Open Access

Baghdad Science Journal **Vol.13(3)2016**

DOI: http://dx.doi.org/10.21123/bsj.2016.13.3.0498

Spectrophotometric Determination of Carbofuran with Diazotized Benzidine in Environmental Water Samples

Saadiyah A. Dhahir ***Noor J. Mohammed*** ***Shetha F. Narren***

Department of chemistry, College of science for women, University of Baghdad

E-mail:sadiataher@yahoo.com.

Received 25/5 /2015
Accepted 10/ 6/2015

Abstract:

A simple, rapid, accurate and sensitive spectrophotometric method has been developed for the determing carbamate pesticides in both pure and water samples. The method is appropriate for the determination of carbofuran in the presence of other ingredients that are usually available in dosage forms. The effect of organic solvents on the spectrophotometric properties of the azo dye and the structure of the resulting product have also been worked out and it is found to be 1:1 benzidine :carbofuran. The method can be successfully applied to determination of carbofuran in water samples. The method is based on diazotization of Benzidine (4, 4 – diamino biphenyl) with sodium nitrite and hydrochloric acid followed by coupling with carbofuran in alkaline medium to form a yellow colored azo dye having the absorption maximum at 429nm against reagent blank solution. Beer's law is obeyed in the concentration range of (0-14) µg of 10mL carbofuran. Molar absorptivity of 1×10^4 $L.mol^{-1}.cm^{-1}$ which depend on the concentration level of carbofuran.

Key words: Carbofuran, Benizidine, Determination, Azo Dye, Spectrophotometery

Introduction:

Carbofuran (2, 3-dihydro-2, 2-dimethyl-7- benzofuranol N-methy carbamate) is one of the carbamate pesticides, a large family of pesticides derived from carbamic acid [1] is shown in Figure (1) The toxicity of pesticides and their degradation products are making these chemical substances a potential hazard by contaminating our environment [2-3] Due to a highly toxicity of carbofuran , it is essential to develope accurate and reliable methods of monitoring their levels for safety purposes. Earlier techniques used for carbofuran assassment were including [4-5] Gas Chromatography(GC) [6-7] ,GLC [8-9] .High Performance Liquid Chromatography (HPLC) [10], and spectrophotometric techniques [11]. Some of these reported methods need costly instruments, laborious procedure and less sensitive these facts have promoted the authors to develop sensitive and cost effective method. The proposed method is based on the coupling of hydrolyzed carbofuran with diazotized benzidine in alkaline medium which gives a yellow product having the absorption as medium at 429nm.

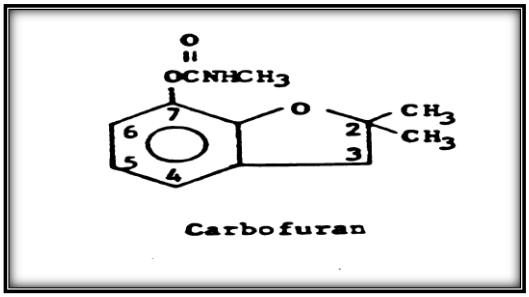


Fig. (1) The Structure of Carbofuran [12]

Materials and Methods:

Apparatus

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

Hotplate Stirrer (Hotplate stirrer Model L-81 Labincobv).

Electric Balance (Sartorius, 4digitals, made in Germany).

Oven (Memmert, maximum temperature 250,made in western Germany).

Chemicals and Reagent

A Standard Carbofuran (99% purity) is purchased from USA (Accustandard) and Carbofuran-3-hydroxy (98.8% purity) is purchased from Sigma-Aldrich.

All other chemicals used in the study are of analytical reagent (AR) grade.

Preparation of Standard Solutions:

All glassware used are supplied and cleaned with distilled water and dried at50˚C for 30min prior to use. Batch experiments are carried out to ensure the reproducibility of results and the average value. All reagents used are of the highest purity and most solutions are prepared in ultra pure water and Dieonized water.

A standard stock solution of 250 ppm of carbofuran is prepared by dissolving 0.25g of the solid carbofuran in 1000ml of deionized water. A working standard solution of 100 ppm of carbofuran is prepared by diluting the stock one with deionized water.

A standard solution of Benzidine of 100 ppm is daily prepared by dissolving 0.01g of the solid product in 5mL of ethanol and filled to the mark with deionized water in to 100mL volumetric flask.

A standard solution of sodium nitrite (1%) is prepared by dissolving (1,00g) of the solid product in 100 mL of deionized water.

A standard solution of sodium carbonate (1M) is prepared by dissolving (11.6g) of the solid product in 100mL of deionized water

A standard solution of hydrochloric acid (1M) is prepared by 10 mL of stock solution was add to 100mL volumetric flask diluted up to the mark by deionized water .

A standard solution of sulphamic acid (0.1%) is prepared by 0.1 mL of stock solution added to 100mL volumetric flask diluted to mark with deionized water.

Interference Solutions of 10 ppm

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

Solutions of Surface Active Substances (0.1%)

These solutions are prepared by dissolving 0.1 g of each substance in distilled water and then completing the volume to 100 mL with distilled water CTAB (Cetyltrimethyl ammonium bromide) SDS (Sodium dodecyl sulphate)

Triton- ×100 (Iso-octylphenoxy-polyethoxy ethanol)

Tween 20(Polyoxyethylenesorbitanmonolauate)

General Procedure for Direct Determination of Carbofuran Using Diazotization Coupling Reaction

0.5mL from 100ppm of Benzidine transferred to 10 mL volumetric flask then 0.5mL of concentrated of 1% $NaNO_2$ is added Then, 0.5 mL of 1M of HCI is added. The mixture is shaken and cooled in ice bath for 5 min then added The following 0.5mL of sulphamic acid ,10ppm of carbofuran , 0.5 mL of 1M of Na_2CO_3 are added and 0.5 mL of 0.1% of Tween 20 is added and the volume was made up to10mL with deionized water. Absorbance measurements are carried out at 429 nm for the yellow color by using a 1.0 cm quartz cell against reagent blank which is prepared in the same way but without carbofuran.

