DETERMINATION OF CARBOFURAN USING J-ACID BY SIMPLE AND SENSITIVE SPECTROPHOTOMETRIC METHOD

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ABSTRACT

A widely used carbamate insecticide carbofuran is determined by simple and sensitive spectrophotometric method. The method is grounded on hydrolysis of carbofuran under alkaline condition to carbofuranphenol followed by coupling with J-acid. The colored dyes formed give absorption maxima at 460 nm. Beer's law is conformed at the concentration range of 0.4 to 3.2 µg in a final solution volume of 25 ml and extracted from iso propyl alcohol. The molar absorptivity and sandell's sensitivity were found to be $1.2x10^4$ (±100) l $mole^{-1}cm^{-1}$ and 0.005 µg cm^{-2} respectively. The standard deviation and relative standard deviation were found to be ± 0.004 and 1.06% respectively. The method is free from interference of other pesticides and diverse ions, simple, sensitive and acceptable for the determination of carbofuran in different ecological, agricultural and biological samples.

KEYWORDS: Agricultural, Biological, Carbofuran, Ecological Samples, J-acid, Spectrophotometer.

Carbofuran (2, 3-dihydro-2, 2-dimethyl-7-benzo (b) furanyl methyl carbamate) is also known as Furadan. It is an effective contact and systemic, broad spectrum carbamate insecticide and acaricide[1]. Carbofuran is registered for use on a variety of fruits, vegetables, grains and crops. It exhibits high mammalian toxicity. Its toxic properties include inhibitory effect on cholinesterase enzyme, violent convulsions and neuromuscular disturbances on inhatation. The acute oral LD_{50} value for rats proposed for carbofuran is 5.0 mg/kg [2], [3]. The wide applicability and high toxicity of carbofuran has resulted in numerous instrumental method for its determination such as, chromatography–tandem mass spectrometry,[4] fluorimetric multi-optosensor [5] etc. A few spectrophotometric methods are also reported [6]-[11]. In the present method carbofuran is first hydrolyzed by sodium hydroxide to carbofuranphenol followed by coupling with J acid. The absorption maxima of the dyes formed is measured at 460 nm by spectrophotometrically.

EXPERIMENTAL

Apraratus and Reagent

A Systronics UV-Vis spectrophotometric model 104 with matched silica cells was used for all spectral measurements. A Systronic pH meter model 335 was used for pH measurements. A Remi C-854/4 clinical centrifuge force of 1850 g with fixed swingout rotors was used for centrifugation.

All reagents used were of Anala R grade or of the best available quality. Double distilled demineralized water was used throughout.

Carbofuran (Rallis, India): A stock solution of 1µg ml^{-1} was prepared in ethanol. Working standard solution was prepared by appropriate dilution of the stock standard solution with water.

Sodium nitrite: A 1% m/V solution was prepared in 10 V/V hydrochloric acid.

Sodium hydroxide: A 1.5 mol l^{-1} aqueous solution was used .

J-acid (6-amino-1-naphthol)-3-(sulphonic acid) : 0.2% in conc. H_2SO_4.

PROCEDURE

Preparation of Calibration Graph

An aliquot of test solution containing 0.4 to 3.2 µg of carbofuran was taken in a 25 ml graduated tube and to it 1.0 ml of 1.5 mol l^{-1} sodium hydroxide was added. The solution was kept for 15 min at room temperature for complete hydrolysis. Then 1 ml of J acid and extracted from iso propyl alcohal. The solution was then diluted to the mark with water and absorbance was measured at 460 nm against a reagent blank.

RESULTS AND DISCUSSION

Spectral Characteristics

The dye formed in the proposed reaction shows maximum absorption at 460 nm. All spectral measurements were carried out against deionised water as the reagent blank showed negligible absorption at this wavelength. The colour system obeys Beer's law in the range of 0.4 to 3.4 µg of dichlorvos in 25 mL of final solution. The molar absorptivity and sandell's sensitivity

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were found to be $1.2x10^4$ (±100) l $mole^{-1}cm^{-1}$ and 0.005 µg cm^{-2} respectively. The standard deviation and relative standard deviation were found to be ± 0.004 and 1.06% respectively.

