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Spectrophotometric determination of Carbofuran in neutral and alkaline medium of environmental water samples

Noor J. Mohammed	Department of chemistry, College of science for women, University of Baghdad
Kareem. D. Khalaf	Department of chemistry, College of science for women, University of Baghdad
Saadiyah A. Dhahir	Department of chemistry, College of science for women, University of Baghdad

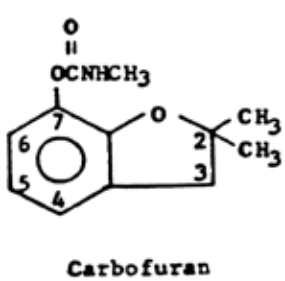
ABSTRACT

A simple, sensitive, rapid and accurate spectrophotometric method was developed for determination of parts per million levels of widely used Carbamate pesticide carbofuran. The proposed method is based on the direct determination of Carbofuran residue in environmental water samples with and without alkalin medium. Carbofuran shows an absorption maximum at a wave length of 279 nm with apparent molar absorptivity is 5.5 ×104 L mol-1cm-1 and obeyed Beer's law in the concentration range of (0- 20µg/ml) In alkaline medium Carbofuran shows an absorption maximum at a wave length of 290 nm with apparent molar absorptivity is 1.5 ×104 L mol-1cm-1 and obeyed Beer's law in the concentration range of (0- 20µg/ml) A simple procedure was employed for the spectrophotometric determination of the presence of trace quantities of carbofuran in environment water samples. Particularly in the river, tap, Rain and underground water samples.

KEYWORDS :Carbofuran , UV- Spectrophotmetry ,Carbamate pesticides

Introduction:

Carbofuran (2, 3-dihydro-2, 2-dimethyl-7- benzofuranol N-methylcarbamate),also known as furadan , an anticholinesterase carbamate, is commonly used as an insecticide, nematicide, and acaricide in agricultural practice throughout the world [1]. The toxicity of pesticides and their degradation products is making these chemical substances a potential hazard by contaminating our environment [2] . Risks from exposure to carbofuran are especially high for persons with asthma, diabetes, cardiovascular disease, mechanical obstruction of the gastrointestinal or urogenital tracts [3]



Carbofuran

Figure (1) The structure of carbofuran[4]

Carbofuran

is a broad spectrum carbamate pesticide that kills insects, mites and nematodes on contact or after ingestion. It is used against soil and foliar pests of field, fruit, vegetable and forest crops. Carbofuran is available in liquid and granular formulations[5]. Carbamate pesticides are extensively used in agriculture due to their rapid degradability and low toxicity to non-target species. Their widespread and indiscriminate application poses serious health hazard to humans and animals [6]. Carbamates have been reported to have high mammalian toxicity, and the main target organs are brain, liver, skeletal muscles, and heart [7]. The most sensitive and appropriate effect associated with the use of carbofuran is its toxicity following acute exposure[8] It is high water solubility and low adsorption coefficient[9] Due to its high toxicity, carbofuran has already been banned in many countries[10] Commonly used analytical methods for the determination of carbofuran are high performance liquid chromatography ,gas chromatography coupled to mass spectrometry ,and spectrophotometry[11]

2.Experimental Parts

2.1.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 1cm path length was used for absorbance measurements
- *Hotplate Stirrer* (*Hotplate stirrer Model L-81 Labinco bv*)
- Electric Balance (Sartorius, 4digitals, made in Germany)
- Oven (Memmert , maximum temperature 250,made in western Germany.)

2.2.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. All glassware was used cleaned with distilled water and dried at 50˚C for 30 minute 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 ultra pure water and Dieonize water.
- A standard stock solution of 250 µg $ml^{-1}$of carbofuran was prepared by dissolving 0.25g of the pesticide in 1000ml Dieonize 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 stock solution of sodium carbonate Na_2CO_3 (1M) was prepared by dissolving (29 g) of the solid product in 250ml of deionized water.

2.3.Real water sample collection

Real water samples of river were taken from different parts of tigers river ,Baghdad in Iraq and mixed together to form a homogenous representative sample .Three underground water samples were taken from three well from different regions and mixed together to obtain a representative water sample. Tap water sample was taken from tap. The three real water samples were kept in brown glass containers and kept in refrigerator at 8 ˚C.

2.4.Procedure for direct determination of carbofuran in neutral environmental water

UV-spectrum of Carbofuran in dieonize water which presents The absorbance at 279 nm This was done by carrying out a calibration graph through the preparation of a series of standard solutions of 0 , 2, 4, 6 ,8,10,12 and 14 µg ml^{-1} of carbofuran in volumetric flasks of 25 ml diluting to the mark with dieonize water.

