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Facile and Sensitive Spectrophotometric Technique for the Determination of Carbofuran in its Formulations, Water and Grain Samples with Substituted Anilines

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Abstract: Methods are described for the determination of carbofuran in its formulations, in water and grain samples by the diazotization coupling spectrophotometric technique, using substituted anilines such as 4-bromoaniline, 4-methylaniline and 4-aminobenzaldehyde as the coupling agents. The orange red colour formed with 4-bromoaniline shows maximum absorption at 478 nm, yellow colour obtained with 4-methylaniline have maximum absorption at 465 nm whereas a red colour derivative formed with 4-aminobenzaldehyde shows $\lambda_{\max}$ at 472 nm. The methods could be successfully applied for the determination of carbofuran in its formulations, water and grain samples.

Key words: Carbofuran, substituted anilines, 4-bromoaniline, 4-methylaniline, 4-aminobenzaldehyde, spectrophotometry, water and grain samples

Introduction

Carbofuran (2,3 - dihydro-2,2-dimethyl-7-benzofuranyl methyl carbamate) is a systemic acaricide, insecticide and nematicide, applied to foliage to control insects and mites. Its formulations are commercially available under the trade names "Furadon", "Curraterr", and "Yaltox". It is found to be highly toxic to mammals¹ and wild birds²⁻³. As a result of extensive usage there is a possibility of contamination of environment in water, soil, food etc., by this

insecticide. Because of this importance several analytical procedures have been developed for the determination of carbofuran in its formulations and environmental samples, such as GC⁴⁻⁷, GLC⁸⁻⁹, HPLC¹⁰⁻¹³ and Spectrophotometric¹⁴⁻²³ methods for determination of carbofuran. The reported methods has several disadvantages like poor sensitivity, selectivity, less stability of colour derivatives and few are required solvents for the extraction of colour derivative. We report here three facile, simple and sensitive spectrophotometric methods for the analysis of carbofuran. Diazotized 4-bromoaniline, 4-methylaniline and 4-aminobenzaldehyde are being first time applied for the determination of carbofuran.

Experimental

Apparatus

An Elico – SL 159 UV VIS Spectrophotometer with 10 mm path length glass cells were used.

An Elico CL-110 digital pH meter, with combined glass electrode, was employed for *pH* measurement.

Reagents

- Carbofuran - Analytical and Technical grade sample (99.4%) supplied by Rallis India Ltd., Bangalore.
- Standard Carbofuran solution - 50 µg/ml each in methanol.
- Sodium nitrite, 0.5% (w/v) aqueous
- Sodium hydroxide, 2% (w/v) aqueous
- 4-bromoaniline, 4-methylaniline and 4-aminobenzaldehyde, 0.2% solutions were prepared by dissolving 0.2 g each of these reagents first in methanol and diluted to 100 ml with distilled water.

Procedure

Aliquots of standard carbofuran (0, 0.5, 1.0, 6.0 ml) pesticide solution were taken into a series of 25 ml standard flasks. To each one of these 2.5 ml of 2% NaOH, 2.4 ml of NaNO₂ and 2.0 ml of 4-bromoaniline was added. The solutions were made upto the mark with distilled water. The resulting orange red coloured derivative had a maximum absorption at 478 nm against a reagent blank and remain stable for more than 48 h. Absorbance values were recorded spectrophotometrically. The plot between concentration vs absorbance was linear over the composition studied. Similarly 4-methylaniline and 4-aminobenzaldehyde were used for the color development as described above.

Recovery of carbofuran from spiked grains

100 g of each grain (rice and wheat) were spiked with 200 ml chloroform for 5 min. The samples were fortified with different concentrations of insecticide in methanol and blended for 3 min. Chloroform was filtered into 250 ml standard flask through Whatman No.1 filter paper and the residue was retained. The residue was washed twice with 10 ml chloroform and blended for 2 min. Chloroform extracts were combined and made up to the mark. Known aliquots of the chloroform extracts were used for colour development after evaporating chloroform on a steam bath. The residue was dissolved in methanol and the amount was determined spectrophotometrically.

