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## **EFFECTIVENESS OF OXIDISING AGENT IN THE DETERMINATION OF CARBARYL PESTICIDE**

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### **Abstract**

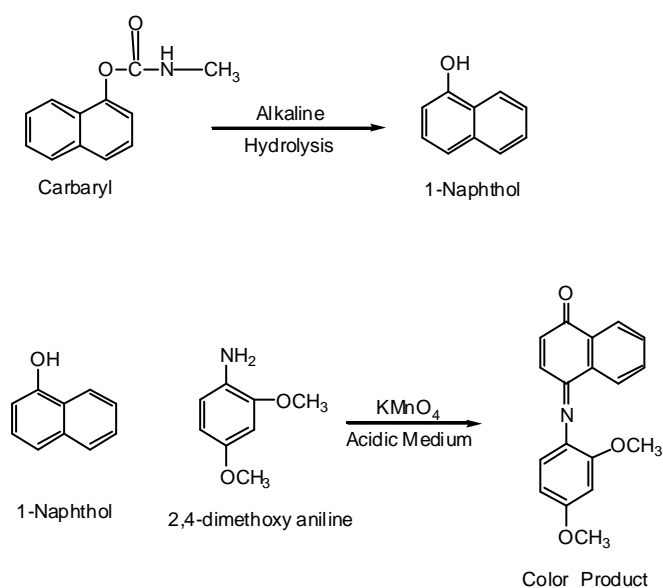
*A simple, convenient, sensitive spectrophotometric technique is reported for the determination of carbaryl pesticide in its formulations in various environmental samples. 2,4 dimethoxy aniline was employed as a new coupling agent in the presence of oxidising agent as potassium permanganate (KMnO<sub>4</sub>) in acidic medium. The formation of colour with the coupling agent is instantaneous and stable for more than 24 h. The absorbance of coloured product was observed at 470 nm.*

### **Introduction**

Carbaryl (1-Naphthyl-N-methyl Carbamate), a toxic pesticide to human system finds a wide applicability to control a number of pests of various crops like paddy, sugar and potato. It is therefore essential to find a simple, sensitive and reliable technique to analyse the residues of carbaryl pesticides in air, water samples and in other environmental systems.

Several analytical methods like colorimetric<sup>1-3</sup> and spectrophotometric technique<sup>4-9</sup> were employed for the analysis of these pesticides using various coupling agents in their formulations, air, water and environmental samples. p-aminophenol, p-Dimethyl phenylenediamine dihydrochloride and 1-Amino-2-naphthol-4-sulphonic acid are the coupling agents available in literature to analyse carbaryl residues. We are now reporting a new coupling agent, 2,4-dimethoxy aniline for spectrophotometric determination, and the method is based on reaction of phenolic product with 2,4 dimethoxy aniline in presence of an oxidising agent (KMnO<sub>4</sub>) to produce a yellow coloured dye as shown in Fig. 1 The colored product is extracted into organic solvent. Extraction of the dye from aqueous solution into a 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 colored product in organic solvents is more when

compared with the aqueous phase. The method is extended to the determination of carbaryl in commercial formulations and water samples.



**Fig.1 : Scheme of Reaction with 2,4-dimethoxy aniline**

### **Experimental**

#### **Reagents :**

All chemicals and reagents used were of analytical grade. Deionised water was used throughout the experiments.

#### **Carbaryl stock solution (1000 Fg/ml) :**

Insecticide (0.10g) was dissolved in 100ml of carbonyl free methanol. The stock solution was progressively diluted with the solvent to obtain standard solution of desired concentration (0.1 Fg/ml).

**2,4-Dimethoxy aniline(2%):** 2,4 dimethoxy anilene (2g) was first dissolved in a few ml of methanol and made up to 100ml with distilled water.

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

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

**Potassium permanganate solution:** Potassium permanganate (8g) was dissolved in distilled water and diluted to 100ml.

**Instrumentation :** A HITACHI U 2001 Spectrophotometer was employed in the present studies.

**Recommended procedure :**

Carbaryl solution (20 ml) was taken in a clean dry 100 ml beaker. 2% sodium hydroxide solution (5 ml) was added and allowed to stand for 5 min for complete hydrolysis, the pH of the solution was adjusted to 9.5 by adding 5 ml buffer solution and the requisite amount of HCl and ammonia solution. The solution was transferred into a 50 ml separating funnel and allowed to stand for 2 min, and then 3 ml of 2,4 dimethoxy aniline and 3 ml of potassium permanganate added and mixed well. The yellow coloured dye formed was extracted into 10 ml chloroform. The absorbance of the layer was measured at 470 nm, against a reagent blank.

**Determination of carbaryl in formulations :**

The well mixed formulation (equivalent to about 100 Fg of the active insecticide) was shaken with 25ml 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 10ml portions of methanol. The filtrate and washing were diluted to 100ml with methanol. Analysis was carried out using the aforesaid procedure.

**Recovery of Carbaryl residues from spiked water sample :**

Water samples (100 ml) spiked with 2.0, 3.0, 4.0, 5.0 and 6.0 Fg of insecticide were taken, the pH of these samples adjusted to 3-4 with 2% sulphuric acid and 2g of anhydrous sodium sulphate. The mixture was transferred into a separating funnel and insecticide extracted using approximately 15 ml of chloroform for each extraction by shaking 5-10 min. Combined extracts were washed with 2ml 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 aforesaid procedure.

**Results and Discussion**

Carbaryl pesticide was hydrolysed and the resultant product converted in to yellow coloured dye by reacting with 2,4- dimethyl anilene in presence of an oxidising agent, potassium permanganate.

