

SPECTROPHOTOMETRIC DETERMINATION OF CARBOFURAN BY USING p-AMINO PHENOL AS A REAGENT

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ABSTRACT

A rapid high sensitive and inexpensive economic method has been developed for the determination of carbofuran by using molecular spectrophotometry. The method is based on the coupling of carbofuran by reagent of p-amino phenol and soduim carbonate in an alkaline medium. The coupling conditions were selected to enhance the sensitivity and the stability of the blue colored species, which shows an absorption maximum at 637 nm. The Beer'slaw was obeyed for carbofuran concentration range from 1 to 20 μ g mL⁻¹ with 0.2813 μ g mL⁻¹ detection limit and molar absorptivity is 2.0 x 10⁴ L mol⁻¹ cm⁻¹. Thismethod was successfully applied for the determination of carbofuran in aqueous samples.

Key words: Carbofuran, Spectrophotometry, p-Amino phenol.

INTRODUCTION

Carbofuran (2, 3-dihydro-2, 2-dimethyl-7-benzofuranol N-methylcarbamate) is shown in Fig. 1. Carbofuran is one of the carbamate pesticides, a large family of pesticides derived from carbamic acid¹.

It is one of the most toxic carbamate pesticides in agriculture. It is applied to alfalfa, com, peanuts, peppers, strawberries, tobacco, bananas, sorghum. Dosage of carbofuran in mammals is found to be 5-50 mg/Kg². The toxicity of pesticides, made it essential to have accurate and reliable methods of monitoring their levels for safety purposes. Earlier techniques used for pesticide detection were chromatographic methods³ like gas chromatography (GC)⁴⁻⁷, GLC⁸⁻¹², high performance liquid chromatography (HPLC)¹³⁻¹⁵, flow injection spectrophotometric¹⁶ and spectrophotometric techniques¹⁷⁻²⁰, LC-MS²¹⁻²³, GC-MS^{24,25}. Some of these reported methods need costly instruments, laborious procedure

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and less sensitive. These facts promoted us to develop sensitive and cost effective method, which is sensitive and reliable²⁶.



Fig. 1: The structure of carbofuran²⁷

p-Amino phenol is also called p-hydroxyaniline, 4-amino-1-hydroxy benzene and p-amino phenol (Czech)²⁸. Amino phenols have been considered as priority pollutants because of their high toxicity at low concentrations. Many efforts have been made for the removal or treatment of amino phenols in industrial wastewater²⁹.

In present research, p-aminophenol is used as reagent that coupling with carbofuran in an alkaline medium of sodium carbonate to produce the blue colored species at absorption maximum at 637 nm.

EXPERIMENTAL

Materials and methods

Apparatus

UV-Visible recording Spectrophotometer (1986) Shimadzu Model (160A) (Japan) with a response time of 0.1s, was used for spectrophotomatric determination. A quartz cell of 5 mL internal volume and 1 cm path length was used for absorbance measurements.

- Hotplate Stirrer (Hotplate stirrer Model L-81 Labincobv)
- Electric balance (Sartorius, 4 digitals, made in Germany)
- Oven (Memmert, maximum temperature 250, made in Western Germany)

Chemicals and reagent

• A standard carbofuran (99% purity) was purchased from USA (Accustandard) and carbofuran-3-hydroxy (98.8% purity) was purchased from Sigma-Aldrich.

- All other chemicals used in the study were of analytical reagent (AR) grade.
- p-amino phenol (99% purity) was purchased from Sigma-Aldrich.

Preparation of standard solutions

All glassware used was supplied and was cleaned with distilled water and dried at 50°C for 30 min prior to use. Batch experiments were carried out in to ensure the reproducibility of results and the average value. All reagents used were of the highest purity and most solutions were prepared in dieonized water.

