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E-J.Chem
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ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
Vol. 3, No.13, pp 250-256, October 2006

Highly Sensitive Reaction for the Estimation of Carbaryl Using 4-4'-Diaminodiphenyl Sulfone in Environmental Samples

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Received 8 June 2006; Accepted 31 July 2006.

Abstract: A rapid, sensitive Spectrophotometric method for the determination of ultra trace amount of carbaryl (1-Naphthyl-N-Methyl Carbamate) is proposed. The method is based on an alkali hydrolysis of carbaryl in the presence of methanolic KOH, followed by coupling with diazotized 4-4'-diaminodiphenyl sulfone in an alkaline medium. The water soluble pink dye obtained shows an absorption maximum at 540 nm. The system obeys Beer's law over the range of 0.06-2.0 $\mu\text{g ml}^{-1}$. The absorptivity of the coloured product is $7.014 \times 10^4 \text{ l mol}^{-1}\text{cm}^{-1}$ and the developed colour is stable for 48h. The detection limit of Carbaryl is 0.0102 $\mu\text{g ml}^{-1}$. This method is a very good alternative tool and it can be used successfully for the determination of carbaryl residue in environmental water and grain samples.

Keywords: Spectrophotometric, carbaryl and dapsone, highly sensitive reaction.

Introduction

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 enzymes¹, sub chronic neurotoxicity², changes on immunological function in in-vitro culture³ and the combination of cyano- bacteria with Carbaryl and 1-Naphthol showing more toxicity when compared to cyano- bacteria alone⁴.

A detailed survey of literature reveals few methods including chromatographic⁵⁻⁸, immunoassay⁹⁻¹⁰ and Spectrophotometric methods¹¹⁻¹⁹ 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. It involves coupling of carbaryl with diazotized dapsone in KOH media.

Experimental

Materials and methods

SYSTRONICS SPECTROPHOTOMETER – 106 Model with 10mm matched quartz cells was used throughout the spectral measurement.

Reagents

Analytical grade sample of Carbaryl pesticide (99.9%) was obtained from Bayer India Ltd. India. 4-4'-diaminodiphenyl sulfone (dapsone) was obtained from Merk (Germany), Pesticide grade methanol and acetone were obtained from Sigma, (USA), Sodium nitrite, Potassium hydroxide, Sulphamic acid, were from BDH, AnalR. Double distilled water was used throughout the experiment.

A stock solution of carbaryl ($1000 \mu\text{g ml}^{-1}$) was prepared by dissolving 100mg of carbaryl in acetone in 100 ml calibrated flask and diluted with acetone. 5 M KOH solution was prepared in methanol. Sodium nitrate 1.0% solution in water, 0.2% dapsone was prepared in 1M hydrochloric acid, 2% Sulphamic acid was prepared in water.

Recommended procedure

An aliquot of the standard solution of carbaryl containing 1.5-50 μg of carbaryl was transferred into a series of 25 ml of calibrated flasks, 5ml of 5M KOH solution was added to each flasks and allowed to stand for 5 min for complete hydrolysis, followed by the addition of 2ml of 0.2% dapsone, 2 ml of 1.0 % sodium nitrate and 2 ml of 2% Sulphamic acid and kept aside for 2min to complete the reaction with occasional shaking. Pink coloured azo dye was formed. Dilution was made with water up to the mark and the absorbance was recorded at 540 nm against the corresponding reagent blank and calibration graph was constructed.

Results and Discussion

Spectral characteristics

The proposed method involves the formation of a pink azo dye having λ_{max} of 540 nm. The reagent blank had negligible absorption at this wavelength. The absorption spectrum of the coloured dye and the corresponding reagent blank are given in the Figure 1.

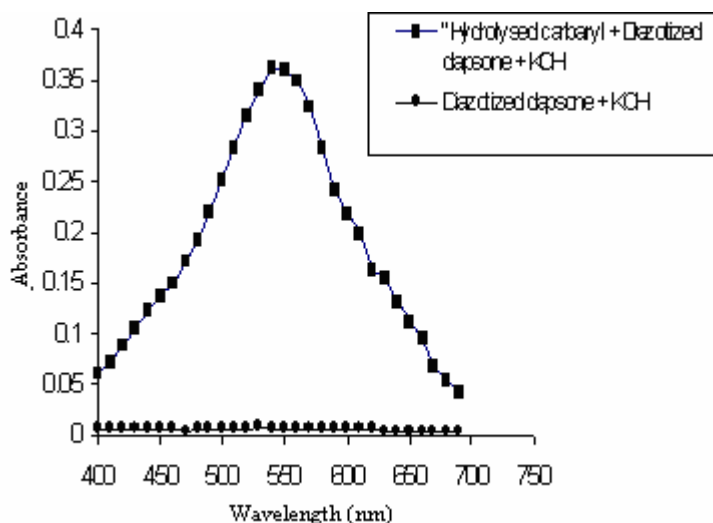


Figure 1. Absorption spectra of the reaction Product of Hydrolyzed Carbaryl and Reagent blank

Optimization of the reagent concentration

Various concentration and volume ranges for all the reagents were studied in detail. It was found that dapsone in the range of 1-2 ml, sodium nitrite in the range of 0.5-4.0 ml, sulfamic acid in the range of 0.5-4.0 ml and KOH 2- 5.0 ml were necessary to obtain a stable pink colored product with maximum colour intensity.

