Rao, Y.Koteswara, K. Lokanath Swaroop, P.Chiranjeevi & B. Rangamannar "Spectrophotometric Determination Of Carbosulfan In Various Environments Using Novel Oxidative Coupling" in Martin J. Bunch, V. Madha Suresh and T. Vasantha Kumaran, eds., *Proceedings of the Third International Conference on Environment and Health, Chennai, India, 15-17 December, 2003*. Chennai: Department of Geography, University of Madras and Faculty of Environmental Studies, York University. Pages 400 – 403.

SPECTROPHOTOMETRIC DETERMINATION OF CARBOSULFAN IN VARIOUS ENVIRONMENTS USING NOVEL OXIDATIVE COUPLING

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Abstract

A novel method for the determination of carbosulfan in environmental samples using oxidative coupling is being described. The method comprises of alkaline hydrolysis of the pesticide and the resulting phenol is reacted with 2,4-di-methoxy aniline in presence of acidified $K_2Cr_20_7$. The dye product formed is extracted into $CHCl_3$ and the absorbance measured at 430nm.

Introduction

The pesticidal property of carbosulpfan, a member of carbamate familty, was reported in literature [1,2]. Bruce et al [3] studied the pesticidal properties of carbosulfan in water, soil and plants. The presence of pesticides was estimated in water and food grains using colorimetric technique [4,5]. These methods were based on the alkaline hydrolysis of the pesticide and coupling the phenolic product with various diazo compounds and the subsequent determination was in an aqueous medium. The methods have their inherent drawbacks due to lower sensitivity and also due to the reaction of the diazo reagent with other species present in the medium resulting in the instability of the coloured compound. The present investigation envisages the determination of carbosulfan, by coupling the phenoliic product formed by alkaline hydrolysis, with 2,4-dimethoxy aniline in presence of acidified $K_2Cr_20_7$ to yield colored cyanogen compound (Fig.1). The cynogen compound is then extracted into $CHCl_3$ and analysed by spectrophotometry. The method developed is applied for the determination of the pesticide in environmental samples.

Materials and methods

- 25% seed treat and 91.4% technical grade samples of carbosulfan supplied by M/s Rallis India Ltd., Bangalore, were used in the present work.
- Carbofuran, if generated by the reaction of carbosulfan with 0.1mL of 2N H_2S0_4 and 2% NaOH is used to hydrolyze carbofuran to yield corresponding phenol.
- 3g $K_2Cr_20_7$ was dissolved in 100mL distilled water.
- 4N H_2SO_4 was used in the course of the experiments.

- 2g of 2,4-dimethoxy aniline dissolved in distilled water and diluted to 100mL.
- Shimadzu UV-240 recording spectrophotometer was employed for the absorbance measurements.

Procedure

20mL of insecticide solution was taken in a 100mL beaker to which 5mL of 2% NaOH was added and allowed to stand for 5minutes for complete hydrolysis. The pH of the resulting solution is adjusted to 3.5 by sulphuric acid and ammonia solution. The solution was transferred into a 50mL separating funnel and allowed to stand for 2minutes and then 3mL of 2,4-dimethoxy aniline was added followed by 3mL of dichromate solution, and equilibrated. The orange colored dye formed was extracted into 10mL chloroform. The absorbance of the chloroform extract was measured at 472nm, against a reagent blank.

Formulations

Samples of formulations, equivalent to about 100µg of the active insecticide were treated with 25mL methanol and the supernatant solution was separated by decantation into a 100mL standard flask. The residue was repeatedly washed with 10mL portion of methanol. The combined methanol extracts were made up to 100mL. Analysis was carried out as described.

Water and food grain samples

Distilled and tap water, and food grains, wheat and rice, samples were fortified with 0.5 – 3.0 ppm of carbosulfan. These fortified samples were extracted independently with chloroform and the residues were dissolved in methanol and analyzed as per the method described.

Results and discussion

Carbosulfan on alkaline hydrolysis produces a phenolic compound, which on coupling with 2,4-dimethoxy aniline in the presence of oxidizing agent forms a colored cyanogen compound. The cyanogen compound extracted at pH 3.5, into chloroform exhibits absorbance maximum at 430nm.

The reaction of the phenolic compound with 2,4-dimethoxy aniline was studied in the pH range 1 – 6, and the absorabance of the colored cynogen was maximum at pH 3.5.

Among the solvents, benzene, MIBK, CCl_4 and chloroform, extraction of the colored dye was maximum into chloroform. Further, the dye solution was stable in this solvent for more than 2 days.

Beer's law was obeyed over the concentration range, 0.1 – 1.0 ppm of the pesticide. Calibration plot is presented in Fig.2.

The colored dye has a molar absorptivity of 3.09×10^5 $Lmol.^{-1}cm.^{-1}$. The absorption data of the dye is presented in Table.1.

Table – 1

Determination of carbosulfan with oxidative coupling with 2,4-dimethoxy aniline

1. Concentration range	0.1 – 1.0 ppm
2. ? $_{max}$	430 nm
3. Color stability	> 24 hrs.
4. Molar absorbivity	$3.09x10^5$L/mol.,cm.
5. Sandell's sensitivity	0.0235 µg/cm^2
6. Relative standard deviations (10 samples)	0.61
7. Correlation coefficient	0.9998
8. % Relative error	0.48

Data relating to the analysis of the pesticide in 25% seed treat and 91.4% technical formulations, 8 samples each, is presented in Table.2

Table – 2

Determination of carbosulfan – Insecticidal formulations

Sample Number	Labelled amount	
	25% seed treat	91.4% Technical
1	24.76	89.20
2	24.87	89.59
3	24.75	90.56
4	24.81	89.98
5	24.87	90.76
6	24.86	90.59
7	24.56	90.78
8	24.63	90.45
Average	24.56	90.24
SD	0.12	0.58

The percentage recoveries along with their fortification level are incorporated in the Table 3.

Table. 3

Recovery of carbosulfan from fortified water samples and grains

		Water samples		Grains	
Sample	Fortification	Tap water	Distilled water	Rice	Wheat
		Recovey			

number	level (ppm)	Amount (ppm)	%	Amount (ppm)	%	Amount (ppm)	%	Amount (ppm)	%
1	0.8	0.77	95.75	0.76	95.00	0.75	93.25	0.76	95.00
2	1.6	1.54	96.26	1.52	95.00	1.50	95.77	1.53	95.75
3	2.4	2.33	97.05	2.27	94.54	2.26	94.16	2.31	96.25
4	3.2	3.13	97.83	3.06	94.63	2.99	93.50	3.09	96.75
5	4.0	3.92	98.01	3.84	96.00	3.76	94.10	3.88	97.08
6	4.8	4.72	95.33	4.64	96.66	4.54	94.58	4.66	97.08

This method has the advantages over the earlier methods in that, the dye formation is instantaneous and the recoveries are better as they are in the range of 95.02 - 97.8%. Further, other ingredients of the sample do not interfere and the sensitivity of the method is fairly high.

The method developed can be adopted for the assay of commercial insecticide formulations and also environmental samples, water and food grains and serves as a complimentary technique.

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