**Effect if pH :**

The reaction of the hydrolysed product with 2,4-dimethoxy aniline was carried out in the pH range 2-6. The absorbance of the coloured dye was greater in the pH range 2-6. Hence, pH 4.0 was selected for the extraction of dye in to organic layer.

**Effect of solvent :**

Extraction of coloured dye was carried out in benzene, chloroform, methyl isobutyl ketone and carbon tetrachloride and their absorption spectra are shown in Fig. 1. Absorbance for the benzene extractant was more than the other solvents. The extraction with carbon tetrachloride was less efficient. though absorbance with chloroform extraction was slightly less than benzene, chloroform was selected for further extraction because of convenience of extraction.

**Stability :**

The stability of the coloured dye was studied in various solvents. It was stable for more than 24 hrs in chloroform, benzene and methyl isobutyl ketone, but faded quickly in carbon tetrachloride. Beer's law was obeyed over the concentration range of 0.09 to 1.0 Fg/ml of carbaryl . The Molar absorption co-efficient was  $3.06 \times 10^5$  Sandell's sensitive is  $0.0113 \text{ Fg cm}^2$  correlation co-efficient 0.991, relative error is 0.01%. The method was employed for the determination of carbaryl in commercial formulations. Results are shown in Table 1. It indicates that the active insecticide obtained in formulations was in agreement with the reported results by the manufacturers and the recovery of carbaryl residues from spiked water samples was quite good. The results further demonstrate that the method is suitable for the analysis of formulations and field water samples.

**Conclusion :**

It is evident from the above results that the proposed method with 2,4-dimethyl aniline are simple, rapid and sensitive, the oxidising agent, potassium per manganate, provides suitable method for the formation of color compound, offers high sensitivity and do not involve other reagents present in technical samples.

This proposed method does not required any elaborate clean up procedure as the oxidation process is unique compared to other methods. The pH at 4.0 serves additional advantage for the stability of the colored product of 1:1 and stable for more than 24h. Hence the described proposed would serve as additional technique for the estimation of carbaryl in field water and spiked water sample which are quite satisfactory.

**Table -1 : Analysis of commercial formulations and spiked water samples.**

S.No.	Added (F g)	Found (F g)	% RSD <sup>a</sup>

1.	15.0	14.7	0.38
2.	30.0	29.6	0.48
3.	45.0	44.4	0.56
4.	60.0	59.5	0.61
5.	75.0	74.1	0.71
6.	90.0	89.0	0.57

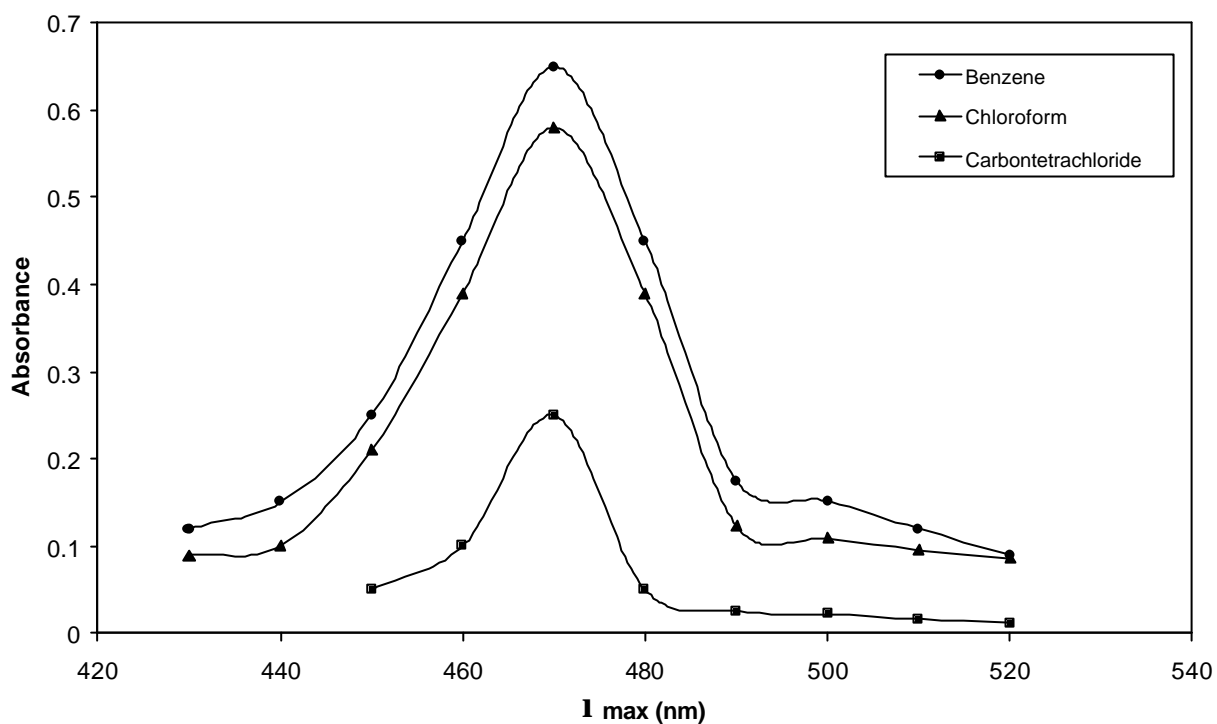
a = RSD for five independent determinations.

**Table - 2 : Recovery of carbaryl residue from spiked water samples**

S.No.	Added (ppb)	Found (ppb)	% Recovery	% RSD <sup>a</sup>
1	15.0	14.9	99.3	0.62
2	30.0	29.4	98.0	0.57
3	45.0	44.2	98.2	0.53
4	60.0	59.3	98.8	0.56
5	75.0	74.2	98.9	0.52

a = RSD for five independent determinations.

Fig.2: Effect of solvents



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