Quantification

Adherence to Beer's law by the coloured product of diazotized dapsone with hydrolyzed carbaryl (sevin) was determined by measuring the absorbance at appropriate wavelength (540 nm) for a set of solutions containing varying amounts of analyte and specified amounts of reagents against colorless reagent blank. Beer's law was obeyed over the hydrolyzed carbaryl range of 0.06-2.0 $\mu\text{g ml}^{-1}$. Limit of quantification (LOQ) is determined by taking the ratio of standard deviation (σ) of the blank with respect to water and the slope of the calibration curve (a) multiplied by a factor 10. LOQ is approximately 3.3 times the limit of detection (LOD). Naturally, the LOQ slightly crosses the lower limit of the Beer's law range. But LOD is well below the lower limit of the Beer's law range. The upper limit of the Beer-Lambert range is determined by a plot of absorbance against concentration at the value of λ_{max} . Beyond this limit, the correlation results were really affected. Hence, the measurements were excluded above these limits to keep the relationship linear. The optical characteristics and precision data are given in Table 1.

Precision and Accuracy

The precision of the proposed method was ascertained from the absorbance values of five replicates. The percentage relative standard deviation was calculated for the proposed method. The accuracy of the method was confirmed by recovery methods.

Table 1. Optical characteristics and precision data for the product

Optical parameters	Dapsone method
Colour	Pink
λ_{\max} (nm)	540
Stability (h)	48
Beer's law range $\mu\text{g ml}^{-1}$	0.06-2.0
Molar absorptivity $\text{l mol}^{-1}\text{cm}^{-1}$	7.014×10^4
Sandell's Sensitivity ng cm^{-2}	2.8
Limit of detection (LOD) $\mu\text{g ml}^{-1}$	0.0102
Limit of Quantification (LOQ) $\mu\text{g ml}^{-1}$	0.342
Regression equation Y*	
Slope (a)	0.349
Intercept (b)	0.0001
Correlation Coefficient (r) ^b	0.9998
Relative standard deviation (%) ^b	0.00114
Range of error(95%) confidence level	0.248

* Y= ax + b, Where x is the Concentration of carbaryl (Sevin) in $\mu\text{g ml}^{-1}$

^bn = 5

Proposed reaction mechanism

Carbaryl undergoes an alkali hydrolysis in the presence of alcoholic KOH to give α - Naphthol, which coupled with Diazotized dapsone to give water soluble pink azo dye having maximum absorption at 540nm. Tentative reaction mechanism is shown in Scheme 1.

Effect of temperature and colour stability

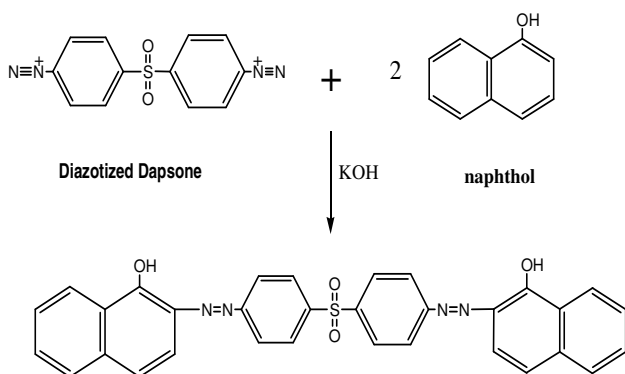
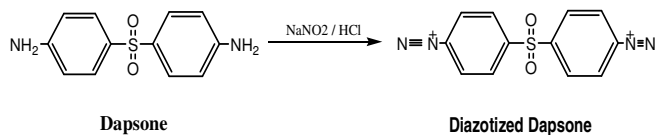
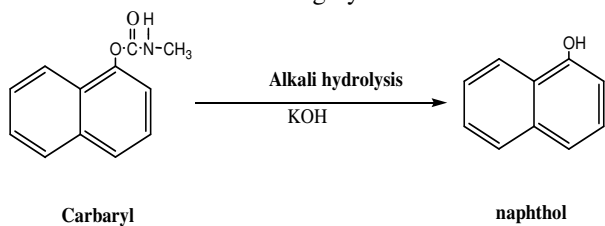
Under the optimized condition, 5 min was given for complete colour development. The intensity of the colour developed was stable at the temperature range from 20°C to 70 °C and up to 48 h at room temperature.

Effect of Foreign ions

Under the diazotized condition reactions used, other pesticides and other common expedients which are present in water were studied thoroughly. It is significant to note that various common ions did not interfere even when added in excess to a known amount of hydrolyzed carbaryl. Table 2 shows the results of interference on the determination of carbaryl. An error of 2 %in the absorbance reading was considered tolerable.

