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Spectrophotometric determination of Carbendazim in its Formulations and Environmental samples

Purushotham Naidu K, Niranjan T and V. S. Naidu N*

Dept of Chemistry, S.V.University, Tirupati – 517 502, A.P, India.

***Corres.author: nvsn69@gmail.com, +91-94407 22881.**

Abstract: Two simple, sensitive, rapid, accurate and precise spectrophotometric methods were developed for the analysis of parts per million levels of widely used carbamate pesticide Carbendazim. The first proposed method A is based on the Oxidation followed by complex formation product with 2,2-Bipyridyl – Fe(III) to form orange colored chromophore exhibiting absorption maximum at 512 nm with apparent molar absorptivity 3.82×10^3 L $mol^{-1}cm^{-1}$ and obeyed Beer's law in the concentration range of 10 - 60µg/ml. The second method B is based on the extraction of pesticide and potassium Ferricynide - Fe (III) to form bluish green colored product exhibiting absorption maximum at 478 nm with apparent molar absorptivity 4.46×10^3 L $mol^{-1}cm^{-1}$ and obeyed Beer's law in the concentration range 4- 40 µg/ml. The high percent recoveries indicates the accuracy and reliability of the validate methods. The proposed methods are highly sensitive, precise and accurate and therefore can be used for determination of carbendazim in its formulations and environmental samples.

Keywords: Spectrophotometer, Carbendazim, 2,2-Bipyridyl, Potassium ferricynide, Formulations, Spiked water samples, soil samples.

INTRODUCTION

Trace contamination of pesticides present in the natural aquatic systems creates a lot of pollution problem due to their toxicity and bioaccumulation property[1, 2]. Fungicides are chemical compounds or biological organisms used to kill or inhibit fungi or fungal spores. Carbendazim (methyl 1H-benzimidazole-2-ylcarbamate) (MBC) is a sort of extensive and inside adsorbing antiseptic. It was used to prevent and cure of disease on crop. Structure of carbendazim is shown in **Fig.1.** Carbendazim is pesticide used to control a broad range of diseases on cereals, fruits, cotton, tobacco, turf, ornamentals and vegetables. It is also used in post harvest food storage, as a seed pre - planting treatment and as a timber treatment fungicide. In addition to being a fungicide in its own right carbendazim is a metabolite of thiophanate – methyl. Thiophanate breaks down rapidly in the environment to carbendazim and the use of thiophanate – methyl can lead to residue of carbendazim in treated commodities. Its resistance is a very serious problem and it is listed in toxicity class IV pesticides.

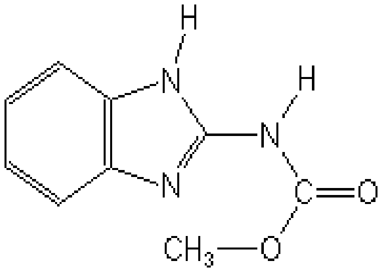

Fig.1: Structure of Carbendazim

The available determination methods of Carbendazim , such as fluorescence analysis [3,4], UV – Vis spectrophotometric[5], solid phase extraction – high performance liquid chromatography[6], HPLC[7], microwave – assisted extraction[8], liquid – mass spectrum[9,10], Voltammetry[11-13] . These methods need expensive equipment and materials. Here, we report sensitive UV-Vis Spectrophotometric methods for analysis of Carbendazim in its formulation, spiked water samples and soil samples.

EXPERIMENTAL

Instrumentation

Shimadzu UV- Visible double beam spectrophotometer (model 2450) with matched quartz cells were used for all the spectral measurements

Chemicals and reagents

Dimethyl formamide, 2,2-Bipyridyl, Potassium Ferricyide, Orthophosphoric acid, Double distilled water. All Chemicals used were of AR grade only.

Technical grade Carbendazim certified to be 98% pure was kindly supplied by Hyderabad chemicals Ltd, Hyderabad, India, and used as the reference standard.

Pesticide formulations of carbendazim such as bavastin, carbendazim were purchased from local markets.

Ferric Chloride (0.2%): The aqueous solution of 0.2% ferric chloride (S.D.Fine Chem., Mumbai, India) was prepared by dissolving 200 mg of chemical in 100 ml of distilled water and stored in dark bottle.

