

A novel spectrophotometric method for the determination of Carbaryl in Environmental samples

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ABSTRACT

A novel, rapid, robust and sensitive spectrophotometric method was developed for the determination of carbaryl in its formulations, water and grain (rice and wheat) samples with newly synthesised reagent. The proposed method was based on the alkaline hydrolysis of carbaryl pesticide and thus resulted 1-naphthol was coupled with diazotised 4-bromoaniline to give dark pink colored product having λ_{max} 518 nm for diazonium method (DM). The formation of colored derivatives with the coupling agent is instantaneous and stable for 48 h (DM). Beer's law was obeyed in the concentration range of 0.5–10.0 $\mu\text{g}\cdot\text{mL}^{-1}$ for DM. Molar absorptivity and Sandell's sensitivity were found to be $6.596 \times 10^4 \text{ l mol}^{-1}\text{cm}^{-1}$ and $0.0305 \mu\text{g cm}^{-2}$ respectively. The experimental results indicate that the procedure can eliminate the fundamental interferences caused by other pesticides and non-target ions, which made the methods more sensitive and selective. The method was applicable to the determination of carbaryl residue in water and food grain samples up to μg level.

Keywords: carbaryl, 4-bromoaniline, spectrophotometer.

INTRODUCTION

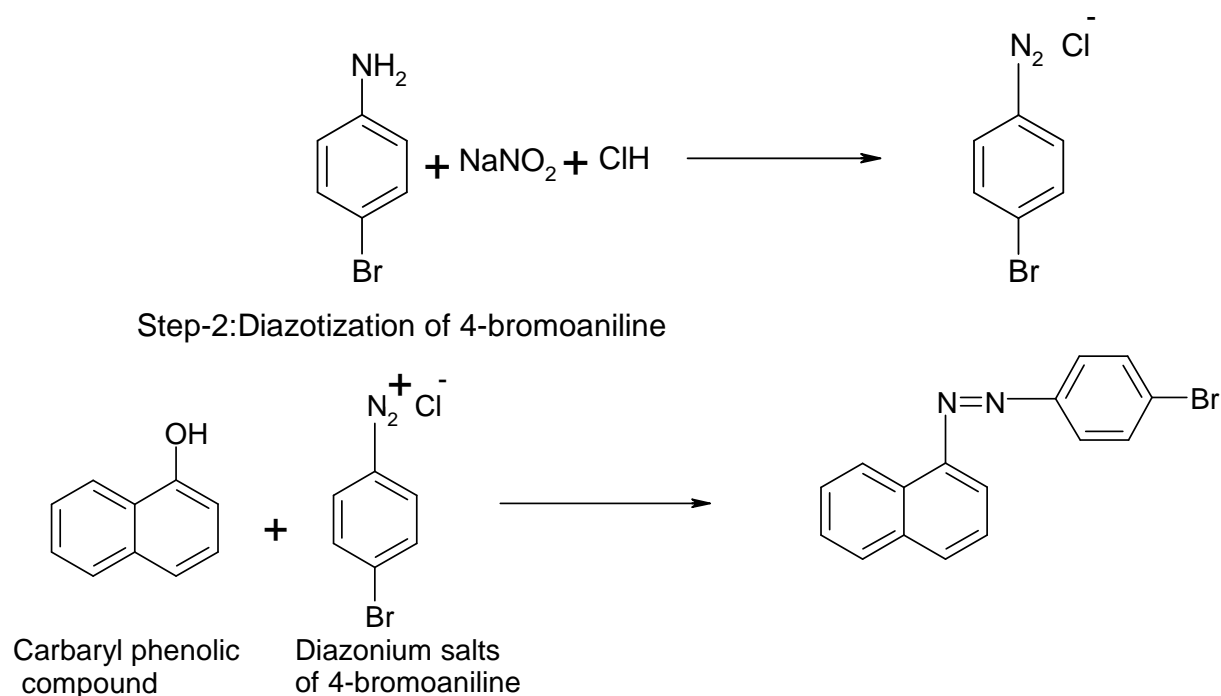
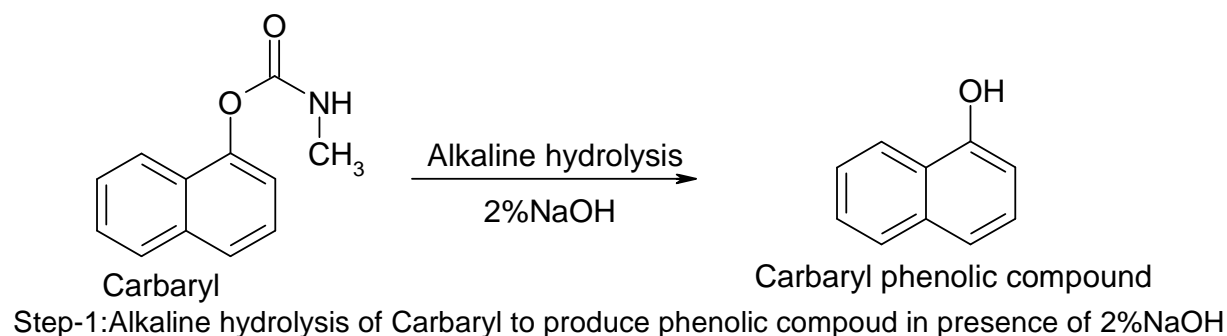
With the world population predicted to rise from 6 billion to over 9 billion by 2050, population growth is a driver of increased demand for agricultural products. Pesticides are used in agriculture mainly for the purpose of increasing plant productivity. Synthetic organic Insecticides, fungicides and herbicides are agrochemicals designed to combat the attacks of various pests on agricultural crops. However, in many cases hazardous residues are left, becoming a permanent danger to quality of food, environment and consumers health [1]. Among all the pesticides used, carbamates are most common.[2-4].