Recovery of the carbaryl residues from spiked water samples

Water samples (100ml) spiked with known amount of carbaryl ($\mu\text{g ml}^{-1}$) is added, the pH of these samples adjusted to 3-4 with 2M Sulphuric acid. The mixture was transferred into a separating funnel and insecticide was extracted using approximately 15 ml of Chloroform in each occasion till complete extraction. The combined extracts were washed with 2ml of 0.1M potassium Carbonate to break any emulsion formed during the extraction. The extracted insecticide was dried over anhydrous sodium sulphate. Chloroform was evaporated and residue was dissolved in methanol. Determination was carried out by above procedure and data are shown in Table 3.



Pink Azo Dye

Proposed reaction mechanism scheme 1

Table 2. Effect of excipients on the determination of carbaryl

Excipients	Amount of excipients added $\mu\text{g ml}^{-1}$	Mean recovery in %
Parathion	5000	99.50
Malathion	3000	99.70
Chloride	200	100.10
Lead (Pb^{2+})	400	99.08
Ca^{2+}	200	99.50
Mg^{2+}	250	99.45
SO_4^{2-}	220	98.99
NO_2^-	150	99.85
CO_3^{2-}	230	100.06

Table 3. Recovery of carbaryl residue from spiked water samples

Water sample	Carbaryl added $\mu \text{ gml}^{-1}$	Carbaryl found $\mu \text{ gml}^{-1}$	Mean Recovery in % and $\pm \text{SD}^b$
Well water (1)	1.0	0.97	97.00 \pm 0.43
Well water (2)	0.8	0.81	101.25 \pm 0.39
River water(1)	0.5	0.48	96.00 \pm 0.48
River water(2)	1.5	1.46	97.33 \pm 0.45
Tap water (1)	1.0	0.99	99.00 \pm 0.51
Tap water (2)	0.5	0.51	102.00 \pm 0.42

^bn = 5*Recovery of Carbaryl residues from grain samples*

Grain samples such as wheat and rice were taken of about 20g each in a warming blender and blended for 15 min with 50 ml of chloroform. These samples were fortified with carbaryl in methanol and again blended for about 5 min. Chloroform was filtered and evaporated on water bath. Thus obtained residue was dissolved in methanol and estimation of carbaryl was carried out by proposed method and results are presented in the Table 4.

Table 4. Recovery of Carbaryl residues from grain samples

Samples	Amount of carbaryl added $\mu \text{ gml}^{-1}$	Amount of carbaryl found $\mu \text{ gml}^{-1}$	Mean recovery in % and $\pm \text{SD}^b$
I wheat 1	0.75	0.74	98.66 \pm 0.45
2	1.0	0.98	98.00 \pm 0.52
3	1.25	1.23	98.44 \pm 0.35
II Rice 1	1.0	1.01	101.00 \pm 0.35
2	1.5	1.47	98.00 \pm 0.50
3	0.8	0.81	101.25 \pm 0.42

^bn = 5**Table 5.** Comparison of Other Spectrophotometric methods with proposed method

Methods	λ_{max} nm	Beer's law range $\mu \text{ g ml}^{-1}$ and Molar absorptivity. $1 \text{ mol}^{-1} \text{ cm}^{-1}$	Remarks
P – Aminobenzoic Acid ⁽¹⁶⁾	470	0.1- 0.8 and 2.00×10^4	Extraction is necessary Dye stability up to 24 h
P-Dimethylphenylene Diamine dihydrochloride ⁽¹⁵⁾	600	0.7-8.0 and 1.41×10^4	Reagent itself toxic
P- Aminophenol ⁽¹⁵⁾	600	0.8-10 and 1.33×10^4	Not much sensitive
2- Amino 4- Nitrophenol ⁽¹⁹⁾	520	0.4-10 and 3.018×10^4	Moderately sensitive Dye stable up to 24h
2,4 - dimethoxy aniline ⁽¹⁹⁾	505	0.4-10 and 3.42×10^4	Moderately sensitive Dye stable up to 10h
4-4 ¹ -diaminodiphenylsulfone (Present method)	540	0.06-2.0 and 7.014×10^4	Highly sensitive Dye stable up to 48 h

Comparison of Other Spectrophotometric methods with proposed method

The data presented in the Table 5 suggests the present method is very sensitive and facile when compare with other officially reported method.

Conclusion

The proposed spectrophotometric method is simple to perform, cheaper and sensitive when compared to many other existing methods which are shown in Table 5. The sensitivity, simplicity, temperature independence and stability of the colored product are the advantages of this method. This method can be used to detect 0.0102 $\mu\text{g ml}^{-1}$ and quantitatively detect 0.0342 $\mu\text{g ml}^{-1}$ of carbaryl and 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.

Acknowledgements

One of the authors (B.L.B.) thanks the University of Mysore for providing the laboratory facilities.

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