Volume-3, Issue-12, Dec-2014 • ISSN No 2277 - 8160

Research Paper | Medical Science

Direct UV-Spectrophotometric determination of Bendiocarb in Environmental water samples.

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ABSTRACT

*A simple, sensitive, rapid and accurate spectrophotometric method was developed for the analysis of parts per million levels of widely used Carbamate pesticide Bendiocarb .The proposed method is based on the direct determination of bendiocarb residue in environmental water samples .Bendiocarb shows an absorption maxima at a wave length of (271) nm with apparent molar absorptivity (1.830*103) L mol-1cm-1 and obeyed Beer's law in the concentration range of(0.1-20) µg/ml. And it shows an absorption maxima at a wave length of (279) nm in alkaline medium with apparent molar absorptivity (2.25*104) L mol-1cm-1 and obeyed Beer's law in the concentration range of(0.1-10)µg/ml. A simple procedure was employed for the spectrophotometric determination of the presence of trace quantities of bendiocarb in environment water samples. Particularly in the tap, river and underground water samples.*

KEYWORDS : UV- Spectrophotometry; bendiocarb, Pesticide.

Introduction

Bendiocarb,(2,2-dimethyl-1,3-benzodioxol-4-yl-methylcarbamate) and other chemical name of bendiocarb **,(** 2,2-dimethyl-2 H-1,3-benzodioxol – 4 -yl methyl carbamate) **,** (2,2dimethyl-1,3 benzodioxol-4-yl *N*-methyl carbamate).(2,3 iso propylidenedioxy phenyl methyl carbamate*)* Empirical formula ($C_{11}H_{13}NO_4$) Relative molecular mass*(*223.25 g/mole)(1).

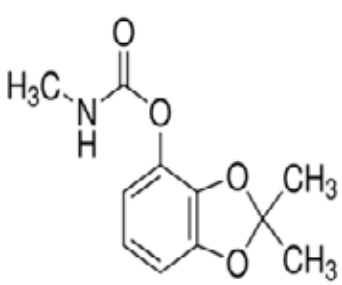


Figure (1) The structure of bendiocarb.

Bendiocarb is a carbamate insecticide. Like other carbamates, so inhibitsreversible acetyl cholinesterase, an enzyme necessary for normal transmission of impulses nervous. Bendiocarb binds to the active center of this enzyme causes a buildup of acetylcholine, necessary for transmission of nerve impulses in the body at the jointsneuromusculares(2). It is a systemic insecticide with contact and stomach action and is active against many public health, industrial and storage pest. This active ingredient is especially useful inside buildings, due to its low odor and lack of corrosive and

Staining properties (3). Bendiocarb disrupts the normal functioning of an insect's nervous system and may kill by either contact or ingestion (4). It is used to control disease vectors such as mosquitoes and flies, as well as household and agricultural pests. Most formulations of bendiocarb are registered for general use, except to Turcam,2.5 G and the best known product Ficam (5) The blockage of enzyme cholinesterase (ChE) caused by bendiocarb persists for approximately 24 hours and subsequently the situation returns to normal after acute exposure because the insecticide does not accumulate in mammalian tissues (6)It is effective against a wide range of nuisance and disease vector insects. It is used to control mosquitoes, flies, wasps, ants, fleas, cockroaches, silverfish, ticks and other pests in homes, industrial plants, and food storage sites. In agriculture it is used against a variety of insects, especially those in the soil. Bendiocarb is also used as a seed treatment on sugar beets and maize and against snails and slugs(7-8) Pesticides containing bendiocarb are formulated as dusts, granules, ultra- low volume sprays, and as wet table powders (9). Several Techniques have been reported for the determination of bendiocarb , such as Spectrophotometry (10).Liquid chromatographic (11), A gas chromatographic method(12,13,14) and different chromatographic techniques were used . A novel method (15): The aim of this search is to determination of bendiocarb in different neutral water by action it with reagent (PAP) and syntheses a color compound in alkaline medium which easily detect the percent of pollutions environmental water samples with pesticides (bendiocarb).

Experimental part

1- Instrumentation

A Shimadzu Model C160A UV-Vis recording spectrophotometer (1986) (Japan) with a response time of 0.1s was used for spectrophotometric absorbance measurements . A quartz cell of 5 ml internal volume and 1cm path length was used for absorbance measurements.

2- Chemicals and Reagent.