- A standard stock solution of 250 μ g mL⁻¹ of carbofuran was prepared by dissolving 0.25 g of the pesticide in 1000 mL dieonized water. This solution was kept in referigetor to prevent any hydrolysis or exposing to sun light and solution stable more than two months.
- A standard solution of PAP of 100 ppm is daily prepared by dissolving 0.05 g of the solid product in 500 mL of volumetric flask of boiled and cooled deionized water. Boling the deionized water for 10 min is very important in order to avoid the oxidation of PAP by the dissolved oxygen. This solution is stable for more than 8 hr.
- A standard solution of sodium carbonate (0.5 M) was prepared by dissolving (29 g) of the solid product in 500 mL of deionized water.
- A standard solution of sodium perioded (0.1 M) was prepared by dissolving (5.35 g) of the solid product in 250 mL of deionized water

Interference solutions of 10 ppm

These solutions were prepared by dissolving 0.001 g of each substance in a suitable solvent (water or ethanol) and then the volume was made up to 100 mL with distilled water.

General procedure for direct determination of carbofuran after coupling with p-amino phenol in waters

1 mL of (10 ppm) of carbofuran was transferred to 25 mL volumetric flask and 1 mL of 0.5 M Na_2CO_3 solution was added. The mixture was shaken with 0.1 mL of 0.1 M solution of $NaIO_4$ was added and the volume was made up to 25 mL and 2.5 mL of (10 ppm) of reagent PAP. Absorbance measurements were carried out at 637 nm for the blue color by using a 1.0 cm quartz cell against reagent blank, which was prepared in the same way but without carbofuran.

RESULTS AND DISCUSSION

The spectrum of carbofuran with reagent PAP

The spectrum (190-1100 nm) of 1 mL of 10 ppm of carbofuran with p-amino phenols reagent shows an absorbance at a wave length at 637 nm. The molar absorptivity value is 2.0×10^4 Lmol⁻¹ cm⁻¹. The value of molar absorptivity enables to carry out the quantitative analysis of carbofuran in environmental water sample directly as shown in the Fig. 2.





Optimization of alkaline medium

A series of solution were prepared by using known concentrations (0.5 M) of Na_2CO_3 (0.5, 1, 2, 3, 4, 5, 10 mL) in to a 25 mL volumetric flask. Then added 1 mL of 10 ppm of carbofuran and added 2.5 mL of (10 ppm) of p-amino phenol and added 0.1 mL of $NaIO_4$ and filled to the mark with deionized water and the measurements were carried at 637 nm in triplicate manner. The absorbance measurements are illustrated in Table 1.

From the effect of Na_2CO_3 concentration on the absorbance in Table 1, we choose the best concentration is (2 mL). The above data of Table 1 and Fig. 3 demonstrates that 2 mL the best concentration of alkaline Na_2CO_3 that depend for further optimization.

Vol. of	-	Absorbance	Mean	
Na ₂ CO ₃ (mL)	A ₃	A ₂	A ₁	absorbance
0.5	0.512	0.510	0.511	0.511
1	0.567	0.560	0.562	0.563
2	0.598	0.591	0.593	0.594
3	0.587	0.585	0.586	0.586
4	0.576	0.569	0.574	0.573
5	0.561	0.559	0.560	0.560
10	0.523	0.518	0.522	0.521

Table 1: The effect of Na₂CO₃ concentration on the absorbance

Fig. 3: The effect of alkaline concentration on absorbance of complex of carbofuran with p-amino phenol

Optimization of NaIO₄

A series of solution were prepared by using known concentrations (0.1 M) of NaIO₄ (2.5, 5, 10, 15, 20 mL) into 25 mL volumetric flasks and added 1 mL of 10 ppm from carbofuran then added 2.5 ml of 10 ppm from reagent of p-amino phenol then added 1 mL of 0.5 M Na₂CO₃ and filled to the mark with deionized water and the measurements were carried at 637 nm in triplicate manner. The absorbance measurements are illustrated in the Table 2.

Vol. of NaIO ₄	Absorbance			Mean	
(mL)	A ₃	A ₂	A ₁	absorbance	
2.5	0.004	0.002	0.003	0.003	
5	0.009	0.004	0.005	0.006	
10	0.011	0.009	0.01	0.01	
15	0.003	0.001	0.002	0.002	
20	0.002	0.001	0.001	0.001	

Table 2: The effect of NaIO₄ concentration on the absorbance

From the effect of $NaIO_4$ concentration on the absorbance in Table 2, We choose the best concentration, which is 10 mL.