Determination of recovery in fortified water samples

After collection of the water samples, (minimum volume one litre) the *pH* values were adjusted below 4 with 20% sulphuric acid. Then fortified with different concentrations of insecticide dissolved in methanol. Next extract each sample in a 250 ml separating funnel with 100 ml of chloroform. The chloroform extract were transferred into a funnel and re-extracted the aqueous phase twice with further 50 ml of chloroform. The second chloroform extract was added to the first and washed the combined extract with 0.1 M potassium carbonate solution, then dried the chloroform by passing it through anhydrous sodium sulphate in a filter funnel and collected the extract in a 250 ml flask. The chloroform extract was reduced to 100 ml.

Results and Discussion

The optical characteristics, accuracy and precision data of the carbofuran with substituted anilines namely 4-bromoaniline, 4-methylaniline and 4-aminobenzaldehyde were shown in **Table 1**. The method was based on the alkaline (NaOH) hydrolysis of carbofuran to form carbofuran phenol. The carbofuran phenol was coupled with diazotized salts of 4-bromoaniline, 4-methylaniline and 4-aminobenzaldehyde to produce coloured derivatives. The colour derivatives are formed instantaneously and stable for longer period than the earlier methods. The Calibration curves for all the aromatic substituted amines followed Beer's law, which obeyed over the concentration range 0.5 to 16 µg/ml for 4-bromoaniline, 0.4–14 g/ml for 4-methylaniline and 0.2–10 µg/ml for 4-aminobenzaldehyde. The methods are free from the interference of the other pesticides.

Table 1. Optical characteristics, precision and accuracy of the method using diazotized reagents.

Optical parameters	4-Bromoaniline	4-Methylaniline	4-Aminobenzaldehyde
Concentration range (µg ml ⁻¹)	0.5 – 16.0	0.4 – 14.0	0.2 – 10.0
Color of the complex	Orange red	Yellow	Red
Stability (h)	48	36	30
$\lambda_{\max}$ (nm)	478	465	471
Limit of detection (µg ml ⁻¹)	0.645	0.564	0.355
Limit of quantification (µg ml ⁻¹)	3.065	2.678	1.355
Molar absorptivity (l mol ⁻¹ cm ⁻¹)	$5.361 \div 10^4$	$3.765 \div 10^4$	$6.698 \div 10^4$
Sandell's sensitivity (µg cm ⁻²)	0.0132	0.0114	0.0105
Regression equation	0.1874	0.4675	0.3254
Slope (a)			
Intercept (b)	0.0156	0.2541	0.0126
Correlation coefficient (r)	0.9998	0.9879	0.9997
Relative standard deviation ^b	1.234	0.8421	1.3561
Relative error	0.98	1.02	0.87

^a $y = ax + b$, where "x" is concentration of carbofuran in µg ml⁻¹.

^b n=10.

The recovery percentage of carbofuran in its formulations ranges between 98 to 99.2% using diazotized reagents and shown in **Table 2 – 4**. **Table 5 – 7** indicates the percentage recovery of carbofuran from fortified water (distilled and tap) samples in the range of 95 to 99.3% Percentage recovery of carbofuran from vegetable samples (potato and tomato) ranges between 96.1 to 99.3%. It is evident from above tables that the proposed methods are very simple, facile, sensitive, rapid and inexpensive than the reported methods in the literature. The performance of the present methods can be successfully compared with the reported methods.¹⁸

Table 2. Determination of carbofuran in insecticidal formulations using 4-bromoaniline as a coupling agent.