Bendiocarb (purity 99.9%) was obtained from Accustandard (USA) .A standard stock solution of 20 µg $ml^{-1}$of

bendiocarb was prepared by dissolving 0.02g of the pesticide in 1L distilled water . This solution was kept in Refrigerator to prevent any hydrolysis or exposing to sun light which being stable for more than two months. A standard stock solution of sodium carbonate Na_2CO_3 (1M) was prepared by dissolving (2.6g) of the solid product in 25ml of demonized water.

3- Collection of Environmental spiked water samples

A (500 ml) of Real water samples were directly taken from tap, Irrigation water was Irrigation collected from Tigris River under Jadria bridge. Underground water samples were collected from well in Baghdad (Jadria). All the environmental water samples were kept in glass containers.

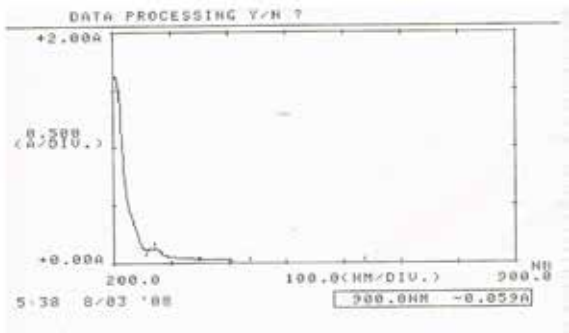
4- Recommended Procedure in neutral water samples.

A series of solution were prepared by taking a known volume of bendiocarb in to a 25ml volumetric flask and filled to the mark with environmental water to Obtained (2,4,6,8,10 ppm) concentrations of bendiocarb . Other series of solution were prepared by taking a known volume of bendiocarb in to a 25ml volumetric flask and added 5ml of 1M sodium carbonate Na_2CO_3 and filled to the mark with environmental water to Obtained (2,4,6,8,10 ppm) concentrations of bendiocarb in alkaline medium. and measurements the absorbance .

Results and discussion :

UV-Spectra of bendiocarb in distilled water.

Most Absorption Spectroscopy of organic compounds is based on transition of n and $\pi \rightarrow \pi^*$ electrons to the excited state .This in because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200- 800) nm These Transitions need an unsaturated group in the molecules to provide The π electrons.20 ppm of bendiocarb show an absorbance at a wave length at(271)nm with an absorbance of (0.132) **.** The molar absorptivity ε value is ($1.830*10^3$) L mol^{-1} cm^{-1} which means that the electronic transitions are due to the $\pi \rightarrow \pi^*$. The value of molar absorptivity enable to carry out the quantitative analysis of bendiocarb in environmental water sample directly as shown in the figure (2).



Figure(2) UV-absorption spectra of 20 µg ml^{-1}bendiocarb in distilled water.

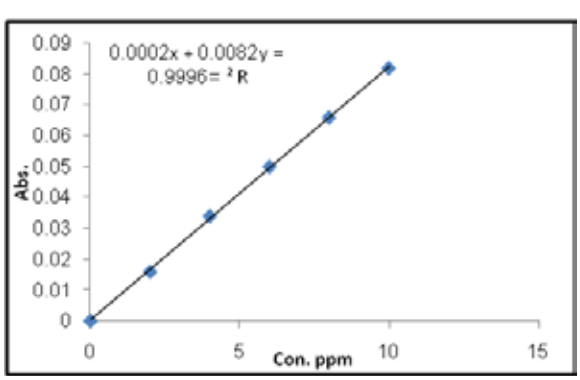
Calibration carve in neutral deionized water.

A series of solution were prepared by taking a known volume of bendiocarb in to a 25ml volumetric flask and filled to the mark with environmental water to Obtained (2,4,6,8,10 ppm) concentrations of bendiocarb and the measurements were carried at (271 nm) in triplicate manner. The absorbance measurements are illustrated in table (1)and figure(1).

Table (1) The absorbance measurements of standard solution of bendiocarb.

Con .of Spiked water samples ppm	Absorbance			Mean Absorbance	RSD%
	R1	R2	R3		
2	0.018	0.019	0.019	0.018	3
4	0.034	0.034	0.035	0.034	1.6
6	0.049	0.050	0.051	0.050	1.4
8	0.065	0.066	0.067	0.066	1.07
10	0.081	0.082	0.083	0.082	0.08

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 bendiocarb in deionized water.

Optical characteristics Features of the calibration curve.

Table(2) Show the main features of the calibration curve carried out in deionized distilled water.

Table (2) Optical characteristic features of calibration curve.

