan pesticide in formulations and water samples is described. The method is based on the alkaline hydrolysis of the pesticide and the resultant phenol is reacted with 4-aminoantipyrine in the presence of an oxidizing agent. The resultant colored dye is extracted into chloroform and the absorbance is measured at 480 nm.

INTRODUCTION

Carbosulfan, a systemic and contact insecticide belonging to the class of carbomates, is recently developed. (It was introduced by FMC Corporation as Code No. FMC 35001, trade mark Marshal). Carbosulfan is a derivative of carbofuran. It acts as cholinesterase inhibitor. It is widely used for the control of soil dwelling insects and foliar pests on maize, corn, citrus, paddy, potatoes and sugar beet and also employed as nematicides. In view of its wide applications and toxicity there is a need for the development of sensitive and reliable methods for the assessment of quality of insecticidal formulations and to quantify the insecticide residues in water.

There are several chromatographic and colorimetric methods for the determination of carbosulfan. The spectrophotometric methods are based on the alkaline hydrolysis of the insecticide followed by coupling the resultant phenol with reagents such as diazotized 3-nitroaniline-4 sulphonic acid,^{1,2} sulphanilic acid,³ 4-aminoantipyrine,⁴ 3,5-dibromo-*p*-benzoquinone chloramine⁵, 4,4-diamino-diphenyl sulphone,⁶ *p*-dimethylphenyl benzaldehyde and *p*-dimethylamino cinnamaldehyde,⁷ 3-methyl-2-benzothiazolinone hydrazone hydrochloride,⁸ *p*-dimethylphenyl-enediamine hydrochloride⁹ and 2-aminobenzophenone.¹⁰ In the above spectrophotometric methods hydrolysed phenolic product was diazotized in aqueous solution and the colour of the aqueous solution was measured. Hence, the sensitivity was less and also there was a possibility of the coloured product reacting with other reagents present in the aqueous phase which leads to instability of the compound.

We now report a spectrophotometric method based on the reaction of hydrolysed phenolic product with 4-aminoantipyrine in the presence of an oxidizing agent to produce an orange-coloured dye as shown in Fig. 1. The dye

is extracted into organic solvent. Extraction of the dye from aqueous solution into small quantity of organic solvent increased the sensitivity of the method by several-fold compared with the reported methods and also the stability of the coloured dye in organic solvents is more when compared with the aqueous phase. The method is extended to the determination of carbosulfan in commercial formulations and water samples.

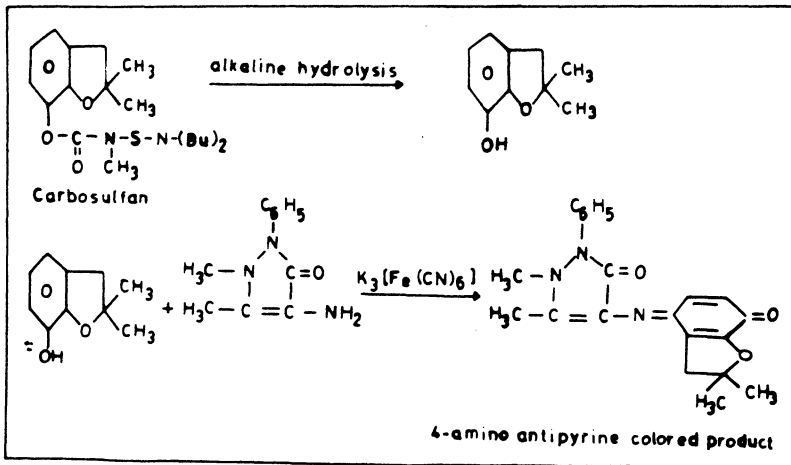


Fig. 1. Reaction mechanism of the coloured product formed (carbosulfan with 4-aminoantipyrine)

EXPERIMENTAL

Apparatus: A Shimadzu UV-240 Scanning Spectrophotometer with 1 cm glass cells and Elico pH-meter were employed.

Reagents: All chemicals used were of analytical grade.

Carbosulfan Stock Solution (100 $\mu\text{g/mL}$): Pesticide (109.8 mg of 91.1% technical grade sample of carbosulfan) was dissolved in 100 mL of methanol. 10 mL of this solution was subsequently diluted to 100 mL methanol. This solution contains 100 $\mu\text{g mL}^{-1}$ carbosulfan. The stock solution was progressively diluted with the solvent to obtain standard solution of desired concentration.

4-Aminoantipyrine (2% w/w): 4-Aminoantipyrine (2 g) was dissolved in distilled water and diluted to 100 mL.

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

Buffer solution: Dipotassium hydrogen phosphate (10.5 g) and 7.3 g of potassium dihydrogen phosphate were dissolved in distilled water and diluted to 100 mL.

Potassium ferricyanide solution: Potassium ferricyanide (8 g) was dissolved in distilled water and diluted to 100 mL.