Results and Discussion:

Absorption Spectra

A yellow -colored oxidizing coupling product with maximum absorption at 429 nm after studing of the Optimum Reaction Conditions is formed when carbofuran is allowed to react with benzidine in basic medium (sodium carbonate). Figure (2) shows the absorption spectra of yellow product formed so the absorption maximum at 429nm is used in all subsequent experiments.

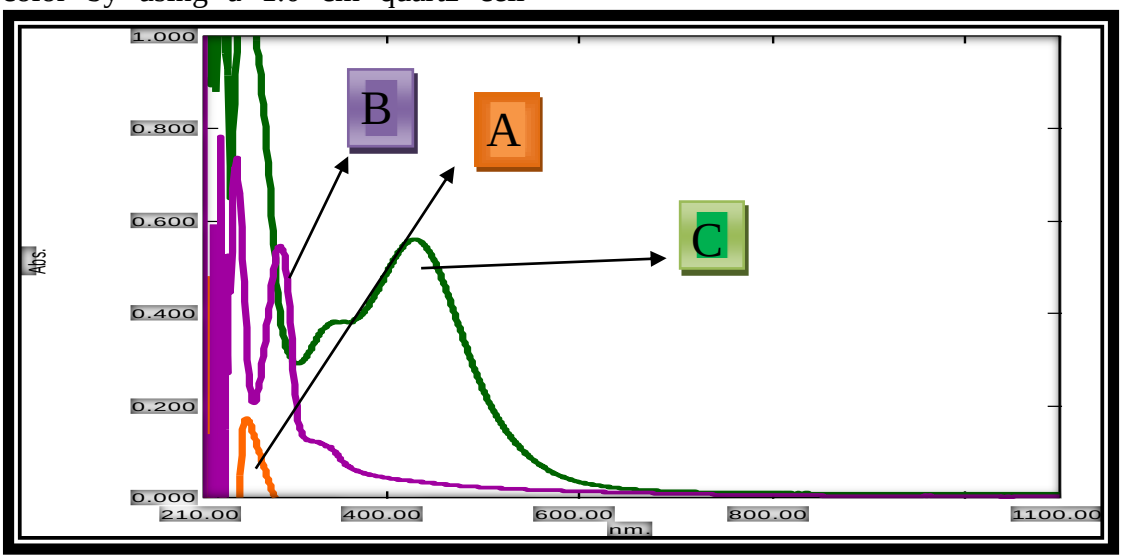


Fig. (2): A. The Absorption Spectrum of the Carbofuran Versus Distilled Water
B. The Absorption Spectrum of the Benzidine Versus Distilled Water
C. The Absorption Spectrum of Carbofuran With reagent Benzidine Versus Blank

Study of the Optimum Reaction Conditions

The effect of various parameters on the absorption intensity of the aso dye formed is studied and the reaction conditions are optimized. The factor affecting color development, reproducibility, sensitivity and conformity with Beers law is carbofuran with reagent benizdine.

Effect of Type of Acid on Diazotization

In order to select the most suitable acid used in the diazotization of carbofuran, different types of 1M acids (HCl, H_2SO_4, HNO_3, H_3PO_4, and CH_3COOH) are investigated in the presence of 0.5mL of (100ppm) benzidine, 0.5mL of (1%) $NaNO_2$, 0.5mL of (0.1%) sulphamic acid, 1mL of carbofuran and 0.5mL of (1M) Na_2CO_3

Table (1): Effect of Different Acids on Diazotization of Carbofuran

Type of acid	Absorbance			Mean Absorbance
	A_1	A_2	A_3	
HCl	0.553	0.568	0.600	0.573
HNO_3	0.072	0.093	0.082	0.082
CH_3COOH	0.566	0.545	0.515	0.542
H_2SO_4	0.220	0.230	0.202	0.217
H_3PO_4	0.314	0.330	0.340	0.328

It is found that 1mL of 1M HCl acid give the maximum absorbance more than other acids Table (1) and is used in all subsequent experiments.

Effect of Volume of Hydrochloric Acid

The effect of different volumes of 1M HCl solution on the absorbance of the colored product was studied as shown in Table (2)

Table (2): Effect of Volume of Hydrochloric Acid and Time in Absorbances intensity of aAzo Dye

Volume add of HCL	A_1.1min	A_2.2min	A_3.3min	A_4.4min	A_5.5min	Mean Absorbance
0.1	0.527	0.522	0.520	0.519	0.517	0.521
0.2	0.553	0.559	0.561	0.562	0.570	0.561
0.3	0.670	0.669	0.655	0.645	0646	0.657
0.4	0.689	0.699	0.704	0.714	0.719	0.705
0.5	0.069	0.072	0.078	0.082	0.089	0.079
0.6	0.070	0.072	0.074	0.076	0.078	0.074
0.7	0.067	0.064	0.060	0.058	0.055	0.061
0.8	0.050	0.046	0.040	0.034	0.030	0.040
0.9	0.022	0.029	0.038	0.033	0.042	0.033

