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SPECTROPHOTOMETRIC DETERMINATION OF CARBOFURAN IN COMMERCIAL SAMPLES BY OXIDATION WITH POTASSIUM FERRICYANIDE

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ABSTRACT

A spectrophotometric method for the determination of carbofuran has been studied. Method comprises of alkaline hydrolysis of the pesticide and the resulting phenol is reacted with potassium ferricyanide. The dye product formed has maximum absorption at 475 nm. Various factors affecting the formation of complex have been investigated. A linear calibration curve, over the range 17.7 µg ml^{-1} to 106.22 µg ml^{-1} with molar absorptivity $4.66X10^{2}$ l $mol^{-1}cm^{-1}$, is obtained. Correlation coefficient, slope and intercept have been calculated as 0.992, 198.112 and 1.552 respectively. The performance of the proposed method has been determined in terms of sensitivity and reproducibility.

Keywords: Spectrophotometer, Carbofuran, Potassium ferricyanide, Complexation, Alkaline hydrolysis.

INTRODUCTION

Carbofuran a member of carbamate family (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methyl carbamate) is a broad spectrum pesticide with a high biological activity against various forage pests [1]. Its primary application is for pretreatment of sowing seeds as well as against soil nematodes [2]. The pesticidal properties of carbosulfan were reported in literature [3,4]. The quantitative determination of carbofuran and carbofuran metabolite residues could be performed by various methods such as spectrophotometry [5,6], gas and liquid chromatography [7-9], GC/MS [10]. Bruce studied the pesticidal properties of carbosulfan in water, soil and plants [11]. The presence of pesticides could be estimated in water and food grains using colorimetric technique [12,13]. These methods were based on the alkaline hydrolysis of the pesticide and coupling the phenolic product with various diazo compounds and the subsequent determination was in an aqueous medium. The majority of these methods, however, requires expensive equipment and highly qualified personnel that limit their extensive use for analytical purposes.

The aim of present investigation envisages the determination of carbofuran, by oxidation of the phenolic product formed by alkaline hydrolysis, with potassium ferricyanide in aqueous media to yield colored compound. The colored compound formed after the oxidation could be analyzed by applying spectrophotometric technique for the determination of the pesticide in commercial and standard samples.

RESULT & DISCUSSION

Effect of Alcoholic Potassium Hydroxide

Different volumes of alcoholic potassium hydroxide were used keeping the concentrations of carbofuran and potassium ferricyanide constant as described in procedure. Absorption measurements were compared at 475 nm against the reagent blank as shown in Fig. 1. The experimental results indicated that the absorbance of the complex increased gradually with an increase in the volume of alcoholic potassium hydroxide. Further increase in its volume, more than 1.2 ml, caused the turbidity and the transparency of the solution was disappeared.

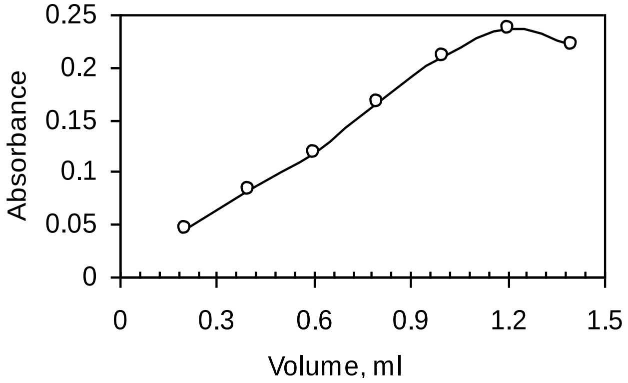


Fig. 1: Effect of alcoholic potassium hydroxide on iron-carbofuran complex using carbofuran (60µg/ml), potassium ferricyanide (5ml, 0.25%), observed at 475 nm.

Effect of Potassium Ferricyanide

The volume of potassium ferricyanide, required for the oxidation of phenolic product obtained from alkaline hydrolysis, was varied keeping the concentrations of carbofuran and alcoholic potassium hydroxide constant. The absorbance of the colored solution was measured at 475 nm using the reagent blank as shown in Fig. 2. The experimental results indicated that the absorbance of the complex increased up to 5 ml of (0.25%) potassium ferricyanide, while further increase in its concentration resulted in a decrease in the absorbance of the complex probably due to the structural isomeric changes.