Procedure: Insecticide solution (20 mL) was taken in a clean dry 100 mL beaker. Two per cent sodium hydroxide solution (5 mL) was added, stirred and

allowed to stand for 5 min for complete hydrolysis; the pH of the solution was adjusted to 8.0 by adding 5 mL of buffer solution and the requisite amount of HCl and ammonia solution. The solution was transferred to a 50 mL separating funnel and allowed to stand for 2 min and then 3 mL of 4-aminoantipyrine and 3 mL of potassium ferricyanide were added and mixed well. The orange-coloured dye formed was extracted into 10 mL of methylisobutyl ketone. The absorbance of the methylisobutyl ketone solution was measured at 480 nm against a reagent blank.

Formulations: Well mixed formulation (equivalent to about 100 µg of the active insecticide) was shaken with 25 mL of methanol for 5–10 min. The supernatant solution was filtered by decantation into a 100 mL standard flask. The residue was washed twice with 10 mL portions with methanol. The filtrate and washings were diluted to 100 mL with methanol. Analysis was carried out using the above procedure.

Water Samples: Water samples (100 mL) spiked with 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 µg of insecticide were taken; the pH of the samples was adjusted to 3–4 with 2% sulphuric acid and 2g of anhydrous sodium sulphate was added. The mixture was transferred into a separating funnel and insecticide extracted using approximately 15 mL of chloroform for each extraction by shaking for 5–10 min. Combined extracts were washed with 2 mL of 0.1 M potassium carbonate to break any emulsion formed during the extraction, then dried over anhydrous sodium sulphate. Finally, chloroform was evaporated and residue dissolved in methanol. Determination was carried out by developing colour using the above procedure.

RESULTS AND DISCUSSION

Carbosulfan pesticide was hydrolysed and the resultant phenol converted into orange-coloured dye by reacting with 4-aminoantipyrine in the presence of an alkaline oxidizing agent, potassium ferricyanide.

The reaction of the phenolic product with antipyrine was carried out in the pH range 6–11. The absorbance of the coloured dye was greater in the pH range 8.0–10. Hence, pH 8.0 was selected for the extraction of dye into the organic layer.

Choice of solvent: Extraction of colored dye was carried out in the methyl isobutyl ketone, benzene, chloroform and carbon tetrachloride and their absorbance spectra are shown in Fig. 2. Absorbance for the methyl isobutyl ketone extractant was more than the other solvents. Hence methyl isobutyl ketone was selected as a suitable solvent for further extractions.

The stability of the coloured dye was studied in different solvents. It was stable for more than 24 h in methyl isobutyl ketone, CHCl_3 and C_6H_6 but faded quickly in CCl_4 .

Beer's law was obeyed over the concentration range of 0.5 to 3.0 µg/mL of carbosulfan. The molar absorption coefficient of the coloured dye was $2.10 \times 10^5 \text{ L mole}^{-1} \text{ cm}^{-1}$.

The method was applied for the determination of carbosulfan in commercial formulations and spiked water samples. Results are shown in Tables 1 and 2.

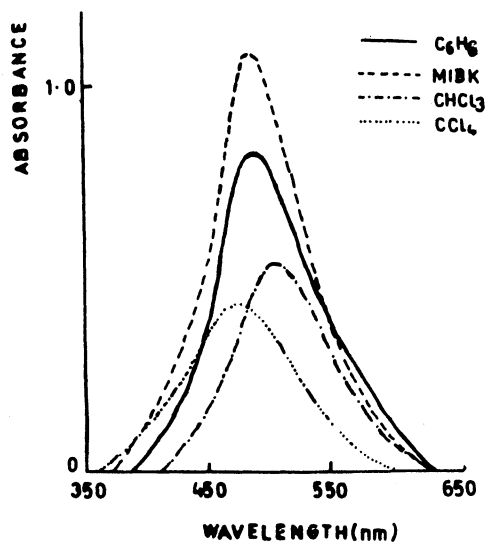


Fig. 2. Extraction of coloured product (carbosulfan with 4-aminoantipyrine) in different solvents.

TABLE-1
DETERMINATION OF CARBOSULFAN ACTIVE INGREDIENT
IN FORMULATIONS (25% emulsion)

S. No.	Amount of pesticide taken (μg)	Active ingredient		RSD*
		Calculated (μg)	Found (μg)	
1.	50.00	12.50	11.40	0.65
2.	60.00	15.00	14.04	0.64
3.	70.00	17.50	17.03	0.62
4.	80.00	20.00	19.26	0.63
5.	90.00	22.50	22.09	0.60
6.	100.00	25.00	24.55	0.59

*RSD for five determinations.

TABLE-2
RECOVERY OF CARBOSULFAN RESIDUE FROM SPIKED
WATER SAMPLES (Tap Water)

S. No.	Added ($\mu\text{g}/100\text{ mL}$)	Found ($\mu\text{g}/100\text{ mL}$)	% Recovery	RSD
1.	25.0	24.2	96.6	0.64
2.	50.0	48.9	97.7	0.61
3.	75.0	73.5	98.0	0.56
4.	100.0	97.9	97.9	0.58
5.	125.0	120.5	96.4	0.67
6.	150.0	146.0	97.3	0.62

% Recovery and RSD are for five determinations.

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