It is found that 0.4mL of 1M HCl acid is adequate for completing diazotization, and it give a maximum absorbance at 5min. Increasing in the volume of HCl solution causes a decrease in the absorbance of the reaction product (Table 2)

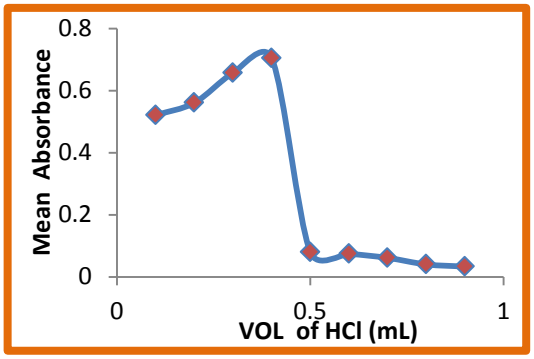


Fig. (3): The Effect of Hydrochloric Acid Volume The Absorbance of Carbofuran Which Demonstrates That The Best Volume of HCl is 0.4 mL. That Dependent for Further Optimization

Effect of the Type of the Alkaline Medium

Typically, coupling reaction of diazotized reagent with phenols is carried out in alkaline solution; therefore, the yellow colored product which is formed between carbofuran and benzidine has developed only in alkaline medium. The effect of different alkaline solutions (1M) such as potassium hydroxide, sodium carbonate, ammonium hydroxide, potassium carbonate and sodium hydroxide is studied.

Table (3):The Effect of the Type of Alkaline Medium on Diazotization of Carbofuran

Type of base	A_1	A_2	A_3	Mean Absorbance
KOH	0.011	0.012	0.015	0.012
NaOH	0.017	0.02	0.019	0.018
Na_2CO_3	0.301	0.310	0.307	0.306
K_2CO_3	0.150	0.154	0.159	0.154
NH_4OH	0.005	0.009	0.01	0.008

The maximum sensitivity and stability are obtained, when the reaction is carried out in the presence of 1mL of 1M sodium carbonate solution as shown in (Table3).

Effect of Volume of Sodium Carbonate

The effect of different volumes of (1M) Na_2CO_3 solution on the absorbance of the colored product is studied keeping other conditions constant.

Table (4) : Effect of volume of sodium carbonate and Time in absorbance intensity of dye

Volume add of Na_2CO_3	A_1.1min	A_2.2min	A_3.3min	A_4.4min	A_5.5min	Mean Absorbance
0.1	0.511	0.500	0.535	0.555	0.534	0.527
0.2	0.546	0.579	0.578	0.580	0.578	0.572
0.3	0.612	0.622	0.620	0.665	0.678	0.639
0.4	0.650	0.659	0.686	0.681	0.667	0.668
0.5	0.665	0.679	0.848	0.655	0.680	0.705
0.6	0.803	0.709	0.611	0.665	0.622	0.682
0.7	0.501	0.406	0.444	0.512	0.522	0.477
0.8	0.470	0.468	0.436	0.435	0.400	0.441
0.9	0.411	0.309	0.415	0.337	0.356	0.365

It was found that a maximum absorbance and stable color is established with 0.5 mL of sodium carbonate (Table 4). Thus 0.5 mL of 1M Na_2CO_3 is chosen in all subsequent experiments as shown in Figure (4).

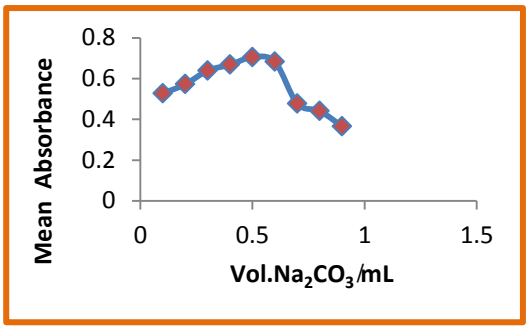


Fig. (4): The Effect of Alkaline Volume on Absorbance of Complex of Carbofuran with Benzidine

Effect of Nitrite Time and Amount on Absorbance of Azo Dye

The effect of different amounts 0.1- 0.9 mL of 1% sodium nitrite with time on the absorbance of the consequential azo dye has undergone a careful study.

Table (5): Effect of Sodium Nitrite Time and Amount on Absorbance

volume add of $NaNO_2$	A_1.1min	A_2.2min	A_3.3min	A_4.4min	A_5.5min	Mean Absorbance
0.1	0.413	0.411	0.415	0.420	0.422	0.416
0.2	0.450	0.451	0.465	0.453	0.460	0.455
0.3	0.512	0.490	0.499	0.560	0.597	0.531
0.4	0.618	0.630	0.670	0.673	0.875	0.693
0.5	0.709	0.715	0.630	0.675	0.612	0.668
0.6	0.560	0.573	0.570	0.523	0.524	0.550
0.7	0.525	0.468	0.489	0.478	0.412	0.474
0.8	0.434	0.456	0.472	0.424	0.406	0.438
0.9	0.422	0.426	0.413	0.420	0.337	0.403

The results in (Table 5) show that 0.4 mL of 1% sodium nitrite solution at 5 min as a reaction time is optimal and it is recommended for the subsequent experiments shown in Figure (5).