Carbaryl (1-Naphthyl –N-Methyl carbamate) is a broad-spectrum pesticide, extensively used as contact and systemic insecticide on agricultural products, introduced in the year 1957. Even though it is a cholinesterase inhibitor, it has been accepted to have low mammalian toxicity. This type of concept is due to upon chemical hydrolysis and biodegradation carbaryl producing metabolites, among which 1-Naphthol is a major product which does not accumulate in the body, but it excretes in urine and faeces. Despite these merits, recent data shows that some adverse effects have also been reported. It includes, alteration of liver microsomal enzymes [5], sub chronic neurotoxicity [6], changes on immunological function in in-vitro culture [7] and the combination of cyano- bacteria with Carbaryl and 1-Naphthol showing more toxicity when compared to cyano- bacteria alone [8].

A detailed survey of literature reveals few methods including chromatographic [9-12], immunoassay [13-14] and Spectrophotometric methods [15-23] are reported. But these reported methods are having their own demerits; example HPLC methods are very expensive due to high cost of solvents and other spectrophotometric methods are of low sensitivity and multiple steps involved. Therefore the present paper describes simple, sensitive and rapid method for carbaryl estimation.

In this paper, a simple and sensitive spectrophotometric method is proposed for the determination of carbaryl using diazotized 4-bromoaniline as a coupling agent. The reaction mechanism is shown in Fig. 1. The developed method is extended to the determination of propoxur in commercial formulations and environmental samples

Fig-1: Reaction Mechanism



MATERIALS AND METHODS

Reagents

All reagents used were of AnalaR grade and doubly distilled water was used throughout the experiment.

Preparation of Standard solutions

A stock solution containing 1 mg/ml Carbaryl (Bayer, India) was prepared in 20% methanol and working standards

were prepared by appropriate dilution of the stock solution. Sodium nitrite: 0.5% aqueous solution. Sodium hydroxide: 2% aqueous solution. Hydrochloric acid: 1N aqueous solution. 4-bromoaniline: 0.2% solution prepared in methanol. Diazotized 4-bromoaniline: 0.2% 4-bromoaniline, 0.5% sodium nitrite and 1N hydrochloric acid were added with continuous shaking. The solution was stable for 48 h.

Apparatus

A Hitachi U-3400 spectrophotometer with 10 mm glass cells was used for all spectral measurements; pH measurements were made with an Elico pH meter Model CL-110.

Preparation of calibration curve

An aliquot containing 0.5 – 10 µg/ml of carbaryl was taken in a 25 ml standard flask and diazotized 4-bromoaniline has been added, followed by 2% sodium hydroxide solution, with continuous shaking in an ice bath. A yellow dye formed. The solution was made up to the mark and kept for 15 min for full color development. The absorbance of the colored solution was measured at 518 nm against the reagent blank.

Determination of carbaryl in water samples

pH of each water samples was adjusted to 3-4 with 20% sulphuric acid, one liter samples of distilled water and tap water was fortified with different concentrations of insecticide dissolved in methanol. Each sample was extracted with chloroform (2 × 100 ml). The extracts were combined and washed with 20 ml of 0.1 M K₂CO₃ solution to break any emulsions. The chloroform extracts were dried over anhydrous sodium sulfate in a filter funnel and the filtrate was collected in a 250 ml calibrated flask. The filter funnel was washed with 20 ml of chloroform and the volume of the filtrate was made up to the mark, known aliquots of chloroform extracts were taken and evaporated on a water bath at about 50°C. The residue was dissolved in 10 ml methanol. The solution was then transferred into a separating funnel with 25 ml of water. To this, diazotized 4-bromoaniline and 2% sodium hydroxide were added, then the yellow color developed spontaneously.

Determination of carbaryl in food samples

Different samples of plant materials like grains (rice and wheat) 25 g of each were collected from the fields where carbaryl had been sprayed. The samples were weighed, macerated and blended in a mixer. It was extracted using 25 ml of chloroform blended sample and it was extracted using 25 ml of chloroform. After extraction, the samples were spiked with different concentrations of carbaryl in 5 ml of methanol. The spiked samples were blended for a further 2 min. The chloroform solution was then decanted into a 250 ml calibrated flask through Whatman No. 1 filter paper. Blending and decanting was repeated twice with 10 ml portions of chloroform. The extracts were combined and diluted to the mark. The chloroform extract was evaporated off, under reduced pressure using a water bath at about 50°C. The residue was dissolved in 10 ml of methanol and the color developed as described before.