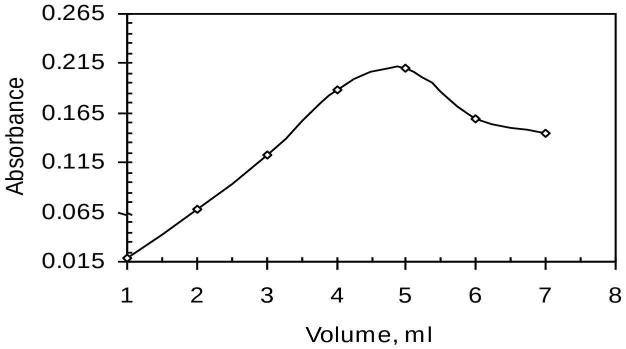


Fig. 2: Effect of potassium ferricyanide on iron-carbofuran complex using carbofuran (60µg/ml), alcoholic potassium hydroxide (1.2ml, 2%) observed at 475 nm.

Calibration Curve

Under the optimum conditions of the reagents along with other parameters, the results were found to obey Beer –Lambert's law from 17.7 µg ml^{-1} to 106.22 µg ml^{-1} of carbofuran as shown in Fig. 3. The results indicate that the appropriate dilutions must be carried out as the linearity of the curve gets disappeared at higher concentrations of carbofuran. The possible reaction mechanism for the formation of iron carbofuran complex is shown in scheme 1.

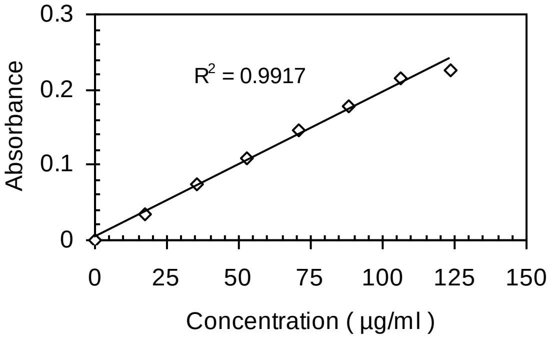
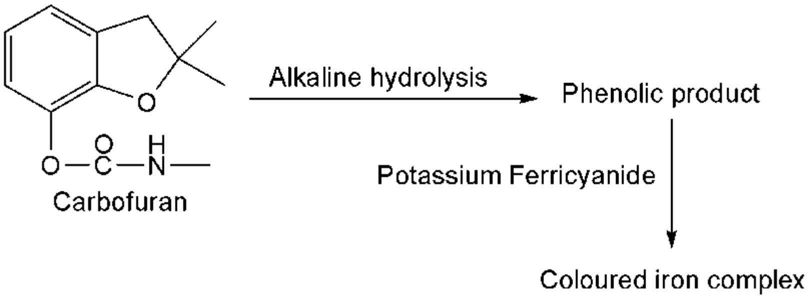


Fig. 3: Calibration curve of carbofuran using alcoholic potassium hydroxide (1.2ml, 2%) potassium ferricyanide (5ml, 0.25%), observed at 475 nm.



Scheme 1.

Validity of Proposed Method

The absorbance measurements of the yellowish brown complex were carried out against the reagent blank at 475 nm as shown in Table-1. Standard deviation of reference and proposed method was found to be 0.051, which showed a good agreement between the methods. The statistical analysis of the results indicates that the proposed method is relatively economical regarding the use of chemicals as well as the time for analysis.

Table-1: Results of carbofuran analyzed by developed and reference method.

No.	Reference method	Developed method
1	3.06±0.51	3.02±0.67
2	2.99±0.41	2.92±0.51
3	3.0±0.56	3.08±0.52
4	3.03±0.32	3.01±0.22
5	2.97±0.48	2.93±0.64

Effect of Interferences on the Analysis of Carbofuran

The experimental results indicated that, in the presence of possible interferences in carbofuran formulations, the recovery of carbofuran was more than 98%. The results show that the effect of excepients on the analysis of carbofuran is not significant as shown in Table-2.

Table-2: Determination of carbofuran in the presence of excepients.

Excepient	Amount taken µg/ml	% recovery±RSD (n=6)
Silica	500	98.5±0.21
Talc	200	98.8±0.56
Poly vinyl acetate	150	97.5±0.64

30µg/ml of cartbofuran was used for interference studies.

Recovery of Carbofuran from Spiked Samples

Samples of 100 g silica sand (from Northern areas of Pakistan) were contaminated with 20, 30, 40, 50, and 60 µg of carbofuran. Six determinations of each concentration were performed. The percentage ratio between the spiked and the experimentally determined concentrations was calculated as shown in Table-3. The percentage recovery of carbofuran by the suggested method varies within 96 to 98 % for concentrations between 20 and 60 µg. Small losses of carbofuran may be due to its extraction with ethanol.

