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# Spectrophotometric Determination of Propoxur and Carbosulfan with 2,4,6-Trichloroaniline as the Coupling Agent

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A new spectrophotometric method is described for the determination of propoxur (O-isopropoxy phenyl, methyl carbamate) and carbosulfan (2,3-dihydro-2,2-dimethylbenzofuran-7-yl (dibutylaminothio) methyl carbamate) by the diazotization-coupling reaction using 2,4,6-trichloroaniline as the coupling agent. The phenols of the insecticides are generated by alkaline hydrolysis. The absorption maximum of orange coloured species were 443 nm and 440 nm. The coloured species obey Beer's law in the concentration range 0–10 ppm.

**Key Words: Spectrophotometric determination, Propoxur, Carbosulfan.**

## INTRODUCTION

Propoxur and carbosulfan are carbamate insecticides. These are now being extensively used to destroy a broad spectrum of insects that affect a wide variety of field crops, fruits, vegetables, ornamental plants and flowers. Propoxur is toxic to silkworms, birds, aquatic organisms and livestock[1–3]. Carbosulfan is toxic to honeybees, birds and mammals[4]. The residues of these insecticides cause air and water pollution. Hence there is a demand for developing simple and precise analytical procedures for the detection and determination of the insecticide residues in surface and sub-surface water systems. Several methods such as chromatography[5–11], colorimetry[12–15] and spectrophotometric[16–25] methods are cited in the literature for their determination.

This paper includes a simple and rapid spectrophotometric method based on azo-coupling. 2,4,6-Trichloroaniline was used as coupling agent, which forms orange coloured derivatives with the phenols of the insecticides produced by alkaline hydrolysis.

## EXPERIMENTAL

Hitachi UV-Vis NIR spectrophotometer model U-3400 with 1 cm glass cells, a Elico digital pH-meter and single pan electronic balance were used. Analytical

and technical grade samples of propoxur and carbosulfan supplied by Bayer India Ltd., Bombay and Rallis India Ltd., Bangalore respectively were employed.

**Preparation of Stock Solutions:** 100 mg of propoxur and carbosulfan were dissolved in 100 mL of methanol (1000 μg per mL).

**Standard propoxur and carbosulfan solutions:** 25 mL of each stock solution was diluted to 100 mL with methanol (250 ppm solution).

**2,4,6-Trichloroaniline (0.1%):** 100 mg of pure 2,4,6-trichloroaniline was dissolved in 100 mL of 2% sulphuric acid.

**Sodium nitrite:** 300 mg of sodium nitrite was dissolved in 100 mL of distilled water to obtain 0.3% solution.

**Sodium hydroxide:** 5 g of sodium hydroxide was dissolved in 100 mL of distilled water to obtain 5% solution.

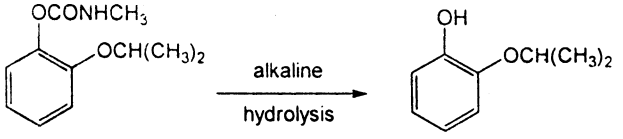
**Preparation of Calibration Graphs**

Aliquots of standard insecticide solutions (0.05, 0.1, 0.2, 0.3, . . . 1 mL) were taken into a series of 25 mL standard flasks. To each of these 2 mL of sodium hydroxide, 1 mL of aqueous sodium nitrite and 1 mL of 2,4,6-trichlonoaniline were added. The solutions were made up to the mark with distilled water. The orange coloured species had a maximum absorption at 443 nm and 440 nm for propoxur and carbosulfan respectively against a reagent blank. The colour remained stable for nearly 96 h and 24 h for the insecticides. Absorption values were recorded using Hitachi UV-Vis NIR spectrophotometer. Dependence of concentration on absorbance was linear over the composition range 0.2–10 ppm.