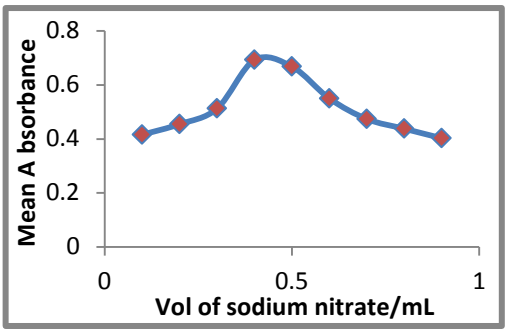


Fig. (5): Effect of Sodium Nitrite Amount and Time on Absorbance

Effect of Sulphamic Acid Amount and Time

The effect of different amounts 0.1- 0.9 mL of 0.1% sulphamic acid with time on the absorbance of the resulting azo dye is studied The excess of nitrite must be removed by adding sulphamic solution due to high blank values.

Table (6): Effect of Sulphamic Acid Amount and Time on Absorbance

Volume . add of sulphamic acid	A_1.1min	A_2.2min	A_3.3min	A_4.4min	A_5.5min	Mean Absorbance
0.1	0.533	0.539	0.537	0.540	0.542	0.538
0.2	0.568	0.566	0.571	0.574	0.576	0.571
0.3	0.657	0.660	0.662	0.664	0.665	0.661
0.4	0.614	0.618	0.619	0.622	0.623	0.619
0.5	0.582	0.583	0.585	0.587	0.589	0.585
0.6	0.515	0.517	0.519	0.525	0.523	0.519
0.7	0.480	0.483	0.485	0.486	0.487	0.484
0.8	0.420	0.421	0.424	0.427	0.430	0.424
0.9	0.358	0.360	0.362	0.365	0.361	0.361

The experimental results reveal that 0.3 mL of 0.1%sulphamic acid with 5 min as time can be incorporated for the development of the formed colored azo dye as shown in Table and Figure (6)

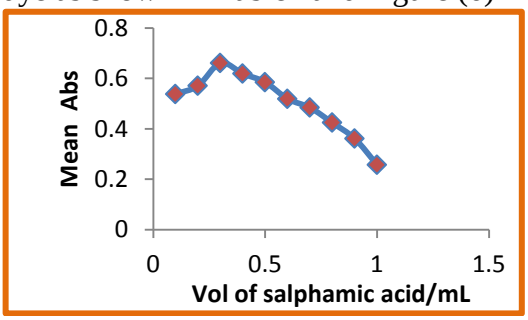


Fig. (6):The Effect of Salphamic Acid Volume on Absorbance of Complex of Carbofuran with Benzidine

Effect of coupling reagent

The effect of varying concentration of coupling reagent is studied using the proposed procedure and adding 0.1-0.9 mL of 100 ppm of benzidine to a series solution.

Table (7): Effect of Benzidine Amount and Time on Absorbance

volume add of Benzidine	A_1.1 min	A_2.2 min	A_3.3 min	A_4.4 min	A_5.5 min	Mean Absorbance
0.1	0.743	0.744	0.745	0.747	0.750	0.745
0.2	0.768	0.771	0.772	0.774	0.776	0.772
0.3	0.767	0.777	0.775	0.776	0.780	0.774
0.4	0.752	0.755	0.758	0.760	0.763	0.757
0.5	0.726	0.730	0.732	0.738	0.739	0.733
0.6	0.721	0.724	0.725	0.729	0.735	0.726
0.7	0.719	0.717	0.715	0.722	0.725	0.719
0.8	0.706	0.709	0.713	0.718	0.714	0.712
0.9	0.691	0.693	0.695	0.698	0.601	0.675

It is found that maximum absorbance and stable color is formed with 0.3 ml at 5min of benzidine in final volume of 10 mL.

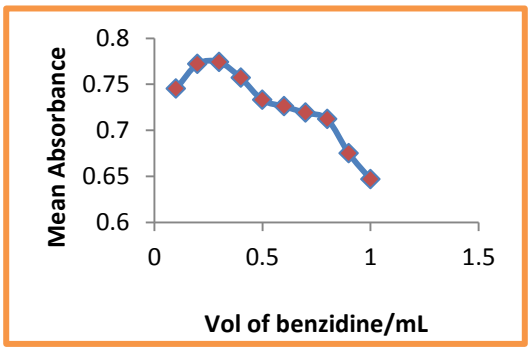


Fig. (7): The Effect of Benzidine Volume on Absorbance of Carbofuran

Effect of Surfactant Type

The experiments are conducted at optimum established conditions according to the general procedure by using various type of surfactants such as, Tween20, SDS. CTAP and Triton X-100 at optimum concentration of 0.1% for each species. In each case, the respective λmax for each surfactant used and absorbance are calculated to choose the best one.

Table .(8) Effect of Surfactant Type on Absorbance

Surfactant	CTAB	SDS	Triton ×-80	Tween 20	Before addition
Absorbance	0.706	0.478	0.556	0.775	0.454

It is observed that Tween 20 which has maximum absorbance at 429 nm is the best one for further study as shown in (Table 8)

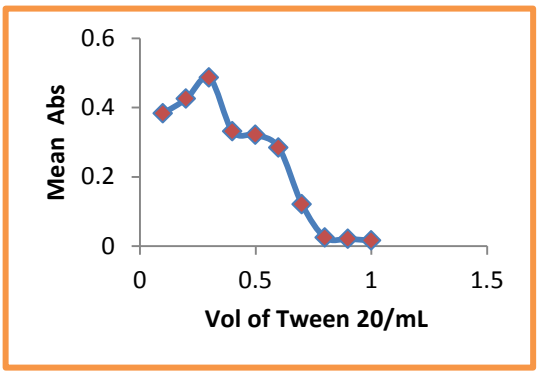


Fig. (8).The Effect of Tween 20 Volume on Absorbance of the Complex of Carbofuran Formed with Benzidine.

