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Spectrophotometric determination of trace carbaryl in water and grain samples by inhibition of the rhodamine-B oxidation

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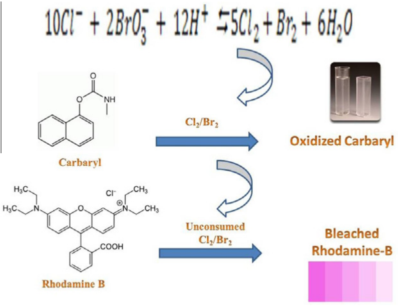
HIGHLIGHTS

- A surfactant assisted spectrophotometric method for carbaryl determination.
- Simple, selective and sensitive method based on a new kinetic approach.
- Rapidity and no interference are distinct advantages of the method.
- Applicable in different water and grain samples with satisfactory results.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel, sensitive, selective and simple kinetic spectrophotometric method has been developed for determination of trace levels of carbaryl based on its inhibitory effect on the oxidation of rhodamine-B by chlorine and bromine released from reaction of potassium bromate with hydrochloric acid in micellar medium. A linear relationship was observed between the inhibitory effect and the concentration of the compound. The absorbance was monitored at the maximum wavelength of 555 nm. The effect of different parameters such as pH, temperature and concentration of rhodamine-B, potassium bromate and surfactant on the reaction were investigated and optimum conditions were established. Under the selected experimental conditions, carbaryl was determined in the range of 0.04–0.4 $\mu g\ mL^{-1}$. Sandell's sensitivity and molar absorptivity were found to be 0.00055 $\mu g\ cm^{-2}$ and $3.658 \times 10^5\ L\ mol^{-1}\ cm^{-1}$ respectively. The proposed method was applied satisfactorily for the determination of carbaryl in water and different grain samples. The results were compared with those obtained by reference method and were found to be in agreement.

Introduction

Synthetic organic insecticides, fungicides and herbicides are agrochemicals designed to combat the attack of various pests on agricultural crops, thereby increasing the agricultural yield. Amongst all the pesticides, carbamates are most common [1–3]. Carbaryl (1-naphthyl-N-methyl carbamate) is used to control more than 100 kinds of pests in crops such as beans, bananas, potatoes and domestic vegetables [4]. It can produce adverse effects on humans by skin contact, inhalation, and ingestion. In plants, a small amount of carbaryl which is deposited on the outer layer, passes to tissues and is metabolised by hydrolysis or oxidation to several hydroxylated metabolites [5]. These pesticides and their degradation product remain as contaminants in environmental samples, such as soil, ground water, surface water and also in food. These substances inhibit the cholinesterase enzyme, impairing the

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function of central nervous system and can cause nausea, vomit, broncho-constriction, blurred vision, convulsions, coma and respiratory failure, in addition to its teratogenic characteristics [6]. Therefore, great attention is given to its monitoring in environment. Analysis of carbaryl in environmental and biological samples is routinely carried out using analytical techniques such as gas chromatography [7], gas chromatography coupled with mass spectrometry [8,9], high-performance liquid chromatography [10]. Other methods like amperometry [11–12], potentiometry [13,14], conductometry [15] have also been reported. Flow injection based on the oxidation of carbaryl by cerium (IV) [22] and with potassium permanganate in sulphuric acid medium [23] has also been reported. Spectrophotometry is considered as the most convenient and economical analytical technique due to its inherent simplicity and wide availability in most of the laboratories. Few spectrophotometric methods [16–21,26] have also been reported for the determination of carbaryl, based on its hydrolysis to 1-naphthol which is subsequently coupled with different reagents. In order to achieve an appropriate selectivity and sensitivity, greener and efficient method using cloud point extraction with Triton X-114,without organic solvents and having pre-concentration steps has also been reported [27]. A method based on oxidation of carbaryl by potassium ferricyanide ($K_3Fe(CN)_6$) is also been reported [24]. Some of the reported methods suffer from interference, poor sensitivity, instability of colour or involve extraction where as other suffers from blank absorption or longer time required for colour development. To overcome these drawbacks a selective and sensitive method has been proposed for the determination of carbaryl. The proposed kinetic spectrophotometric method is based on the inhibitory effect of carbaryl on the decoloration reaction of rhodamine-B by bromate in acidic medium in presence of cetyl trimethyl ammonium bromide (CTAB) surfactant. The method is simple, selective and can be easily applied for the determination of carbaryl in water and different grain samples. The availability of spectrophotometric instrument and the simplicity of the proposed analytical procedure make the technique very attractive for wide range of application.