2, 2 – Bipyridyl (0.2%): Prepared by dissolving 200 mg of 2,2 – Bipyridyl (S.D.Fine Chem., Mumbai, India) in 100 ml distilled water.

0.5% Potassium ferricynide (Qualigens Fine Chemicals, Mumbai, India) was prepared by dissolving 500 mg of potassium ferricynide in 100 ml of distilled water.

Orthophosphoric acid (0.1N): Concentrated acid (Merck, Mumbai, india0 was appropriately diluted with water to get the required concentration

Preparation of standard solution

Accurately weighed 100 mg of Insecticide Carbendazim was dissolved in 100 ml of Dimethyl formamide to give a concentration of 1 mg/ml. It is diluting, 10 ml of above solution to 100 ml with dimethyl formamide. The final concentration was brought to 100 µg/ml for further working standards.

Procedure

Method A

Aliquots of standard working solution of carbendazim ranging from 1-6 ml (10-60 µg/ml) were transferred in to a series of 10 ml graduated tubes. To each tube 1 ml of 0.2 % 2, 2'-Bipyridyl and 1 ml of 0.2% Ferric Chloride solutions were added and the resulting solution was heated for 15 min at 100^0C and cool. To this 2 ml of 0.1N Orthophosphoric acid was added. The volume was made up to 10 ml with distilled water and the absorbance of the orange colored chromophore was measured at 512 nm against the corresponding reagent blank. The amount of carbendazim was computed from the Beer – Lambert's plot shown in Fig.2.

Method B

Aliquots of standard working solution of carbendazim ranging from 0.4 – 4ml (4-40µg/ml) were taken into a series of 10 ml volumetric flasks. To each flask 1ml of 0.2% Ferric Chloride and 1 ml of 0.5% Potassium Ferricynide was kept on water bath for 15 min at 60^0C, for complete color development and cooled complete to volume with distilled water. The transferred the colored solutions in to 125 ml separating funnel. The mixture was extracted twice with 10 ml Chloroform by shaking for two min and then allowed to stand for clear separation of the two phases. The absorbance of the separated Chloroform layer i.e Bluish green colored complex was measured against the reagent blank at 478 nm. The colored species was stable for more than 14 hrs. The amount of Carbendazim present in the sample was computed from the calibration curve (Fig.3).

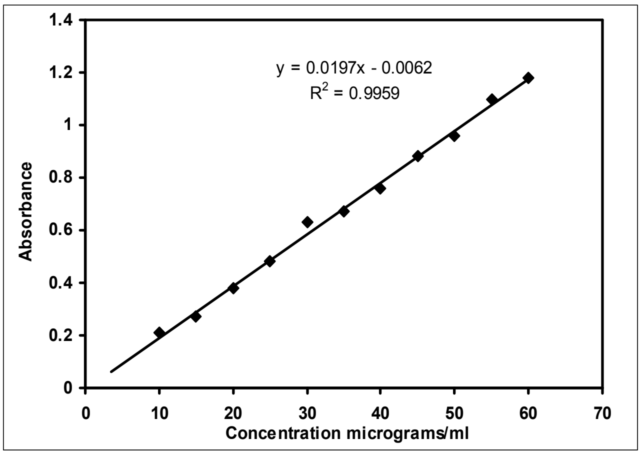

Fig.2 .Calibration plot of carbendazim with spectrophotometry (Method A)

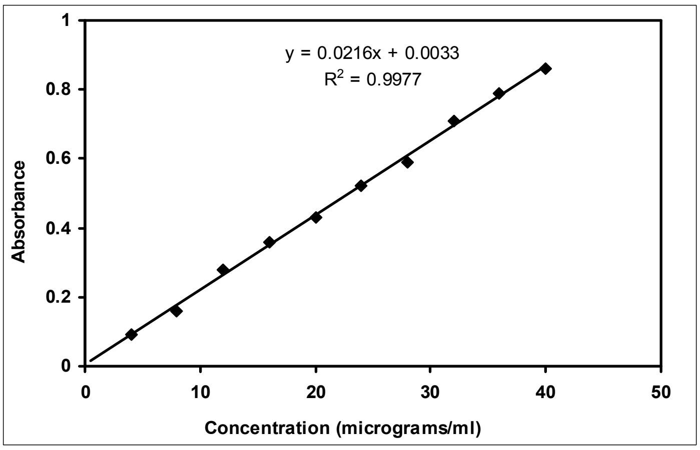

Fig. 3 .Calibration plot of carbendazim with spectrophotometry (Method B)

RESULTS AND DISCUSSIONS

The results obtained in the first method was based on reduction of Fe^{+3} to Fe^{+2} followed by complex formation to form orange colored chromophore exhibit absorption maximum at 512 nm against the reagent blank.