Parameter	Values
Color	Colorless
Wave length λ_{max} (nm)	271
Beer's Law limit (µg ml^{-1})	0-20
Molar absorptivity $Lmol^{-1}cm^{-1}$	$1.830_{*}10^3$
Limit of detection µg ml^{-1}	0.01
Sandell's sensitivity (µg.cm-2/0.001 A.U)	0.0994
Slope (m)	0.008
Intercept (C)	0.001
Regression equation (Y = m X + C)	0.0082x+0.0002
Correlation coefficient (r^2)	0.9996

From the above data in table (2) we can see that the method in suitable for the direct determination of bendiocarb in deionized water.

Direct determination of bendiocarb in spiked natural neutral water samples.

A series of solution were prepared by spiking of different environmental water samples with a known volume of bendiocarb in to a 25ml volumetric flask and filled to the mark with Tap water to Obtained (2,4,6,8,10 ppm) concentrations from a spiked water samples. The absorbance measurements were carried out at a wavelength at 271 nm .The concentrations were obtained from the calibration curve for the spiked solutions are shown in the table (3).

Table (3) Recovery bendiocarb of the Tap water.

Con .of Spiked waters ppm	Absorbance			Mean Absorbance	RSD %	Found	Recovery %
	R1	R2	R3				
2	0.020	0.019	0.019	0.019	2.9	1.9	98
4	0.040	0.042	0.041	0.041	2.4	4.1	102
6	0.060	0.062	0.061	0.061	1.6	6.1	101
8	0.079	0.081	0.080	0.080	1.25	8	100
10	0.098	0.099	0.100	0.099	1	9.9	99

The above table shows quite obviously that the recovery percent is from 98 to 102 % which means that the method is suitable for direct determination of bendiocarb in natural environmental water samples with very low interferences.

Direct determination of bendiocarb in underground water samples:

Determination of bendiocarb in underground water was carried out by the same method as illustrated above. Table (4) shows the absorbance measurements and recovery percentages of bendiocard obtained.

Table (4) Recovery bendiocarb of the spiked real water samples .

Con .of Spiked waters ppm	Absorbance			Mean Absorbance	RSD %	Found	Recovery %
	R1	R2	R3				
2	0.016	0.017	0.017	0.017	3.5	2	100
4	0.034	0.035	0.036	0.035	2.8	4.3	107
6	0.050	0.053	0.054	0.053	1.3	6.5	108
8	0.070	0.068	0.066	0.068	2	8.5	106
10	0.086	0.087	0.088	0.087	1.6	10.8	108

The above results show the recovery percentages of the added ben-

diocarb quantities of 100 to 108 % which mean that the interference is low and the proposed method is validated for measuring this compound directly in environmental water samples.

Direct determination of bendiocarb in Irrigation water samples:

Determination of bendiocarb in Irrigation water was carried out by the same method as illustrated above from by take water from Tigris river in Baghdad under the Jadria bridge .

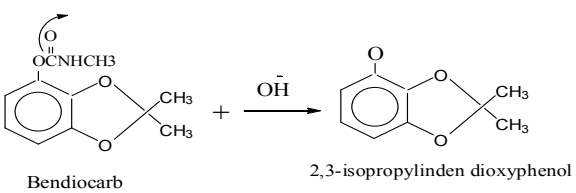
Table (5) shows the absorbance measurements and recovery percentages of bendiocard obtained .

Con .of Spiked waters ppm	Absorbance			Mean Absorbance	RSD %	Found	Recovery %
	R1	R2	R3				
2	0.017	0.016	0.017	0.016	3.4	2.04	102
4	0.033	0.034	0.035	0.034	2.9	4.2	105
6	0.049	0.050	0.051	0.050	2.8	6.2	103
8	0.064	0.066	0.068	0.066	2.1	8.2	102
10	0.081	0.082	0.083	0.082	0.8	10.2	102

The above results show the recovery percentages of the added bendiocarb quantities of 102 to 105 % which mean that the interference is very low and the proposed method is validated for measuring this compound directly in environmental water samples.

UV-Spectrum of bendiocarb in Alkaline Medium.