Experimental

Apparatus and reagent solutions

A Varian Carry 50 Bio UV–Visible spectrophotometer was used for spectral measurements, pH measurements were made with systronics digital pH meter 335. A thermostat water bath was used to maintain the reaction temperature at 30 °C. All chemicals used were of analytical grade and solutions were prepared with double distilled water. Carbaryl (Bayer, India Ltd.), stock solution 1000 $\mu g\ mL^{-1}$ was prepared in ethanol. Working standards were prepared by appropriate dilution of the stock. Potassium bromate ($KBrO_3$) (Merck, Mumbai, India), aqueous solution of 6.0×10^{-3} mol L^{-1} was prepared and stored in amber coloured bottle. Rhodamine-B (Merck, Mumbai, India) aqueous solution 2.0×10^{-4} mol L^{-1} was prepared. A 2 mol L^{-1} aqueous solution of hydrochloric acid (HCl) (Merck, Mumbai, India) was prepared. CTAB (Merck, Mumbai, India) stock solution 1.3×10^{-3} mol L^{-1} was prepared by dissolving in water. The other surfactants cetyl pyridinium chloride (CPC), sodium dodecyl sulphate (SDS) and Triton X-100 were prepared in the similar way.

Procedure

Preparation of calibration curve

Before the measurements all solutions and distilled water were kept in a thermostat water bath at 30 °C for 15 min, for equilibrium. An aliquot of the solution containing 0.04–0.4 $\mu g\ mL^{-1}$ of carbaryl was transferred into a 10 mL volumetric flask and then 1 mL of rhodamine-B, 1 mL of CTAB solution and 0.6 mL of HCl were added to the flask. The solution was diluted to 9 mL with water and then 1 mL of 6.0×10^{-3} mol L^{-1} potassium bromate was added. The solution was mixed and a portion of the mixture was transferred into spectrophotometric cell. The reaction was followed by recording the absorbance of the solution against water at 555 nm at 30 s interval, for five minutes after the initiation of the reaction. Time was measured just after the addition of last drop of potassium bromate solution. This signal (sample signal) was labeled as ΔA_s. The same procedure was repeated without sample solution and the signal (blank signal) was labeled as ΔA_b. Analytical signal ΔA was difference between sample signal and blank signal $\Delta A_s - \Delta A_b$. The standard curve was constructed between ΔA versus carbaryl concentration.

Table 1
Recoveries of carbaryl spiked to water and grain samples.

Sample	Amount added (μg)	Amount found (μg)[a]	Recovery (%)	RSD (%)
Water sample[b]	5	4.91	98.2	1.47
	10	9.93	99.3	0.50
	20	19.87	99.35	0.18
Grain samples[c] wheat	5	5.06	101.20	3.26
	10	10.04	100.40	1.60
	20	19.94	99.70	0.58
Rice	5	4.89	97.80	2.54
	10	9.88	98.80	1.15
	20	19.85	99.25	0.43

[a] Mean of five replicate analyses.
[b] Volume of sample, 5 mL (free from carbaryl).
[c] Volume of sample, 10 g (free from carbaryl).

Determination of carbaryl in pesticide free water samples

To check the recovery, water samples, free from carbaryl, were taken. The samples were spiked with the known amounts of carbaryl and then kept for 24 h. After filtering, the filtrate was transferred into a 100 mL Erlenmeyer flask (with a screw cap), and 15 mL of dichloromethane (CH_2Cl_2) were added. The mixture was then shaken for 10 min. The collected aqueous phase was extracted with another 15 mL dichloromethane. The extracts were combined, and evaporated in rotary evaporator. Finally, the residue was dissolved in ethanol and the amount was analyzed by proposed method (Table 1).

Determination of carbaryl in pesticide free grain samples

To check the recovery, samples of wheat and rice free from carbaryl were taken in a mixer and blended for 15 min, then it is fortified with a known amount of the carbaryl. The samples were blended for further 2 min then aliquot of this sample was transferred to a 100 mL Erlenmeyer flask (with a screw cap), and 20 mL of dichloromethane were added. The mixture was shaken for 30 min then filtered on a Buchner funnel, the residue in the funnel was further washed with 15 mL of dichloromethane. The extracts were combined, and evaporated in rotary evaporator. Finally, the residue was dissolved in ethanol and the amount was analyzed by the proposed method (Table 1).

Results and discussion

Rhodamine-B undergoes oxidation reaction with Cl_2 and Br_2 released by bromate in acidic medium leading to its decolorisation.