Foreign Species

The effect of common foreign species and pesticides were studied to assess the validity of the method. Known amounts of foreign species and pesticides were added to the standard solution containing 2µg of these pesticides prior to hydrolysis and the solution was analysed by the given method.

The effect of various species on the determination of the carbofuran was studied. Most of the metal ions, organic, inorganic compounds and communally used pesticides did not interfere under proposed condition (Table -1).

Recovery of carbofuran from water and grain samples : Water samples free from carbofuran were fortified with known amount of the compounds and extracted with chloroform (2x 5ml) in a separatory funnel by shaking the funnel for 2-3 min. Known aliquots of the chloroform extract were than evaporated to dryness under reduced pressure and the residue dissolved in ethanol[12] (10ml). Carbofuran were then determined as described above; the recoverie of carbofuran are listed in (Table –2, 3).

Grain samples (wheat, rice, apple and cauliflower; 25 gm) were blended with chloroform (2x25ml) in a blender and fortified with known amounts of carbofuran. The chloroform solution was filtered through Whatman No. 1 filter paper into a 25 ml calibrated flask and the volume made up to the mark. Aliquots of chloroform solution were evaporated to dryness and the residue dissolved in ethanol[12](10ml). Carbofuran were determined as described above; the recoveries obtained are listed in Table - 2.

Recovery of carbofuran from biological samples : Since the presence of phenolic pesticides in blood (serum), urine and mother milk has been reported in detectable concentration[13],[14].The method has been applied for the determination of carbofuran in biological samples. Synthetic samples were prepared by adding known amounts of carbofuran to these samples and than analysed after deproteination with trichloroacetic acid [15],[16] as described above (Table -3).

Temperature and pH

There was no change in the absorbance values within the temperture range 20-30^{0}C. The colour was found to be stable for about 10 hr. Constant absorbance values were obtained within pH 12-13 and no buffer was required to stabilize the colour.

Application

The proposed method was satisfactorily applied to the determination of carbofuran in polluted water, wheat, rice, apple, cauliflower and biological (blood, urine and mother milk) samples. The results obtained were in good agreement with the reported method.(Table-4) To check recoveries known amount of carbofuran was added to the samples and then determined by the proposed and the reported method, and recoveries are as follows : water (94.8, 96.8), wheat (94.4, 98.1), rice (91.4, 96.8), apple(85.8, 95.4), cauliflower(81.2, 98.1), blood (92.0, 90.0), urine (88.0, 90.0) and mother milk (92.0, 82.0).

Table 1. Effect of foreign species (2 ppm)

I. Foreign species	Tolerance limit* µg in 25ml	Foreign species	Tolerance limit* µg in 25ml
Formaldehyde, Methanol	450	Fe^{3+} Fe^{2+}, Sb^{3+}	370
DDT, BHC	300	Ni^{2+}, Pb^{2+}, SO_4^{2-}	190
Aldrin, Dichlorovos	350	Al^{3+}, Mg^{2+}, Br^-	140
Monocrotophos, Ethyl parathion, Quinolphos	330	CO_3^{2-}, Ca^{2+}, Cl^-	120
Malathion, Parathion, Phorate	250	Zn^{2+},Co^{2+}, Cu^{2+}	80
1-Naphthol	3**	NO_2^-	60
Phenol,Carbaryl, Propoxur	2**		

* = The amount causing an error of ±2% in absorbance value.

* * = Tolerance limit without its removal from the sample

Table 2. Determination of carbofuran in environmental and agricultural samples

Samples	Amount of carbofuran added[a] (µg)	mount of carbofuran found[a](µg) in	Recovery %
Water[b] A	50	47.4	94.8
B	75	72.6	96.8
Wheat[c] A	50	47.2	94.4
B	75	73.6	98.1
Rice[c] A	50	45.9	91.8
B	75	72.4	96.5
Apple[c] A	50	44.6	89.2
B	75	71.6	95.5
Cauliflower[c] A	50	43.4	86.8
B	75	71.4	95.2

a = Mean of three replicate analyses

b = 250 ml sample (Sample taken from plant field)

c = 25 gm sample (Sample taken from agricultural field)