2.5.Procedure for direct determination of carbofuran in alkaline medium

the Hydrolysis in alkaline medium with Sodium Carbonate Which indicate that carbofuran is readily hydrolysis and yields The absorbance at 290 nm . This was done by carrying out a calibration graph through the preparation of a series of standard solutions of 0, 2, 4,6,8,10,12, and 14 µg ml^{-1} of carbofuran in volumetric flasks of 25 ml diluting to the mark with different water and determination of concentration

3.Results and Discussion

3.1. UV-Spectram of carbofuran in distilled water

The spectrum (200-800nm) 10 ppm of Carbofuran shows an absorption wavelength at 279 nm with an absorbance of 0.248 . From the Chemical The molar absorpitivity value is 5.5×10^4 L mol^{-1} cm^{-1} which means that the electronic transitions are due to the л to л*. This value of molar absorpitivity enables to carry out the quantitative analysis of carbofuran in environmental water sample directly as shown in the figure 2.

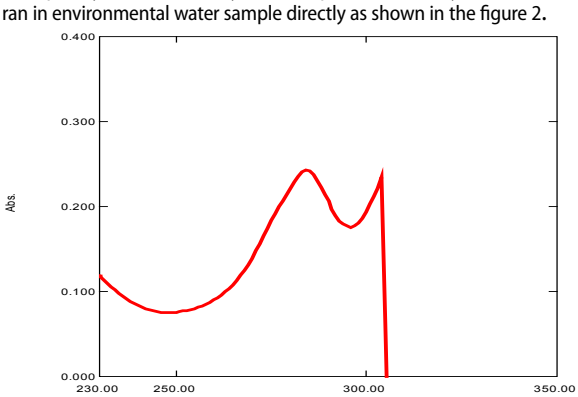


Figure 2: UV- absorption spectrum of 10 ppm of carbofuran in dieonize water.

Calibration carve in neutral deionzed water

A series of solutions were prepared by using known concentration of carbofuran (0,2,4,6,8,10 ppm) in to a 25ml volumetric flask and filled to the mark with deionised water and the measurements were carried at 279 nm in triplicate manner The absorbance measurements are illustrated in table 1.

Table 1: The absorbance measurements of standard solutions of carbofuran

Conc. ppm	Mean Absorbance	RSD%	Found	Recovery%
2	0.049	2. 040	1.806	90
4	0.110	1. 801	4.162	104
6	0.158	1.265	6.015	100
8	0.215	0.465	8.216	102
10	0.265	0.377	10.146	101
12	0.315	0.676	12.077	100
14	0.358	0.323	13.73	98

The calibration curve was draw by using the mean absorbance as a function of concentration (ppm) as shown in figure 3.

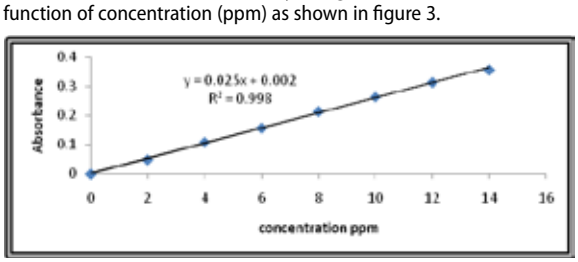


Figure 3: Calibration curve of carbofuran in deionized water

3.2.Optical characteristics Features of the calibration curve.

Table 2 shows the main features of the calibration curve and measuring the absorbance at 279 nm

Table 2: Optical characteristic features of calibration curve

Parameter	Values
Color	Colorless
Wave length λ_{max} (nm)	279
Beer's Law limit a (µg ml^{-1})	0-20
Molar absorpitivity ($mol^{-1}cm^{-1}$ L)	5.5×10^4 L mol^{-1} cm^{-1}
regression coefficient (r)	0.9993
Sand ell's sensitivity (µg cm^{-2})	0.00401
Slope (m)	0.0259
Intercept (C)	0.0022
Regression equation (Y = mX + C)	y = 0.0259x + 0.0022
Correlation coefficient (r^2)	0.9987
Variation coefficient (%)	99.87
Limit of detection(µg ml^{-1})	0.3800
Limit of quantization (mg mL^{-1})	1.2667
Average recovery (%)	99.28

From the above data in table (2) can see that the method in suitable for the direct determination of carbofuran in environmental water samples.