The second method was based on the redox reaction followed by complex formation between pesticide, potassium ferricynide and Ferric chloride to form bluish green colored product exhibiting absorption maximum at 478 nm against the reagent blank.

As fe^{3+} interfere even though to a little extent in the determination of Fe^{2+} in method A, the reactivity of the interfering entity(Fe^{3+}) has to be made insignificant by complexing it with o- Phosphoric acid.

The optical characteristics such as absorption maxima, Beer's law limits, molarabsorptivity and sandell's sensitivity for these methods are presented in Table.1. The regression analysis using the method of least squares was made for the slope and intercept obtained from different concentrations are summarized in Table.1. Recovery experiments were performed by adding a fixed amount of the pesticide to the pre – analysed formulation and results are given in Table .2. The recovery percent was found to be 95.91 – 98.50. The % R.S.D less than 2 indicated that the method was accurate and precise. A representative visible spectrum of carbendazim in a randomly selected sample of formulations diluted to 100 µg/ml. The closeness of mentioned/labeled amount and calculated concentration of pesticide in the formulations proves the validity of the methods and lack of interference from the excipients.

Table.1: Optical characteristics of proposed methods by spectrophotometry

Parameters	Method A	Method B
λmax (nm)	512	478
Beer's Law limit (µg ml^{-1})	10-60	4-40
Molar absorptivity (L. mol^{-1} cm^{-1})	$3.82x10^3$	$0.446x10^4$
Specific absorptivity	0.020	0.0235
Sandell's sensitivity (µg.cm^{-2}/0.001 A.U)	0.05	0.0425
Correlation coefficient (r^2)	0.995	0.997
Regression equation (Y = mX + C)		
Slope (m)	0.197	0.0216
Intercept (C)	-0.0062	0.0033
% Relative Standard deviation	0.5698	0.4731
Color	Orange red	Bluish green

Table.2: Determination of carbendazim in formulations

S.No	Spiked amount of CAR ppm	Method A			Method B		
		Found	% Recovery*	R.S.D	Found	% Recovery*	R.S.D
Bavastin	0.4	0.383	95.91	1.92	0.384	96.16	1.65
	0.6.	0.591	98.50	0.61	0.589	98.27	0.42
Carbendazim	0.4	0.385	96.41	0.91	0.386	96.58	0.97
	0.6	0.581	96.83	1.47	0.583	97.22	1.26

*Each value is an average of five determinations.

Determination of carbendazim in spiked water samples

100 ml of water is spiked with known concentration of the pesticide in dimethyl formamide .The sample was extracted with 20 ml portions of trichloromethane. The extracted insecticide is washed with potassium carbonate dried over sodium sulphate. The organic phase is then evaporated and dissolved in dimethyl formamide in 50 ml flask. Known aliquot of the solution is taken and absorbance was recorded against reagent blank and concentration of Carbendazim was determined using calibration plot already drawn and the results are reported in Table.3.

Analysis of soil samples containing Carbendazim

Soil samples were collected from a paddy field around Tirupati and it was washed repeatedly with water and exposed to the atmosphere. Approximately 50 g of the sieved soil was spiked with 25 ml of 100 µg/ml Carbendazim. The carbendazim was extracted using dichloro methane. The extracted was filtered and evaporated to dryness by gentle heating on a water bath. The residue was transferred into a 250 ml calibrated flask, dissolved in dimethyl formamide and made up to the mark. A 10 ml portion of this solution was transferred into a 50 ml calibrated flask, and 0.002M/L H_2SO_4 containing 50 % aqueous dimethyl formamide was used to dilute the contents of the flask to the required volume. The standard addition method was used. A 0.05 ml aliquot of the Carbendazim solution was added to the solution prepared as previously mentioned. Spectrophotometric studies under the best possible experimental conditions were carried out for the determination carbendazim in the soil sample. Five identical measurements were made and R.S.D. values are presented in Table.4.