Sample No.	3% Granules	10% Formulations	50% Soluble powder	75% Wettable powder
1	2.91	9.95	49.89	74.89
2	2.95	9.94	49.85	74.95
3	2.91	9.96	49.75	74.89
4	2.95	9.97	49.75	74.96
5	2.89	9.96	49.89	74.87
6	2.98	9.93	49.95	74.50
7	2.91	9.90	49.68	74.85
8	2.94	9.94	49.50	74.75
Mean	2.93	9.94	48.84	73.67
SD	0.065	0.089	0.251	0.552

Table 3. Determination of carbofuran in insecticidal formulations using 4-methylaniline as a coupling agent.

Sample No.	3% Granules	10% Formulations	50% Soluble powder	75% Wettable powder
1	2.95	9.93	49.95	74.94
2	2.94	9.96	49.90	74.94
3	2.93	9.94	49.85	74.93
4	2.95	9.93	49.79	74.95
5	2.82	9.92	49.91	74.82
6	2.95	9.97	49.93	74.78
7	2.93	9.95	49.85	74.90
8	2.97	9.96	49.65	74.92
Mean	2.93	9.94	49.85	74.89
SD	0.043	0.016	0.090	0.058

Table 4. Determination of carbofuran in insecticidal formulations using 4-aminobenzaldehyde.

Sample No.	3% Granules	10% Formulations	50% Soluble powder	75% Wettable powder
1	2.95	9.97	49.90	74.90
2	2.97	9.92	49.89	74.85
3	2.93	9.93	49.78	74.94
4	2.95	9.95	49.90	74.93
5	2.94	9.94	49.95	74.90
6	2.92	9.93	49.92	74.75
7	2.90	9.93	49.75	74.85
8	2.93	9.95	49.65	74.85
Mean	2.9362	9.94	49.84	74.87
SD	0.019	0.046	0.097	0.056

Table 5. Recovery of carbofuran from fortified water sample using diazotized 4-bromoaniline as a coupling agent.

S.No.	Fortification level ($\mu\text{g ml}^{-1}$)	Distilled water		Tap water	
		Amount of recovery ($\mu\text{g ml}^{-1}$)	Recovery percentage	Amount of recovery ($\mu\text{g ml}^{-1}$)	Recovery percentage
1	0.5	0.49	98.0	0.48	96.0
2	1.0	0.99	99.0	0.98	98.0
3	1.5	1.48	98.6	1.45	96.6
4	2.0	1.97	98.5	1.95	97.5
5	2.5	2.48	99.2	2.45	98.0
6	3.0	2.94	98.0	2.91	97.0

Table 6. Recovery of carbofuran from fortified water sample using diazotized 4-methylaniline as a coupling agent.

S.No.	Fortification level ($\mu\text{g ml}^{-1}$)	Distilled water		Tap water	
		Amount of recovery ($\mu\text{g ml}^{-1}$)	Recovery percentage	Amount of recovery ($\mu\text{g ml}^{-1}$)	Recovery percentage
1	0.4	0.39	97.5	0.38	95.0
2	0.8	0.78	97.5	0.78	97.5
3	1.2	1.18	98.3	1.17	97.5
4	1.6	1.58	98.7	1.57	98.1
5	2.0	1.96	98.0	1.95	97.5
6	2.4	2.37	98.7	2.36	98.3

Table 7. Recovery of carbofuran from fortified water sample using diazotized 4-aminobenzaldehyde as a coupling agent.

S.No.	Fortification level ($\mu\text{g ml}^{-1}$)	Distilled water		Tap water	
		Amount of recovery ($\mu\text{g ml}^{-1}$)	Recovery percentage	Amount of recovery ($\mu\text{g ml}^{-1}$)	Recovery percentage
1	0.2	0.19	95.0	0.19	95.0
2	0.8	0.79	98.7	0.77	97.4
3	1.4	1.38	98.5	1.36	97.1
4	2.0	1.97	98.5	1.96	98.0
5	2.6	2.58	99.2	2.57	98.8
6	3.2	3.18	99.3	3.17	99.0

Hence, the proposed methods can be adopted for the routine analysis of the purity of the commercial formulations and environmental samples.

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