Fig. 4: The effect of sodium periodade concentration

The absorbance of carbofuran, which demonstrates that the best concentration of $NaIO_4$ is 10 mL that dependent for further optimization.

Optimization of p-amino phenol

A series of solution were prepared by using known concentrations of 100 ppm of p-amino phenol (0.5, 1, 1.5, 2, 2.5, 3, 3.5 mL) into 25 mL volumetric flasks and added 10 ppm from carbofuran then added 1 mL from (0.5 M) of Na_2CO_3 then added 0.1 mL from (0.1 M) of $NaIO_4$ and filled to the mark with deionized water and the measurements were carried at 637 nm in triplicate manner. The absorbance measurements are illustrated in Table 3.

Mean		Absorbance		
absorbance	A ₃	A_2	A ₁	(mL)
0.263	0.265	0.260	0.264	0.5
0.329	0.330	0.328	0.329	1.0
0.411	0.412	0.410	0.411	1.5
0.463	0.466	0.461	0.462	2.0
0.414	0.416	0.411	0.415	2.5
0.315	0.316	0.314	0.315	3.0
0.250	0.252	0.247	0.251	3.5

Table 3: The effect of p-amino phenol concentration on the absorbance

The above results shown in Table 3 shows the best concentration from reagent of pamino phenol is (2 mL) and dependent on accounts.



Fig. 5: The effect reagent of p-amino phenol concentration

On absorbance of carbofuran, which demonstrates that the best concentration of PAP is 2 mL.

Effect of stability time

The color intensity reached a maximum after carbofuran solution had been reacted immediately with p-amino phenol in neutral alkaline and the effect of time was studied regarding the formation of the reaction product and its stability. The color of product was obtained immediately; maximum color intensity was obtained after about 15 min and remains stable for about 65 mins at room temperature. Development time was selected as optimum in the analytical procedure shown in Table 4.

Mean		Absorbanc	e	Time
absorbance	A ₃	A_2	A_1	(min)
0.200	0.202	0.197	0.201	5
0.212	0.211	0.0.215	0.210	10
0.232	0.233	0.234	0.229	15
0.232	0.234	0.232	0.230	20
0.230	0.232	0.230	0.228	25
0.230	0.232	0.231	0.227	30
0.229	0.233	0.228	0.226	35
0.229	0.231	0.229	0.227	40
0.229	0.231	0.232	0.227	45
0.228	0.230	0.228	0.226	50
0.228	0.232	0.227	0.225	55
0.228	0.228	0.230	0.226	60
0.225	0.228	0.224	0.223	65
0.210	0.214	0.209	0.207	70
0.195	0.202	0.193	0.190	75
0.189	0.198	0.185	0.183	80
0.170	0.175	0.169	0.166	85
0.150	0.156	0.149	0.145	90
0.125	0.133	0.122	0.120	95
0.0098	0.0101	0.0098	0.0095	100

Table 4: The effect of stability time

Table 4 shows that on increasing the time of residence of carbofuran with best values from added 2 mL of 100 ppm of PAP, 2 mL of 0.5 M of Na_2CO_3 and addad 10 mL of 0.1 M $NaIO_4$ causes a decreasing in absorbance values due to the further hydrolysis effects and the losing the carbamate group from the compound as illustrated in Fig. 6.



Fig. 6: The stability time of 10 ppm carbofuran in best value of 2 mL of PAP then 2 mL of Na₂CO₃ and 10 mL of NaIO₄ solution as a function of time

The mechanism of coupling of carbofuran with p-amino phenol producing blue color is shown in the following equation.