Table.3: Determination of carbendazim in spiked water samples (Tap water)

S.No	Spiked amount of CAR ppm	Method A			Method B		
		Found	% Recovery*	R.S.D	Found	% Recovery*	R.S.D
1	0.15	0.1479	98.64	0.33	0.1475	98.68	0.32
2	0.20	0.1961	98.05	0.88	0.1962	98.10	0.85
3	0.25	0.2481	99.26	0.28	0.2480	99.30	0.30
4	0.30	0.2976	99.20	0.47	0.2980	99.33	0.30

*Each value is an average of five determinations.

Table.4: Determination of carbendazim in spiked soil samples.

S.No	Spiked amount of CAR ppm	Method A			Method B		
		Found	% Recovery*	R.S.D	Found	% Recovery*	R.S.D
1	0.2	0.1925	96.50	0.259	0.1933	96.66	0.395
2	0.4	0.3905	97.62	0.338	0.3910	97.95	0.194
3	0.6	0.5940	99.00	0.084	0.5925	98.75	0.084

*Each value is an average of five determinations.

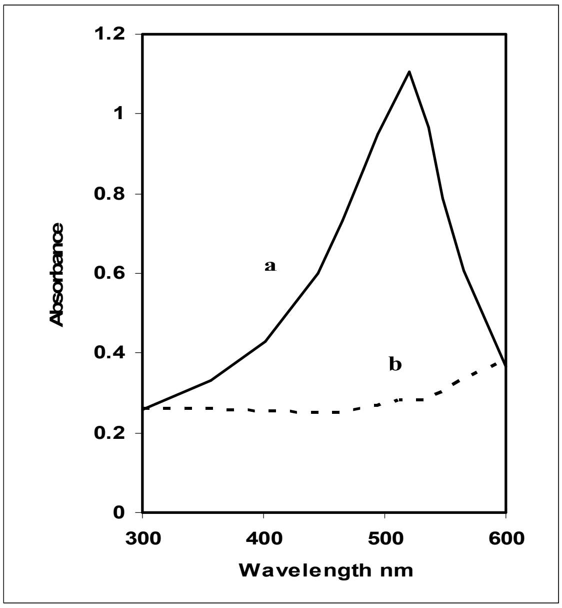

Fig.4. Absorption spectrum of
a) Carbendazim with 2,2-bipyridyl and Ferric chloride
b) 2,2-bipyridyl + Ferric chloride.

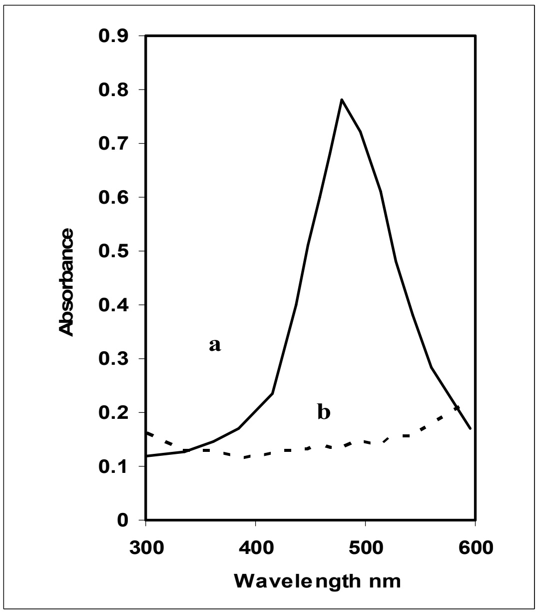

Fig.5. Absorption spectrum of
a) Carbendazim with potassium ferricynide and Ferric chloride
b) Potassium ferricynide + Ferric chloride.

CONCLUSION

The methods developed for the determination of Carbendazim use readily available inexpensive chemicals. The higher λ_{max} of the proposed visible spectrophotometric methods over the reported UV and Visible spectrophotometric methods are decisive and advantageous. Since interference from the excipients should be far less at higher wavelength. The proposed methods were accurate and precise as indicated by good recoveries of the pesticide and low RSD values. The proposed methods were applied for routine analysis and in quality control laboratories for quantitative determination of the cited pesticide both in the pure and formulations.

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