The data above of Table and Figure (8) demonstrate that 0.3ml the best volume of Tween 20 that is dependent on further Study

Effect of Organic Solvents

Different organic solvents are examined to evaluate their effects on the intensity of the azo dye which form the data as shown in(Table 9).

Table (9): Effect of Water and Organic Solvents on the Optical Properties of the Azo Dye

Type of solvent	Absorbance			Average
	A_1	A_2	A_3	
Water	0.501	0.503	0.502	0.502
Chloroform	0.259	0.262	0.260	0.260
Ethanol	0.483	0.485	0.487	0.485
Methanol	0.504	0.508	0.515	0.509
Hexane	0.100	0.101	0.103	0.101
Dichloromethan	0.189	0.190	0.194	0.191
Methyl ethyl ether	0.157	0.161	0.162	0.160
Benzen	0.366	0.365	0.367	0.366
Hydrogen peroxide	0.370	0.369	0.371	0.370

Effect of Interference

The effect of some foreign organic compounds and Inorganic compounds, often found in environmental, are studied by adding equal amount of 1mL of (10ppm) of organic compounds, Inorganic compounds and phenols to 1mL of (10ppm) of carbofuran. The color is developed by following the recommended procedure described earlier.

Table (10) Effect of Interference

Type of interference (1mL)	**Mean Absorbance**	**RSD%**
Non addition	0.572	0.524
Lactose	0.069	1.449
Succrouse	0.083	1.204
Potassium nitrate	0.050	2.0
Potassium chloride	0.041	1.396
Urea	0.092	1.086
Benzoic acid	0.088	2.838
Benzoyl peroxide	0.095	2.785
bendiocarb	0.078	2.657
Magnesium nitrate	0.036	2.777

It is observed the Table (10) above, the foreign organic compounds and inorganic compounds do not interfering with the determination carbofuran

Effect of Additing Order

Different orders of addition are examined, as Shown in (Table11)

Table (11): Effect of Additing Order

number	Addition order	Absorbance
I	R+H+N+ F+C+B+T	0.418
II	R+H+N+F+T+C+B	0.468
III	R+H+T+N+F+R+C	0.530
IV	C+R+N+H+F+T+B	0.562
V	C+H+N+T+ F+R+B	0.490
VI	R+N+H+F+C+B+T	0.463
VII	C+N+H+F+R+T+B	0.429
VIII	C+H+N+F+R+B+T	0.450
IX	C+H+N+F+T+R+B	0.502

C:(carbofuran), R:(benzindine), H:(HCl), N:($NaNO_2$), B:(Na_2CO_3), F:(Sulphamic acid) T:(Tween 20)It is found from the data in Table (11) that the order (C+R+N+H+F+T+B) gives maximum color intensity and was used in all subsequent experiments

Effect of Temperature

The effect of temperature on the color intensity of the product is studied (Table 12). Maximum absorbance is obtained when the color is developed at room temperature

Table (12): Effect of Temperature on the Color Intensity of the Product Was Studied .

Time. (min)	0.0	Room.T 25°C	40°C	50°C
5	0.679	0.607	0.660	0.698
10	0.618	0.627	0.651	0.629
15	0.633	0.630	0.635	0.646
20	0.640	0.634	0.628	0.606
25	0.648	0.636	0.640	0.607
30	0.656	0.657	0.663	0.681
35	0.660	0.698	0.698	0.685
40	0.665	0.700	0.718	0.695
45	0.667	0.714	0.720	0.694
50	0.666	0.720	0.690	0.720
55	0.665	0.725	0.700	0.700
60	0.670	0.726	0.710	0.714

From the data in Table (12) it is recommended that the color reaction should be carried out at room temperature (25°C). Maximum absorbance is obtained when the color is developed at room temperature (25°C) more than when the color is developed in an ice-bath (0°C) or in a water-bath (40 °C).and in a water-bath (50 °C).In addition a loss in color intensity and stability is observed with increasing the temperature .

Selected Optimum Conditions

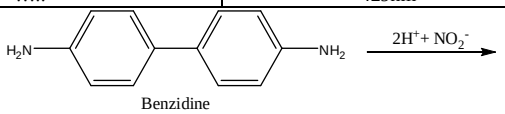
After studying the effect of different parameters that have impact on the absorbance intensity of the colored product, the optimum conditions for the proposed procedure are summarized in (Table 13) and are used in all subsequent experiments.

Table (13): The Optimum Conditions for the Determination of Carbofuran

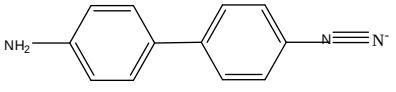
Optimum	Concentrations	Optimum quantities of solutions used	Observations
HCL	1M	0.4mL	Standing 5 minute time
$NaNO_2$	1%	0.4mL	Standing 5 minute time
Sulphamic acid	0.1%	0.3mL	Standing 5 minute time
Carbofuran	100ppm	1mL	……
Benzidine	100ppm	0.3mL	Standing 5 minute time
Na_2CO_3	1M	0.5mL	Standing 3minute time
Tween 20	0.1%	0.3mL	Standing 3 minute time
Total volume of solution	…..	……	3.2mL in volumetric flask (10mL)
Temperature	……	…..	Room.T
Order of addition	…..	….	IV
λ max	….	…..	429nm

Structure of the Dye

The stoicheiometry of the complex formed between carbofuran and benzidine is studied ,it is observed that benzidine reacts with increasing amount of nitrite ion in the acidic medium to from Diazonium ion