Table-3: Recovery rate in control 100 g silica sand samples contaminated with carbofuran.

Amount of added carbofuran in µg/100 g	Measured concentration µg/ 100 g (mean±Std)	Recovery %
20	19.6±0.12	98
30	29.1±0.23	97
40	38.8±0.31	97.2
50	48.5±0.53	97
60	57.9±0.72	96.5

Sensitivity and Reproducibility of Proposed Method

Six consecutive determinations for 20, 30, 40, 50, and 60 µg of carbofuran per 100 g of silica sand were performed. The mean values, the standard deviation and coefficient of variation were calculated. The accuracy was determined as the percentage difference between mean measured concentrations and the added concentrations as shown in Table-4. The coefficient of variation between 0.60 % (for 20 µg/100 g sample) and 1.2 % (60 µg/100 g sample) indicates that the precision (reproducibility) of the suggested method is satisfactory as it is within –15 % to + 15%. Using the proposed method, the statistical parameters for the determination of carbofuran by iron complex formation are given in Table-5.

Table-4: Precision (repeatability) and accuracy of proposed method.

Amount of added carbofuran in µg/100 g	Measured concentration µg/100 g (mean±Std)	CV (%)	Accuracy (%)
20	19.6±0.12	0.6	-2.0
30	29.1±0.23	0.7	-3.0
40	38.8±0.31	0.8	-3.0
50	48.5±0.53	1.1	-3.0
60	57.9±0.72	1.2	-3.5

Table-5: Determination of carbofuran by iron complex formation.

Parameters	Results
Concentration range	17.7 µg ml^{-1} to 106.22 µg ml^{-1}
λ max	475 nm
Molar absorptivity	$4.66X10^{2}$ l mol^{-1} cm^{-1}
Coefficient of variation	0.60 – 1.2 % (20 µg , 60 µg /100 g)
Correlation coefficient	0.992
Standard deviation of reference and proposed method	0.051
% Recovery	96 % - 98 %
Accuracy and precision	-2.0 – 3.5 % (20 µg , 60 µg /100 g)
Slope	520.46
Intercept	-2.00
Variance	0.0020
F test	0.245

EXPERIMENTAL

Apparatus

All the absorbance measurements were made on a Light Wave Diode Array Spectrophotometer (S- 2000). Matched pairs of 10 mm glass cells were used throughout the analysis of carbofuran.

Reagents and Solutions

All the reagents were analytical grade and doubly distilled water was used. Solutions were prepared in ethanol and doubly distilled water. 2.213 mg ml^{-1} of carbofuran (Solex chemicals Pvt. Ltd Pakistan, mol. wt. 221.3 and purity 98%) was prepared by dissolving 0.0601 g in 25 ml of ethanol. Potassium hydroxide (Merck) 2% was prepared in ethanol. Potassium ferricyanide 0.25% (Merck) was prepared in water.

Procedure

In 25 ml Pyrex volumetric flasks, to different aliquots of carbofuran (17.7 µg ml^{-1} to106.22 µg ml^{-1}) 1.2 ml of 2% alcoholic potassium hydroxide was added and allowed to stand for 5 minutes for complete hydrolysis. Then, 5ml of 0.25% potassium ferricyanide was added to oxidize the phenolic product obtained after the hydrolysis of carbofuran. Volume of the measuring flask was made up with distilled water and the absorbance of the yellowish brown solution was measured against reagent blank at 475 nm.

Validity of Proposed Method

To check the labeled composition of carbofuran, five commercial samples of 3% finished product were obtained from the market and analyzed by the reference as well as the proposed method. An aliquot of carbofuran equivalent to 200 mg was stirred with 50 ml of ethanol in a volumetric flask. The solution was filtered using Whatman filter paper # 42 and the residue was washed with ethanol. The filtrate and washings were diluted with ethanol to 100 ml measuring flask. One ml of the sample solution was mixed with 1.2 ml of 2% alcoholic potassium hydroxide in 25 ml volumetric flask and allowed to stand for 5 min for complete hydrolysis. Then, 5ml of 0.25% potassium ferricyanide was added to oxidize the phenolic product. Volume of the measuring flask was made up with distilled water. Six determinations of each commercial sample were performed.

CONCLUSION

The results indicate that the proposed method is economically significant regarding the use of chemicals and time for analysis. The statistical analysis shows that the present method is also sensitive, reproducibility and efficient as it works equally well. It can be used for the assay of standard and commercial insecticide formulations and serves as a complimentary technique.

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