Fig. 7: Carbofuran coupling with reagent PAP

This reaction shows an absorption maxima at 637 nm named the molar absorptivity of 10 ppm is 2.0×10^4 L mol⁻¹ cm⁻¹, which means that the method can be used for direct determination of carbofuran depending on the absorption measurements of the coupling product of carbofuran,

Calibration carve of carbofuran coupling with p-amino phenol in alkaline medium

A series of solution were prepared by spiked sample of carbofuran with deionized water at known concentration of carbofuran 0, 2, 4, 6, 8, 10, 12 ppm into 25 mL volumetric

flasks and added 2 mL from Na_2CO_3 then added 2 mL of p-amino phenol then added 10 mL of $NaIO_4$ and filled to the mark with distilled water to form a spiked samples. The absorbance measurements were carried out at a wavelength at 637 nm. The concentrations were obtained from the calibration curve for the spiked solutions are shown in the Table 5.

Recovery (%)	Found	RSD (%)	Mean absorbance	Conc. of carbofuran (ppm)
102	2.0469	0.5235	0.191	2
98	3.9574	0.5464	0.366	4
103	6.2281	0.3484	0.574	6
95	7.6364	0.4267	0.703	8
102	10.2128	0.3194	0.939	10
99	11.9596	0.0909	1.099	12

 Table 5: The absorbance measurements of standard solution of carbofuran in alkaline medium by using distilled water

The calibration curve was drawn by using the mean absorbance as a function of concentration (ppm) as shown in Fig. 8.



Fig. 8: Calibration curve of carbofuran in deionized water coupling with p-amino phenol

Optical characteristic feature of the calibration carve

The main features of the calibration curve carried out by using the optimum condition were tabulated in Table 6.

Parameter	Values
Color	Blue
Wave length λ_{max} (nm)	637
Beer's law limit a ($\mu g m L^{-1}$)	0-20
Molar absorpitivity (mol ⁻¹ cm ⁻¹ L)	$2.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$
Regression coefficient (r)	0.9989
Sand ell's sensitivity (µgcm ⁻²)	0.01082
Slope (m)	0.0916
Intercept (C)	0.0035
Regression equation $(y = mx + C)$	y = 0.091x + 0.003
Correlation coefficient (r ²)	0.9979
Variation coefficient (%)	99.79
Limit of detection ($\mu g m L^{-1}$)	0.2813
Limit of quantization (mg mL ⁻¹)	0.9376
Average recovery (%)	99.83

Table 6: Optical characteristic features of calibration curve

From the above data in Table 6, we can see that the method in suitable for the direct determination of carbofuran coupled with p-amino phenol.

Dericat determination of carbofuran coupling with p- amino phenol by using neutral water samples

A series of solution were prepared by spiking of different environmental water samples with a known concentration of carbofuran 0, 2, 4, 6, 8, 10, 12 ppm in to 25 mL volumetric flasks and added 2 mL of 0.5 M of Na_2CO_3 then added 2 mL of 100 ppm of p-amino phenol then added 10 mL of 0.1 M of $NaIO_4$ and filled to the mark with (tap, underground, river (and rain) water to form a spiked samples. The absorbance measurements were carried out at a wavelength at 637 nm. The concentrations were obtained from the calibration curve for the spiked solutions are shown in the Table 7.

From the above table, it shows quite obviously that the recovery percent is from 90 to 95% for tap water, 93 to 100% for underground water, 81 to 89% for river water and 82 to

95% for rain water, which means that the method is suitable for direct determination of carbofuran in natural environmental water samples and also that the interference is very low and the proposed method is validated for measuring this compound directly in environmental water samples.

Type water	Conc. (ppm)	Mean absorbance	RSD (%)	Found	Recovery (%)
	2	0.186	1.0752	1.9923	99
	4	0.345	0.2898	3.7281	93
Tap water	6	0.501	0.1996	5.4312	90
	8	0.677	0.3908	7.3526	91
	10	0.877	0.3016	9.5360	95
	2	0.174	0.5747	1.8613	93
	4	0.349	0.7580	3.7718	94
Underground	6	0.556	0.4758	6.0316	100
	8	0.712	0.3715	7.7347	96
	10	0.911	0.1097	9.9072	99
	2	0.167	1.5842	1.7849	89
	4	0.322	0.3105	3.477	86
River weter	6	0.454	0.5827	4.9181	81
NIVEL WALL	8	0.633	0.4179	6.8722	85
	10	0.822	0.3218	8.9355	89
	2	0.154	3.2467	1.6430	82
D • 4	4	0.342	2.0467	3.6954	92
Kain water	6	0.489	0.9371	5.3002	88
	8	0.703	0.8883	7.6364	95
	10	0.831	0.8701	9.0338	90