Benzidine



Diazonium ion

Adding sulphamic acid to prevent the side reactions with the dye formed which may be caused by the increase of sodium nitrite, which reacts with the increase of nitrite and produce free nitrogen gas

$$NHO_2 + NH_2SO_3H \longrightarrow N_2 + H_2O + H_2SO_4$$

Nitrose acid Sulphamic acid

Then coupling Diazonium salt with carbofuran in the alkaline medium to get the yellow Azo Dye

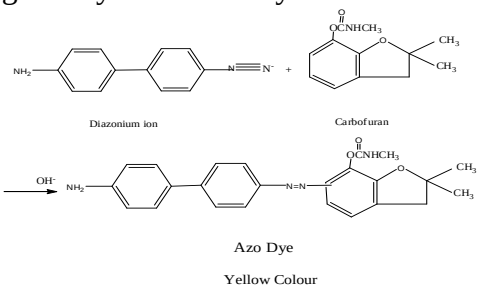


Fig.(9) Carbofuran Coupling with of Reagent

The reaction shows an absorption maxima at 429nm named the molar absorpitivity of 10 ppm is (1×10^4Lmol^{-1}cm^{-1})which means that the method can be used for direct determination of carbofuran depending on the absorption measurements of thecoupling product of carbofuran,

Calibration Curve A series of solution is prepared with deionized water at a known concentration of carbofuran (0, 2,4,6,8,10,12,14 ppm) in to 10mL volumetric flasks and added 0.3mL of benzidine , 0.4 mL of 1% of $NaNO_2$, 0.4 mL of 1M of HCl, 0.3 mL of 0.1% sulphamic acid and then added 0.3mL of 0.1% Tween and then added 0.5 mL of 1M Na_2CO_3 and filled to mark with distilled water to form a spiked samples. The absorbance measurements are carried out at a wavelength at 429 nm. The concentrations are obtained from the calibration curve for the spiked solutions are shown in the (Table 14)

Table (14) The Absorbance Measurements of Standard Solution of Carbofuran in Alkaline Medium by using Distilled Water Samples.

Conc .ppm of carbofuran	Avarage absorbance	RSD%	found	Recovery%
2	0.121	1.65289	1.9907	99
4	0.239	0.63735	4.1639	104
6	0.351	0.4356	6.2265	103
8	0.443	0.46954	7.9208	99
10	0.562	0.27196	10.1123	101
12	0.661	0.30257	11.9355	99
14	0.765	0.27223	13.8508	98

The calibration curve is drawn by using the mean absorbance as a function of concentration (ppm) as shown in Figure (10).

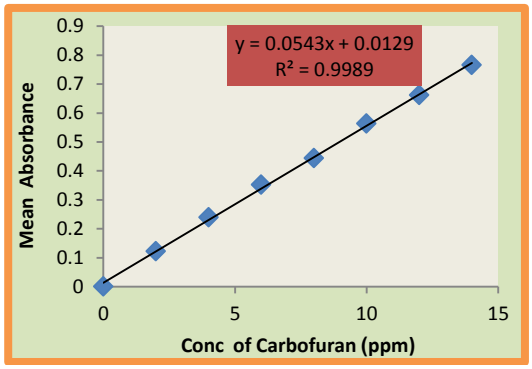


Fig. (10). Calibration curve of carbofuranin deionized water coupling with benzidine

Optical Characteristic Features of the Calibration Curve.

Table(15) shows the main features of the calibration curve and measuring the absorbance at 429 nm

Table (15): Optical Characteristic Features of Calibration Curve

Parameter	Values
Color	yellow
Wave length λ_{max} (nm)	429
Beer's Law limit a (µg mL^{-1})	0-14
Molar absorpitivity (mol^{-1}cm^{-1} L)	1×10^4
regression coefficient(r)	0.9994
Correlation coefficient (r^2)	0.9989
Sand ell's sensitivity (µgcm^{-2})	0.017783
Slope (m)	0.0543
Intercept (C)	0.0129
Regression equation (Y = mX + C)	y = 0.0543x + 0.0129
Variation coefficient (%)	99.89
Limit of detection(µg mL^{-1})	0.314475

Limit of quantization (µg mL^{-1})	1.048250
Average recovery (%)	100.4

From the data above in Table (15) we can see that the method in suitable for the direct determination of carbofuran in environmental water samples.

Direct Determination of Carbofuran in Spiked Neutral Water Samples .A series of solutions is prepared by spiking different environmental water samples with a known concentration of carbofuran (0,2,4,6,8 ppm) into 25mL volumetric flasks and filled to the mark with tap underground , river and rain waters to form spiked samples. The absorbance measurements are carried out at a wavelength at 429 nm.The absorbance measurements and recovery percentages of carbofuran shown in the Table(16)

Table (16) Recovery of Carbofuran in the Spiked Water Sample Solutions.

Type water	present. ppm	Mean Absorbance	RSD%	Found (ppm)	Recovery%
Tap water	2	0.119	1.6806	1.9539	97
	4	0.221	0.4524	3.8324	95
	6	0.334	0.7921	5.9134	98
	8	0.427	0.4871	7.6261	95
Underground water	2	0.122	2.1686	2.0092	100
	4	0.218	0.9534	3.7771	94
	6	0.326	0.6378	5.7661	96
	8	0.446	0.2242	7.9760	99
River water	2	0.115	0.8695	1.8802	94
	4	0.240	0.8685	4.1823	104
	6	0.347	0.5993	6.1528	102
	8	0.455	0.2197	8.1418	101
Rain water	2	0.127	1.6348	2.1012	105
	4	0.229	0.9077	3.9797	99
	6	0.342	0.7736	6.0607	101
	8	0.431	0.2320	7.6998	96

The results in Table (16) reveral that the percent recovery is from 95 to 98% for tap water, 94 to 100 % for underground water,94 to 104 % for River water and96 to 105 % for Rain water .indicating that the method is suitable for direct determination of carbofuran in environmental water samples and with the interference of very low .