RESULTS AND DISCUSSION

The optimum conditions were established by alternating one variable at a time. The yellow colour species formed by carbaryl derivative shows maximum absorbance at 518 nm. The reagent blank has negligible absorbance at this wavelength. Beer's law was obeyed in the range of 0.5 – 10 µg ml⁻¹. Molar absorptivity and Sandell's sensitivity were found to be $6.596 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.0305 \mu\text{g cm}^{-2}$ respectively. The colour of the dye formed was found to be stable for 48h.

The suitability of the proposed method was studied by analysis of six replicate samples containing 5 ppm of carbaryl. The relative standard deviation values are given in Table-1.

Table-1: Optical characteristics, precision and accuracy of the method using diazotized 4-bromoaniline as coupling agent.

Colour of the dye	Dark pink
Beer's law Concentration range	0.5 - 10 µg ml ⁻¹
λ max	518 nm
Stability of the colour	48 hrs
Molar absorptivity	$6.596 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$
Sandell's sensitivity	$0.0305 \mu\text{g cm}^{-2}$

Recovery experiment was performed with known amounts of the compounds added to different samples of grains

and water. Grains samples were spiked by adding a methanol solution of the insecticides to the dry grains and evaporating the solvent.

The results presented in Table-2 and Table-3 show that recovery was in the range 95-99%.

Table-2: Recovery of carbaryl from fortified water samples using diazotized 4-bromoaniline as a coupling agent

Sample No.	Fortification level $\mu\text{g ml}^{-1}$	Distilled water		Tap water	
		Amount recovered $\mu\text{g ml}^{-1}$	Recovery* percentage	Amount recovered $\mu\text{g ml}^{-1}$	Recovery* percentage
1	0.6	0.59	98.6 \pm 1.0	0.591	98.5 \pm 0.9
2	1.0	0.99	99.0 \pm 0.8	0.985	98.5 \pm 0.75
3	1.4	1.38	98.9 \pm 0.7	1.39	99.2 \pm 0.8
4	1.8	1.78	98.1 \pm 0.6	1.76	97.7 \pm 0.7
5	2.2	2.16	98.18 \pm 0.6	2.17	98.6 \pm 0.7
6	2.6	2.55	98.0 \pm 0.6	2.47	95.0 \pm 0.5

* Mean \pm S.D. of five determinations

Table-3: Recovery of carbaryl from fortified grains using diazotized 4-bromoaniline as a coupling agent

Sample No.	Fortification level $\mu\text{g ml}^{-1}$	Rice		Wheat	
		Amount recovered $\mu\text{g ml}^{-1}$	Recovery* percentage	Amount recovered $\mu\text{g ml}^{-1}$	Recovery* percentage
1	0.6	0.58	96.6 \pm 1.0	0.585	97.5 \pm 0.9
2	1.0	0.983	98.3 \pm 0.81	0.979	97.9 \pm 0.79
3	1.4	1.385	96.4 \pm 0.7	1.358	97.0 \pm 0.82
4	1.8	1.78	98.8 \pm 0.65	1.71	95.0 \pm 0.78
5	2.2	2.18	99.0 \pm 0.59	2.10	95.4 \pm 0.65
6	2.6	2.52	97.0 \pm 0.5	2.5	96.1 \pm 0.5

* Mean \pm S.D. of five determinations

Comparison of Other Spectrophotometric methods with proposed method

The data presented in the Table 4 suggests the present method is very sensitive and facile when compare with other officially reported method.

Table 4. Comparison of Other Spectrophotometric methods with proposed method

Methods	λ_{max} nm	Beer's law range $\mu\text{g ml}^{-1}$ Molar absorbtivity. $\text{l mol}^{-1} \text{cm}^{-1}$	Remarks
p-dimethylphenylene diaminodihydrochloride [19]	600	0.7-8.0 and 1.41×10^4	Reagent it selftoxic
p-aminophenol [19]	600	0.8-10 and 1.33×10^4	Not much sensitive
2,4-dimethoxyanilin [23]	505	0.4-10 and 3.42×10^4	Moderately sensitive
2,6-dibromo 4-Metylaniline [20]	505	0.6-10 and 3.42×10^4	Moderately stable
4-bromoaniline (present method)	518	0.5-10 and 6.59×10^4	Highly sensitive. Stable up to 48h.

CONCLUSION

The proposed spectrophotometric method is simple to perform, cheaper and sensitive when compared to many other existing methods which are shown in Table 4. The sensitivity, simplicity, temperature independence and stability of the colored product are the advantages of this method. Does not involve extraction step and the use of carcinogenic solvents. The proposed method does not entail any stringent experimental variables which affect the reliability of the results. From the recovery studies it comes to know that this method can serve as an alternative method for determining carbaryl residues in various environmental samples.

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