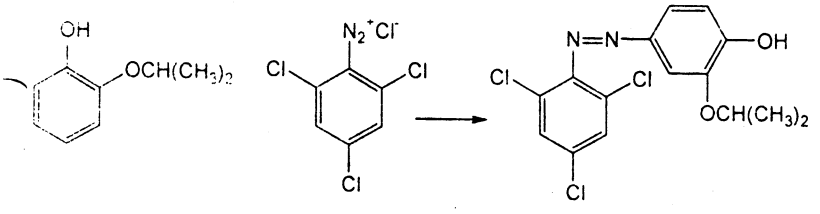
**Scheme-1**

PROPOXUR *vs.* 2,4,6-TRICHLOROANILINE

A. Hydrolysis of Propoxur




B. Coupling reaction

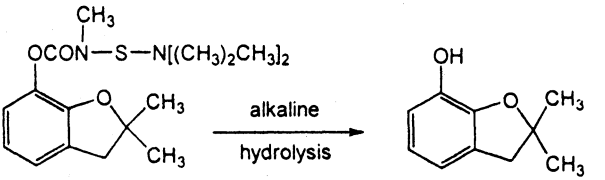



Diazotized
2.4.6-trichloroaniline

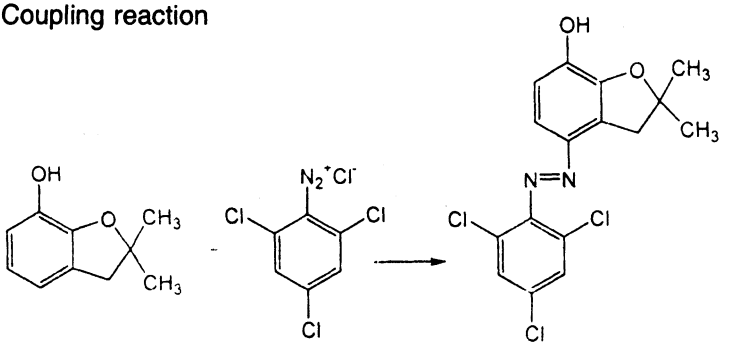
**Scheme-2**

CARBOSULFAN *vs.* 2,4,6-TRICHLOROANILINE

A. Hydrolysis of Carbosulfan




B. Coupling reaction




Diazotized
2,4,6-trichloroaniline

**Determination in Insecticidal Formulations**

The formulations used in the investigation included propoxur in 1% spray, 2% bait and 4% dust and 25% emulsion of carbosulfan. The well mixed formulations equivalent to 100 mg of insecticides were shaken with 25 mL of methanol for 5 min and the mixture was centrifuged. The supernatant solution was decanted and filtered into a 100 mL standard flask. The residue was washed with methanol and diluted to the mark in a 100 mL standard flask. Known aliquots of the solution were used for colour development after suitable dilution as outlined under preparation of calibration graphs. Results pertaining to analyses of these commercial formulations are given in Table-1.

**Recovery from Grains**

50 g of wheat and rice was taken in a conical flask, fortified with a known concentration of the pesticide in 5 mL of methanol and the solvent was evaporated. The sample was shaken for 5 min with 200 mL chloroform and the solution was transferred into a 250 mL standard flask through a Whatman No. 1 filter paper. The grain in the flask was extracted thrice with 10 mL portions of chloroform. The combined extracts were diluted to 250 mL with chloroform. Solvent was evaporated from a known volume of this solution; the residue was dissolved in methanol and the analysis was completed as described earlier.

TABLE-1
ANALYSES OF COMMERCIAL FORMULATIONS OF PROPOXUR AND CARBOSULFAN

| Sample | Propoxur | | | Carbosulfan |
|---|---|---|---|---|
| | 1% spray | 2% bait | 4% dust | 25% emulsion |
| 1. | 0.97 | 1.84 | 3.91 | 24.32 |
| 2. | 0.92 | 1.82 | 3.84 | 24.01 |
| 3. | 0.91 | 1.94 | 3.79 | 23.92 |
| 4. | 0.94 | 1.89 | 3.87 | 24.56 |
| 5. | 0.96 | 1.91 | 3.92 | 24.68 |
| 6. | 0.95 | 1.93 | 3.83 | 24.71 |
| 7. | 0.92 | 1.86 | 3.78 | 24.48 |
| Mean | 0.94 | 1.88 | 3.85 | 24.46 |
| S.D. | ±0.02 | ±0.05 | ±0.06 | ±0.23 |

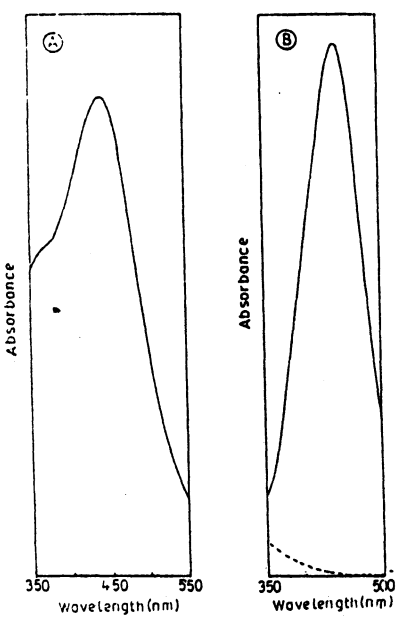



Fig. 1. Absorption spectra: **A.** Carbosulfan *vs.* 2,4,6-trichloroaniline, **B.** Propoxur *vs.* 2,4,6-trichloroaniline,

### Determination of Recovery in Water Samples

250 mL of distilled water were taken and fortified with different amounts of pesticide. pH of the samples was adjusted to 4 with 2% sulphuric acid. 10 g of sodium sulphate was added to prevent emulsion formation and the mixture was transferred to a 500 mL separating funnel. The pesticide was extracted with 150 mL of chloroform. The extract was transferred to another separating funnel and the aqueous phase was re-extracted with 50 mL of chloroform. The combined extracts were washed with 10 mL of 0.1 M potassium carbonate solution to break emulsions if any. Chloroform solution was dried by passing through 15–20 g of anhydrous sodium sulphate in a filter funnel and diluted to 250 mL. Known aliquots of the chloroform was taken and evaporated to dryness in vacuum in a fume cup board, the residue was dissolved in methanol and the colour was developed as described under preparation of calibration graphs.