Continuous Variation Method(Job`s method) [13]

A series of(1, 2, 3, 4, 5, 6, 7, 8, 9) mL of (5×10^{-4}) mol $L^{-1}$of the solution that contain carbofuran is pipette into each of (10mL) volumetric flask then(9,8,7,6,5,4,3,2,1) mL of (5×10^{-4}) mol $L^{-1}$of reagent ,the absorbance of the solutions is measured at λ_{max} 429 nm the stoichiometric ratio between carbofuran and reagent 1:1 results are shown in the Plotting the value of absorbance versus the VC / VT is shown in Figure (11)

Table (17): The Continuous Variation Method of Carbofuran and Benzidine Complex.

VC ml	VR ml	V C / VT	Absorbance at λ= 429forColor compound
1	9	0.1	0.11
2	8	0.2	0.219
3	7	0.3	0.349
4	6	0.4	0.502
5	5	0.5	0.565
6	4	0.6	0.498
7	3	0.7	0.351
8	2	0.8	0.245
9	1	0.9	0.128

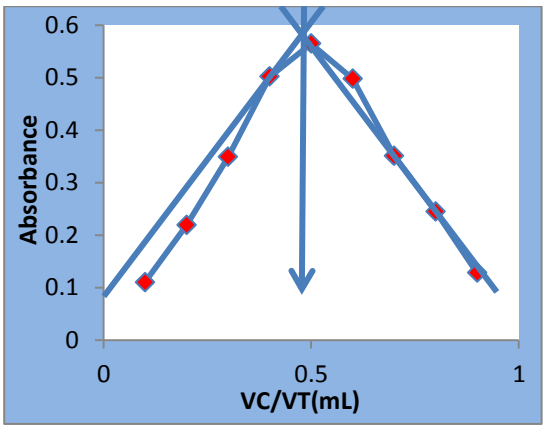


Fig. (11) Continuous Variation Plot.

VC :The values of the compound (carbofuran).
VR :The values of the reagent (benzidine) .
VT: Total (VC+VR)

Mole Ratio Method [13]

Aliquots of 10 ml solution containing 1mL of (5×10^{-4}) mol L^{-1} of (1mL) carbofuran and increasing concentrations (5×10^{-4}) mol $L^{-1}$of (0.1,0.2,0.4, 0.6, 0.8, 1.0,1.2,1.4,1.6 mL) of benzidine (5×10^{-6} -- 8×10^{-6})molL^{-1}reagent. The absorbance of the solutions is measured versus blank at λ_{max}= 429 nm the stoichiometric ratio is of 1:1and results are shown in the Table (18)

Table(18) The Mole Ratio Method of The Carbofuran and Benzidine Complex.

CL	*CL/CM*	Absorbance at λ= 429nm
5×10^{-6}	*0.1*	0.125
1×10^{-5}	*0.2*	0.135
2×10^{-5}	*0.4*	0.178
3×10^{-5}	*0.6*	0.223
4×10^{-5}	*0.8*	0.276
5×10^{-5}	*1.0*	0.304
6×10^{-5}	*1.2*	0.347
7×10^{-5}	*1.4*	0.373
8×10^{-5}	*1.6*	0.389

Plotting the value of absorbance versus the *CL /CM* is shown in Figure (12)

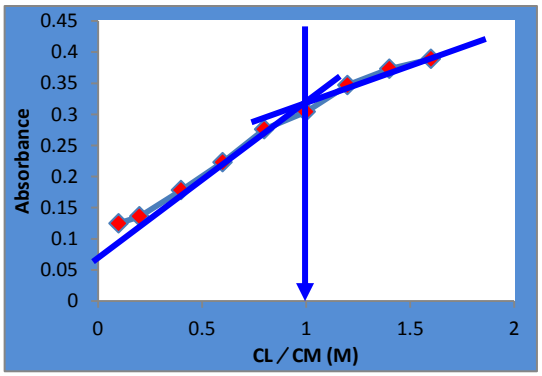


Fig.(12): Mole Ratio Plot of Carbofuran and Benzidine Complex.

CL: The concentration of the reagent(benzidine)
CM: The concentration of the compound (carbofuran)

Stability Constant of Reaction Product [13-14]

The conditional or apparent stability constant of the 1:1 (Reagent and carbofuran) product is evaluated as described

Complete founding the stability constant [K] of colored product Formed imputation of (Regent :carbofuran) as follows :

A series of solution is prepared containing three different concentrations of reagent and carbofuran the concentration (5×10^{-4}) mol L^{-1} for Each reagent and carbofuran when Forming imputation under this condition easily to Hydrolysis and the Intensity absorption are very low.

Another series of solution is prepared containing three different concentration of reagent and carbofuran but with abundance of the reagent (the best concentration) The complex is prepared of the intensity absorption A_m and application the relationship we can calculate the value degree of decomposition follows (α):

$$\alpha = \frac{A_m - A_s}{A_m}$$

Stability constant [K] as follows ;

$$S + R \rightarrow SR$$

$$\alpha c \qquad \alpha c \qquad (1-\alpha)c$$

$$K = \frac{[SR]}{[S][R]}$$

$$K = \frac{(1-\alpha)c}{(\alpha c)(\alpha c)} = \frac{1-\alpha}{\alpha^2 c}$$

Where: K; stability constant
C; the concentration of the product complex and it equivalence the concentration of carbofuran.are shown in the Table19

Table(19) Stability Constant of the Dye Formed

Vol of carbofuran	Absorbance at λ= 429nm			
	A_s	A_m	α	K(l.mol^{-2})
0.5	0.220	0.225	0.0222	4.8×10^{6}
0.7	0.224	0.336	0.3333	1.20×10^{4}
0.9	0.335	0.450	0.2555	2.28×10^{4}

Conclusion:

The proposed method is simple, sensitive and free from drastic experimental conditions such as heating. It is also accurate and precise enough to be successfully adopted as an alternative

to the existing spectrophotometric method and evaluation of carbofuran in an electrophilic compound using Diazotization and in Environmental samples.