3.3.Direct determination of carbofuran in spiked 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 ppm) into 25ml volumetric flasks and filled to the mark with real water of tap water , underground water , river water and Rain water to form a spiked samples. The absorbance measurements were carried out at a wavelength at 279 nm the concentrations were obtained from the calibration curve for the spiked solutions and the absorbance measurements and recovery percentages of carbofuran obtained are shown in the table 3.

Table 3. Recovery of carbofuran in the spiked (Tap, Underground, River and Rain)water sample solutions.

Type water	Conc. ppm	Mean Absorbance	RSD%	Found	Recovery%
Tap water	2	0.048	2.083	1.768	88
	4	0.101	2.619	3.814	95
	6	0.153	2.848	5.822	97
	8	0.189	1.907	7.212	90
Underground	2	0.058	3.448	2.154	107
	4	0.112	1.785	4.239	105
	6	0.167	2.610	6.362	106
	8	0.219	1.646	8.370	104
River water	2	0.058	1.886	1.961	98
	4	0.115	2.608	4.355	108
	6	0.155	1.706	5.899	98
	8	0.201	0.497	7.675	95
Rain water	2	0.045	2.222	1.652	82
	4	0.103	4.231	3.891	97
	6	0.178	1.486	6.787	113
	8	0.234	1.540	8.949	111

From the above table shows quite obviously that the recovery percent is from 88 to 97% for tap water , 104 to 107 % for underground water , 95to 108 % for River water and 82 to 113 % for Rain water .Which means that the method is suitable for direct determination of carbofuran in natural environmental water samples .

3.4.UV-Spectram of carbofuran in Alkaline Medium.

Carbofuran hydrolised in alkaline medium producing phenolate according to the following equation [12]:

The hydrolysis product Phenol derivative carbofuran shows an absorption maxima at 290 nm and the molar absorpitivity of 10 ppm is(1.5 $\times$ 10^4L mol^{-1} cm^{-1}) Which means that the method can be used for direct determination of carbofuran depending on the absorption measurements of the hydrolysis product of carbofuran.

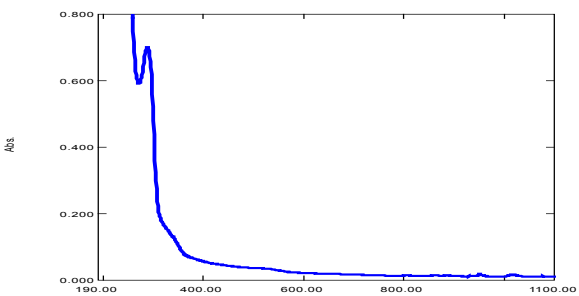


Figure 4. UV-absorption spectrum of 10 µg ml^{-1} carbofuran in 0. 1M of Na_2CO_3

3.5.Optimization of alkaline concentration

Figure 5 shows the effect of alkaline concentration on hydrolysis of carbofuran which demonstrates that the best concentration of Na_2CO_3 is 0. 1 M. The absorbance of 10 ppm of carbofuran is (0.126) and the molar absorpitivity is 1.5 $\times 10^4$L mol^{-1} cm^{-1})

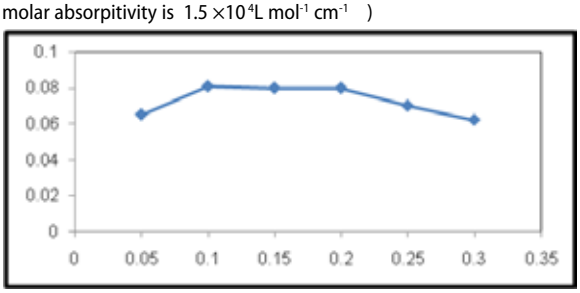


Figure 5. Optimization of the concentration of Na_2CO_3

3.6.Obamization of hydrolysis of carbofuran with Time.

Hydrolysis of carbofuran in alkaline medium used Na_2CO_3 produce the phenolate .Figure 6. shows that on increasing the time of residence of carbofuran in alkaline medium causes a decreasing in absorbance values due to the further hydrolysis effects and the losing the carbamate group from the compound as illustrated in figure 6.

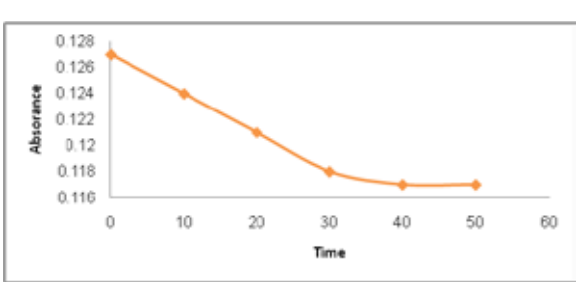


Figure 6: Optimization hydrolysis of 10 ppm carbofuran in 0.1 M Na_2CO_3 solution as a function of time

3.7.Calibration Carve of Carbofuran in Alkaline Medium of Na_2CO_3.