 Table 7: Recovery of carbofuran in the spiked (Tap, underground, river and rain) water sample solutions

Effect of interference

The effect of foreign species was studied by adding 1 mL of (10 ppm) different amounts of species such as organic compounds and inorganic compounds (Table 8), which often found in environmental. It was observed that were not interfering with the determination at levels found in carbofuran form.

Type of interference (1 mL)	Mean absorbance	RSD%
Non addition	0.505	0.3960
Sodium chloride	0.039	2.631
Sodium sulfate	0.056	1.7857
Resorcinol	0.077	1.966
Iron chloride	0.055	1.818
Sodium azid	0.039	2.564
Hydrocatechol	0.097	2.061
Pyrocatechol	0.048	2.083
Salicylic acid	0.085	2.949
Magnesium chloride	0.040	2.5
p-nitro phenol	0.058	2.64

Table 8: Effect of interference

It was observed that the Table 8 was not interfering with the determination at levels found in carbofuran form.

Stoichiometric determination of color compound: Continuous variation method (Job's method)³⁰

A series of 1, 2, 3, 4, 5, 6, 7, 8, 9 mL of 1×10^{-4} mol L⁻¹ of the solution that contain carbofuran was pipette into each of 10 mL volumetric flask then 9, 8, 7, 6, 5, 4, 3, 2, 1 mL of 1×10^{-4} mol L⁻¹ of reagent, the absorbance of the solution was measured by UV-Vis Spectrophotometer at λ_{max} 637 nm. The stoichiometric ratio between carbofuran with reagent 1:1 results are shown in the Table 9.

Absorbance at $\lambda = 637$ for color compound	VC/VT	VR mL	VC mL
0.041	0.1	9	1
0.111	0.2	8	2
0.23	0.3	7	3
0.391	0.4	6	4
0.543	0.5	5	5
0.440	0.6	4	6
0.320	0.7	3	7
0.179	0.8	2	8
0.1	0.9	1	9

Table 9: The continuous variation method of carbofuran and p-amino phenol complex

Plotting the value of absorbance versus the VC/VT, it is shown in Fig. 9.





VC : Values of the compound (Carbofuran).

VR : The values of the reagent (Para-amino phenol).

Mole-ratio method³⁰

The stoicheiometry of the reaction between a series of 1 mL of 3.5×10^{-4} mol.L⁻¹ of carbofuran solution and increasing volume of 1.4, 2, 2.8, 3.5, 4.2, 5, 5.7, 7, 8.5 mL of 3.5×10^{-4} mol.L⁻¹ of 3.5×1

 10^{-4} mol.L⁻¹ p-amino phenol was studied. The absorbance of the solutions were measured by UV-Vis spectrophotometer versus blank at $\lambda_{max} = 637$ nm. The stoichiometric ratio between 1:1 results is shown in Table 10.

CL	CL/CM	Absorbance at $\lambda = 637$ nm
0.5×10^{-4}	0.33	0.046
$0.75 imes 10^{-4}$	0.5	0.071
1×10^{-4}	0.66	0.11
1.25×10^{-4}	0.83	0.133
1.5×10^{-4}	1	0.158
1.75×10^{-4}	1.16	0.164
2×10^{-4}	1.33	0.169
2.5×10^{-4}	1.66	0.175
3×10^{-4}	2	0.179

Table 10: The mole-ratio method of the carbofuran and p-amino phenol complex

Plotting the value of absorbance versus the CL/CM, which is shown in Fig. 10.



Fig. 10: Mole ratio plot of carbofuran and p-amino phenol complex

CONCLUSION

The present method describes simple analytical procedure for the determination of carbofuran in water samples (tap, river, underground, rain). The preparation of the coupling reagent p-amino phenol was simple and in a classical laboratory.

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