References:

[1]Manuel, A.; Garcia, R. L. C. M. J.; Rodriguez, D. P. and Slmanl, G. J. 2005. Influence of Micelles on the Basic Degradation of Carbofuran. J. Agric. Food Chem. 53: 7172-7178.

[2]Mohamed, S. J.; Moamed, A. F. and Ahamed, M. A. 2011. Adsorption of carbofuran insecticide from aqueous solution using commercial activated, Int. J. Chem. Sci. 9(2):557-564.

[3]AL-Rawi, S. M. Sh. 2011. Quantitative Analysis of some nsecticidos and their Mixture in Agricul by using uv-vis Spectrophotometer. Baghdad Sci. J. 8(2): 274-279.

[4]Al-Niaeem, Abd-Alsatar, M. Th. Mahmood, I. A. Adin, H. and Mohammed, A. 2014. Effect of the fungus Metarhizumanisopliae (Metchnikoff) Sorokin and actelic insecticide in the protection of bean seeds packaged in bag from infection by cowpea beetle. Baghdad Sci. J. 11(2): 908-912.

[5]Rama, B.; Swanandi, p.; Vidya, T. and Bipinraj, N. 2011. Developments in Analytical Methods for Detection of Pesticides in Environmental Samples. American J. Chem Analytical. 2:1-15

[6] Cook, R. F.; Stanovick, R. P. and Cassil, C. C. 1969. Chromatographic techniques in the analysis of organochlorine pesticide residues J. Chromatography 754(22): 33-42.

[7]Ling, C. F.; Melian, G. P.; Jimenez-Conde, F. and Revilla, E. 1990. Comparative study of some columns for direct determination of carbofuran by gas—liquid chromatography with nitrogen-specific detection. J. Chromatography A 519(2):359-362.

[8]Agrawal, O. and Gupta, V. K. 1999. Sub-Parts-per-Million Spectrophotometric Determination of Phenol and Related Pesticides Using Diazotized *p*-Amino-acetophenone. J. Microchemical: 62 (1):147-153

[9]Hirokawa, T.; Ohmori, A. and Kiso, Y. 1993. Analysis of a dilute sample by capillary zone electrophoresis with isotachophoretic preconcentration. Journal of Chromatography 634 (1):101-106

[10] McGarvey, B. D. 1993. High-performance liquid chromatographic methods for the determination of N-methylcarbamate pesticides in water. soil, plants and air J. Chromatography A . 642(1): 88-105.

[11] Nagaraja, P. and Bhaskara, B. L. 2006. Sensitive spectrophotometric assessment of carbofuran using dapsone as a new chromogenic reagent in formulations and environmental samples .31(4) 1678-4618

[12] Trotter, D.; Kent, R. and Wong, M. 1991. Aquatic Fate and Effect of Carbofuran. Crit Rev in Environ Cont 21(2): 137-176

[13] de-Levie, R. 1997. Principles of Quantitative Chemical Analysis J. Chromatography A 646 (2): 317–329.

[14] Hadjiioannou , T. P .; Christian, G. D.; Koupparis, M. A. and Macheras, P. E.1993. Quantitative Calculations in Pharmaceutical Practice & Research, VCH Publishers, Inc. USA.

التقدير الطيفي للكاربوفيوران با ستخدام ازوتة البنزيدين في نماذج المياة للبيئة

سعدية احمد ظاهر نور جمال محمد شذى فاضل نارين

قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد، بغداد، العراق

الخلاصة:

تم تطوير طريقة طيفية بسيطة وحساسة لتقدير الكاربوفيوران في نماذج مياه تعتمد الطريقة علئ ازوتة كاشف البنزيدين(4,4-داي امينو ثنائي الفينل) بواسطة نتريت الصوديوم وحامض الهيدروكلوريك ثم اقترانة مع الكاربوفيوران في وسط قاعدي من كاربونات الصوديوم لتكوين صبغة ازوتة ذات لون اصفر ,مستقرة وذائبة في الماء لها اعلئ امتصاص عند الطول الموجي 429 نانومتر وكان حدود قانون بير ضمن مدئ التركيز(14-0) مايكروغرام من الكاربوفيوران في حجم نهائي 10 مل وقيمة معامل الامتصاص المولاري 1×10^4 لتر.مول$^{-1}$ سم$^{-1}$ اعتماد علئ مستوئ تركيز للكاربوفيوران مما يدل علئ ان الطريقة تمتاز بدقة وضبط عالية , وقد تمت دراسة بعض المذيبات العضوية ولم توثر علئ صفات الصبغة المتكونة وان نسبة التفاعل بين كاربوفيوران والبنزيدين هي 1:1 وقد طبقت الطريقة بنجاح لتقدير الكاربوفيوران في نماذج المياة (مياة الشرب، البئر، النهر، المطر)

الكلمات المفتاحية: الكاربوفيوران، تقدير، صبغة الازو، البنزيدين ، المطيافية