Table 3: Recovery from biological samples

Samples	Amount of carbofuran pesticides added (µg)	Carbofuran Pesticide found** (µg) Carbaryl	Recovery %
Urine*	2.5	2.1	84.0
	5.0	4.4	88.0
Blood* (serum)	2.5	2.1	84.0
	5.0	4.2	84.0
Mother milk*	2.5	2.3	92.0
	5.0	4.4	88.0

* Amount of biological Fluid =1ml

** Mean of three replicate analyses.

Table 4: Comparison with other reported methods

Reagent	λmax nm	Beer's law detection limit(ppm)	Remarks
4-amino antipyridine[6]	475	0.5-20	Reagent unstable High blank problem
Sulphanilic acid[7]	470	1.0-40	Poor sensitivity
4- amino benzoic acid[8]	490	0.4-12	Less selective, less sensitive
Conc. nitric acid[9]	345	2-30	Reagent corrosive, less sensitive
Vanillin phosphoric acid[10]	550	1.0-10	Reagent corrosive, poor sensitive
p-anisidine[11]	660	0.1-1.0	Sensitive and selective
Present method	460	0.4-3.2	Highly sensitive

CONCLUSION

The proposed method is rapid, simple and sensitive and reagent described here is sensitive and selective for carbofuran insecticides containing a phenolic group. The method has been compared with other spectrophotometic methods and found to be superior (Table-4)

The proposed method has been applied satisfactorily to the determination of carbofuran in various samples of water, soil, vegetables, fruits, foliages and biological samples. To check the recoveries, known amount of carbofuran were added to various samples of soil, vegetables, fruits and biological samples and then analysed by the proposed method. (Table – 2, 3).

ACKNOWLEDGEMENT

Authors are thankful to the Head School of Studies in Chemistry, Pt. Ravishankar Shukla University and Director Shri Shankaracharya Institute of Professional Management & Technology for providing laboratory facilities and financial assistance.

REFERENCES

D. Chaput, J. Assoc. Off. Anal. Chem., 1988, **71**, 542.

Patty F. A., (1962), " Industrial Hygeine and Toxicology " II$^{nd.}$ Vol. II , Interscience, London, pp. 2105-2169.

G Zweig, Analytical Methods for Pesticides and Plant Growth Regulators, Academic press, NewYork, 1964, **2**, 561.

R. Bravo, L. M. Caltabiano, C. Fernandez, K. D. Smith, M. Gallegos, R. D. Whitehead, G. Weerasekera, P. Restrepo, and A. M. Bishop, Journal of Chromatography B, 2005, **820**, 229-236.

J. F. Garcia Reyes, E. J. Liorent Martinez, P. Ortega Barrales, and A. Molina Diaz, Talanta, 2004, **64**, 742-749.

K. M. Appaiah, R. Ramkrishna, K. R. Subba Rao, K. V. Kagaraja, and O. P. Kapoor, J. Food Sci. Technol., 1982, 19, 211.

C. V. Rajeswari and P. R. Naidu., J. Food Sci. Technol., 1986, 23, 101.

S. K. Handa and A. K. Dikshit., J. Assoc. Off. Anal. Chem., 1978, **61**, 1513.

S. K. Handa , J. Assoc. Off. Anal. Chem., 1980, **63**, 200.

M. C. Quintero, M. Silva and D. P. Bendito, Analyst, 1989, 14, 497.

R. Kesari, J. V. Das and V. K. Gupta, J. Indian Chem. Soc. 1998, 75, 18.

D. Bose, P. Shivhare and V. K. Gupta, Journal of Planar Chromatography, 1994, **7**, 415-418.

K. N. Ramachandran and V. K. Gupta , Z Anal Chem.,1993, **346**, 457-459.

R. Kesari and V. K. Gupta, J. AOAC Intern, 1997, **80**, 388-393.

A. Fukec, K. Amenos and Lijril, Arch. Toxicol, 1996, **70**, 504 –512.

W. N. Aldridge, Analyst, 1994, **69**, 262 – 270.