Bendiocarb hydrolyzed in alkaline medium producing phenolate according to the following equation:



Bendiocarb 2,3-isopropylinden dioxyphenol

Figure (4) Hydrolysis of bendiocarb in alkaline medium.(16)

The hydrolysis product 2,3-isopropyldioxyphenol shows an absorption maxima at

(279) nm and the molar absorptivity of 10 ppm is ($2.25*10^4$) $Lmol^{-1}cm^{-1}$ Which means that the method can be used for direct determination of bendiocarb depending on the absorption measurements of the hydrolysis product of bendiocarb, as shown in the figure (5):

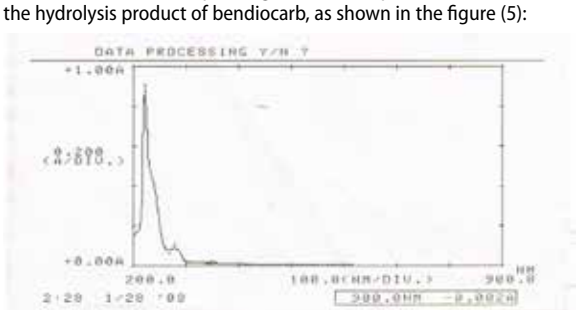


Figure (5) UV-absorption spectra of 10 µg ml^{-1}bendiocarb in 0.2M of Na_2CO_3.

Optimization of alkaline concentration.

Figure 6 shows the effect of alkaline concentration on hydrolysis of bendiocarb which demonstrates that the best concentration of Na_2CO_3 is (0.2 M). The absorbance of 10 ppm of bendiocarb is (0.088) and the molar absorptivity is ($2.25*10^3$) $Lmol^{-1}cm^{-1}$

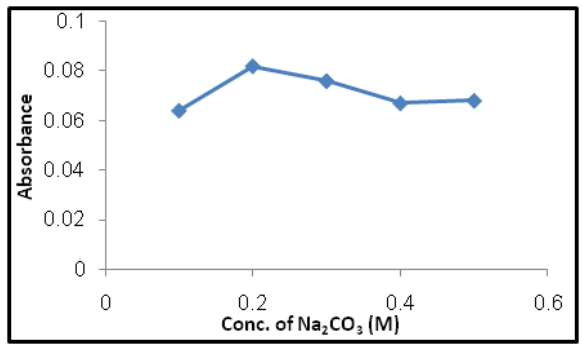
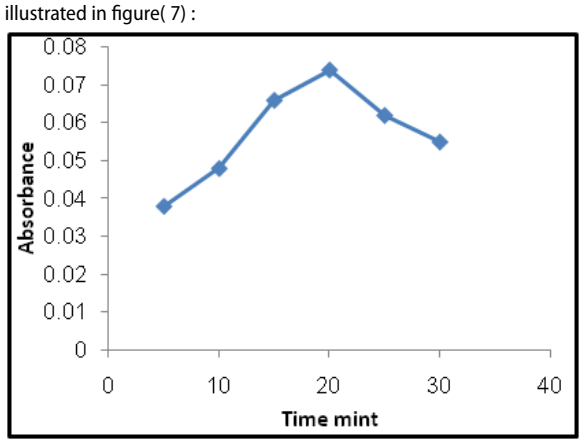


Figure (6) optimization of the concentration of Na_2CO_3

Optimization of hydrolysis of bendiocarb with Time:

Bendiocarb was Hydrolysis in alkaline medium by used sodium carbonate Na_2CO_3 produce the phenolate .Figure 3 shows that on increasing the time of residence of bendiocarb 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(7) :



Figure(7) Alkaline hydrolysis of 10 ppm bendiocarb in 0.2 M Na_2CO_3 solution as a function of time.

Calibration Carve of Bendiocarb in alkaline Medium with Na_2CO_3.

A series of solution were prepared by spiking of different environmental water samples with a known volume of bendiocarb in to a 25ml volumetric flasks and added (0.2M)from Na_2CO_3 and filled to the mark with distilled water to Obtained (2,4,6,8,10 ppm) concentrations to form a spiked water samples the solution left behind for 20 min to ensure a complete hydrolysis . The absorbance measurements for triplicate were carried out at a wavelength at (279) nm as shown in the table (6).and Figure(8).

Table (6) the absorbance measurements of standard solutions of bendiocarb in alkaline medium by used distilled water samples.

Con .of Spiked waters ppm	Absorbance			Mean absorbance	RSD%
	R1	R2	R3		
2	0.020	0.021	0.021	0.020	2.7
4	0.041	0.040	0.041	0.040	1.3
6	0.061	0.062	0.063	0.062	1.6
8	0.081	0.082	0.083	0.082	1.2
10	0.101	0.102	0.103	0.102	0.9
12	0.119	0.120	0.121	0.120	0.8

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

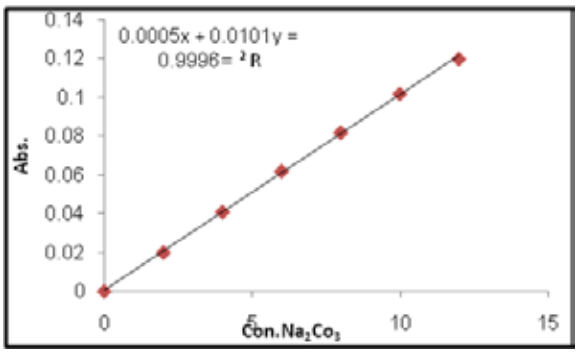


Figure (8) Calibration curve of bendiocarb in alkaline medium .