A series of solution were prepared by spiking of different carbofuran (0,2,4,6 ,8,10,12 ppm) in to 25ml volumetric flasks and added 0.5M from Na_2CO_3 and filled to the mark with distilled water to form a spiked samples. The absorbance measurements were carried out at a wavelength at 290 nm .The concentrations were obtained from the calibration curve for the spiked solutions are shown in the table 4.

Table 4: The absorbance measurements of standard solutions of Carbofuran in alkaline medium in distilled water.

Conc. ppm	Mean Absorbance	RSD%	found	Recovery%
2	0.194	2.246	2.269	113
4	0.335	0.789	4.119	102
6	0.477	0.913	5.982	99
8	0.630	0.572	7.990	99
10	0.774	0.465	9.880	98
12	0.937	0.213	12.019	100

The calibration curve was drawn by using the mean absorbance as a function of concentration (ppm) as shown in figure 6

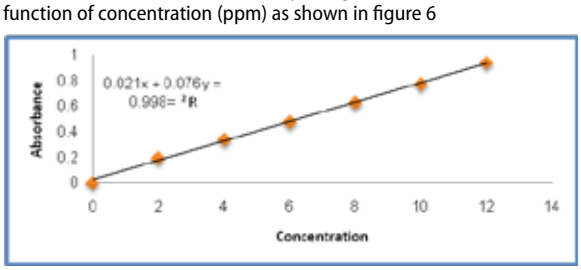


Figure 7: Calibration curve of carbofuran in deionized water in alkaline medium of Na_2CO_3

3.8.Optical Characteristic features of the calibration carve.

Table 5 Show the main features of mart of the calibration curve carried out by using the optimum conditions.

Table 5: Optical characteristic features of calibration curve

Parameter	Values
Color	Colorless
Wave length λ_{max} (nm)	290
Beer's Law limit a (µg ml^{-1})	0-20
Molar absorpitivity ($mol^{-1}cm^{-1}$ L)	1.5 $\times 10^4$
regression coefficient (r)	0.9991
Sand ell's sensitivity (µg cm^{-2})	0.00142
Slope (m)	0.0762
Intercept (C)	0.0211
Regression equation (Y = mX + C)	y = 0.0762 x + 0.0211
Correlation coefficient (r^2)	0.9984
Variation coefficient (%)	99.84
Limit of detection(µg ml^{-1})	0.029
Limit of quantization (mg mL^{-1})	0.096
Average recovery (%)	101.83

From the above data in table 5 one can see that the method in suitable for the direct determination of carbofuran in environmental water samples.

3.9.Dericat determination of carbofuran in Alkaline Medium 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 25ml volumetric flasks and added 5 ml of 1 M Na_2CO_3 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 290 nm .The concentrations were obtained from the calibration curve for the spiked solutions in different natural water and the absorbance measurements and recovery percentages of carbofuran obtained as shown in the table 6.

Table 6: Recovery carbofuran of the spiked solutions in different natural water

Type of water	Conc ppm	Mean Absorbance	RSD%	Found	Recovery%
Tap water	2	0.161	0.621	1.84	92
	4	0.287	0.921	3.48	87
	6	0.417	1.045	5.19	86
	8	0.600	1.013	7.59	94
Underground water	2	0.185	1.948	2.16	108
	4	0.340	0.294	4.18	104
	6	0.479	0.417	6.00	100
	8	0.627	0.318	7.95	99
River water	2	0.154	0.649	1.84	92
	4	0.292	0.684	3.55	88
	6	0.439	0.227	5.48	91
	8	0.587	0.170	7.42	92
Rain water	2	0.176	2.048	2.032	101
	4	0.298	0.887	3.633	90
	6	0.456	0.580	5.707	95
	8	0.611	0.590	7.741	96

The above results show the recovery percentages of the added carbofuran quantities of 86 to 94 % for tap water, 99to108 % for underground water, 88to91 % for river water and 95 to 101 % for rain water which means that the proposed method is validated for measuring this compound directly in environmental water samples

4.Conclusion

The proposed method shows quite obviously two practical facts, the first one proves that environmental water samples (tap, River and country side water are not contaminated and can be used for drinking or River and the second fact is that the proposed method can be used to direct determination of carbofuran with high accuracy as well as the method is fast, economic and accurate.

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