## RESULTS AND DISCUSSION

**Effect of acidity on diazotization:** The optimum concentration of the acid for diazotization in the method is 2%.

**Effect of reagent concentration:** 1.2 mL of 2,4,6-trichloroaniline is necessary for maximum colour development (Fig. 3).

**Effect of sodium nitrite:** The aliquots of 0.1% aqueous sodium nitrite for maximum colour development in the method is 1.0 mL.

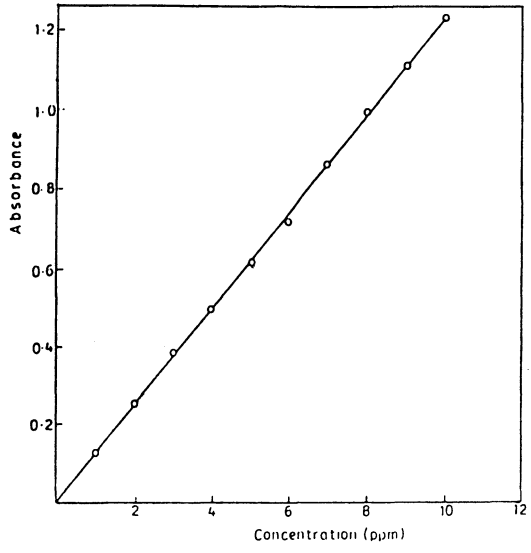



Fig. 2. Calibration plot (Propoxur *vs.* 2,4,6-trichloroaniline)

### Effect of pH on coupling reaction

The reaction of the phenolic product with 2,4,6-trichloroaniline was carried out in the pH range 8–12. The optimum pH range for maximum colour development is between 11 and 12.

Recovery experiments were carried out by adding known amounts of the carbamate to different samples of water and grains and was determined by the

method described. Recoveries of the propoxur and carbosulfan ranged from 95.7 to 98.0%. The data are given in Table-2. The proposed method has an advantage in that the coloured complexes remain stable for longer periods than the methods cited in the literature. The method is simple, rapid, sensitive and colour develops instantaneously. Hence it is concluded that the present method is suitable both for the determination of active ingredients in formulations and also in contaminated water.

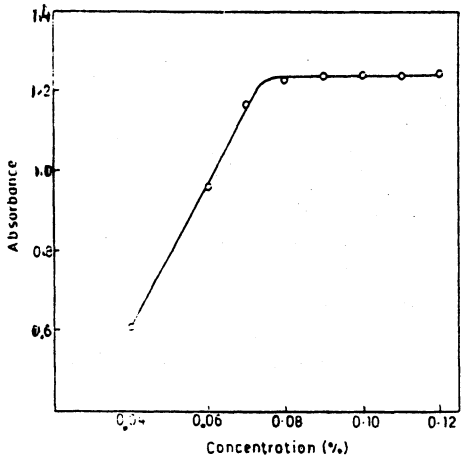



Fig. 3. Effect of reagent concentration on colour development (propoxur vs. 2,4,6-trichloroaniline)

TABLE-2
RECOVERY OF PROPOXUR AND CARBOSULFAN ADDED TO GRAINS AND SPIKED WATER SAMPLES

| Sample | Propoxur | | Carbosulfan | |
|---|---|---|---|---|
| | Fortification level, ppm | Recovery (%) | Fortification level, ppm | Recovery, (%) |
| Wheat | 1.0 | 97.0 ± 1.0 | 1.0 | 97.0 ± 1.2 |
| | 3.0 | 96.8 ± 0.9 | 3.0 | 96.8 ± 1.0 |
| | 5.0 | 96.5 ± 0.6 | 5.0 | 96.4 ± 0.7 |
| | 7.0 | 95.9 ± 0.5 | 7.0 | 96.1 ± 0.6 |
| Rice | 1.0 | 97.0 ± 1.2 | 1.0 | 97.0 ± 1.0 |
| | 3.0 | 96.7 ± 1.1 | 3.0 | 96.7 ± 0.8 |
| | 5.0 | 96.3 ± 0.9 | 5.0 | 96.2 ± 0.7 |
| | 7.0 | 95.7 ± 0.7 | 7.0 | 95.9 ± 0.5 |
| Water | 1.0 | 97.0 ± 1.0 | 1.0 | 98.0 ± 0.9 |
| | 3.0 | 96.8 ± .09 | 3.0 | 97.6 ± 0.7 |
| | 5.0 | 96.5 ± 0.6 | 5.0 | 97.3 ± 0.6 |
| | 7.0 | 95.9 ± 0.5 | 7.0 | 90.8 ± 0.5 |

*Mean ± S.D. of five determinations.

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