Optical Characteristic features of the calibration carve.

Table (7) Shows the main features of the calibration curve carried out by using the optimum condition of alkaline concentration and hydrolysis time.

Table (7) Optical characteristic features of calibration curve.

Parameter	Values
Color	Colorless
Wave length λ_{max} (nm)	279
Beer's Law limit (µg ml^{-1})	0 -10
Molar absopitivity $Lmol^{-1}cm^{-1}$	($2.25*10^4$)
Limit of detection µg ml^{-1}	0.01
Sandell's sensitivity (µg.cm-2/0.001 A.U)	0.000976
Slope (m)	0.0101
Intercept (C)	0.0004
Regression equation (Y = m X + C)	0.0101x+0.0005
Correlation coefficient (r2)	0.9996

From the above data in table(7)one can see that the method in suitable for the direct determination of bendiocarb in environmental water samples without remarkable interferences.

Determination of Bendiocarb in Alkaline Medium by using Tap water samples.

A series of solution were prepared by spiking of different environmental water samples with a known volume of bendiocarb in to a 25ml volumetric flasks and added (0.2M)from Na_2CO_3 and filled to the mark with Tap water to Obtained (2,4,6,8,10 ppm) concentrations to form a spiked water samples the solution left behind for 20 min to ensure a complete hydrolysis . The absorbance measurements for triplicate were carried out at a wavelength at (279) nm as shown in the table (8).

Table (8) Recovery percentages of bendiocarb in the spiked samples.

Con .of Spiked waters ppm	Absorbance			Mean	RSD%	Found	Recovery%
	R1	R2	R3				
2	0.031	0.030	0.030	0.030	1.9	2.1	105
4	0.057	0.058	0.059	0.058	1.72	4.2	105
6	0.081	0.082	0.083	0.082	1.27	6	101
8	0.107	0.108	0.109	0.108	0.92	8	100
10	0.133	0.134	0.135	0.134	0.74	10	100
12	0.154	0.156	0.158	0.156	1.28	11.7	98

The above results show the recovery percentages of the added bendiocarb quantities of 98 to 105 % which mean that the interference is very low and the proposed method is validated for measuring this compound directly in environmental water samples.

Direct determination of Bendiocarb in underground water.

Determination of bendiocarb in alkaline medium of underground water was carried out by the same method as illustrated above . Table (9)shows the absorbance measurements and recovery percentages of bendiocard obtained .

Table (9) Recovery bendiocarb of the spiked solutions.

Con .of Spiked waters ppm	Absorbance			Mean	RSD%	Found	Recovery%
	R1	R2	R3				
2	0.03	0.03	0.031	0.03	1.9	2	100
4	0.059	0.060	0.061	0.058	1.66	4.1	102.5
6	0.090	0.088	0.086	0.087	1.62	6	100
8	0.117	0.118	0.117	0.118	0.49	8.2	102.5
10	0.140	0.142	0.144	0.142	1.40	10	100
12	0.169	0.168	0.167	0.168	0.59	11.8	98.30

The above results show the recovery percentages of the added bendiocarb quantities of 98 to 103 % which mean that the interference is very low and the proposed method is validated for measuring this compound directly in environmental water samples.

Direct determination of bendiocarb in irrigation water samples .

Determination of bendiocarb in Irrigation water was carried out by the same method as illustrated above .

Table (10) Shows the absorbance measurements and recovery percentages of bendiocard obtained .

Con .of Spiked waters ppm	Absorbance			Mean absorbance	SRD%	Found	Recovery%
	R1	R2	R3				
2	0.029	0.030	0.030	0.030	0	2.1	105
4	0.057	0.058	0.059	0.058	1.72	4.1	102
6	0.087	0.088	0.089	0.088	1.13	6.2	103
8	0.119	0.120	0.122	0.120	1.26	8.5	106
10	0.144	0.145	0.146	0.145	0.68	10.3	103
12	0.175	0.176	0.177	0.176	0.56	12.5	104

The above results show the recovery percentages of the added quantities of bendiocarb from 102 to 106 % which mean that the interference is very low and the proposed method is validated for measuring this compound directly in environmental water samples.

Conclusion

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

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