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Analysis Of Fenitrothion Using Novel Reagent In Water Samples By Spectrophotometry

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ABSTRACT

A novel spectrophotometric method was developed for the determination of fenitrothion in its formulations, water samples with newly synthesised reagent. The method was based on the alkaline hydrolysis of fenitrothion pesticide and resultant hydrolysed product of fenitrothion was coupled with diazotised 4,4'-methylene-bis-o-hydroxy aniline in basic medium to give purple coloured product having λ_{\max} 552 nm. The formation of coloured derivative with the coupling agent is instantaneous and stable for 5 days. Beer's law was obeyed in the concentration range of 0.5-18.0 $\mu\text{g ml}^{-1}$. The proposed method is sensitive, easy to operate and permitted the determination of fenitrothion with a detection limits of 0.026 $\mu\text{g ml}^{-1}$. The experimental results indicate that the procedure can eliminate the fundamental interferences caused by other pesticides and non-target ions, which made this method is more sensitive and selective. Performance of the proposed method was compared statistically in terms Student's F and t-tests with the reported method. © 2007 Trade Science Inc. - INDIA

KEYWORDS

Fenitrothion;
4,4'-methylene - bis-o-
hydroxy aniline;
Diazotization method (DM);
Spectrophotometry;
Water samples.

INTRODUCTION

Fenitrothion(o,o-dimethyl-o,p-nitro-3-methylphenyl phosphorothionate) belongs to an organophosphorus pesticide, extensively applied on crops. In agricultural it is used for seed, dressing and granular formulations for the control of soil, pests and some foliar pests particularly effective against rice stem borers and with

some effect against red spider mites. The insecticide activity of Fenitrothion has been summarised by schmitt^[1]. It is slightly toxic to mammals^[2] and also wild birds^[3]. Fenitrothion is a contact and stomach poison and it destroys soil pests, coleoptera, cockroaches and other pests in buildings. Burt^[4] studied the biophysical aspects of nervous activity in relation to the mode of action of organophosphate,

which effect the transmission of nerve impulses from one cell to another. Due to indiscriminate application, it finds a way into surface water bodies, through agriculture runoff and municipal waste water systems by ingestion and inhalation. Finally, it reaches the human system. Many methods have been developed for the determination of fenitrothion^[5-15]. The spectrophotometric methods based on the using diazotization in the presence of oxidising agents and its metabolites by various alkaline hydrolysis of the pesticides have been determined^[16-21].

The present paper deal with a economical spectrophotometric method for the determination of fenitrothion in its formulations, water samples. Here authors successfully synthesised a new reagent, 4,4'-methylene-bis-o-hydroxy aniline for determination of fenitrothion by diazotization. The quantitative and qualitative estimation of the pesticide in their formulations, water (spiked) samples were determined.

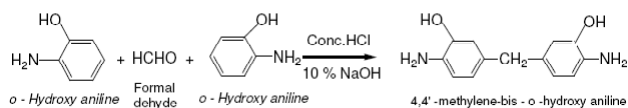
EXPERIMENTAL

Apparatus

A HITACHI U 2001 spectrophotometric with 1.0 cm matched quartz cells were used for all absorbance measurement. An Elico Li-29 model pH meter with combined glass electrode was used for pH measurements. All the chemicals and reagents used were of analytical reagent grade and double-distilled water was used through out experiments.

Synthesis of 4,4'-methylene-bis-o-hydroxy aniline

10.9 g (0.1 mol) of o-aminophenol was dissolved in 125 ml of water and 25 ml of 36.5 % hydrochloric acid at 50°C. The reaction mixture was then treated with 35 ml of 3 % aqueous formaldehyde solution at 60°C with stirring for 1 h and neutralised with 5M sodium hydroxide. The yellow coloured solid obtained was filtered, washed with hot water, dried and recrystallized from acetic acid (m.p., 135°C; yield, 87%), M.F : C₁₃H₁₄N₂O₂ and elemental analysis of Calculated(found): C-67.82 (67.80), H-6.08 (6.05), N-12.17(12.14), O-13.91(13.89) as shown in Scheme. 1a.^[22]



Scheme 1(a) : Synthesis of 4,4'-methylene-bis-o-hydroxyl aniline

Chemicals and Reagents

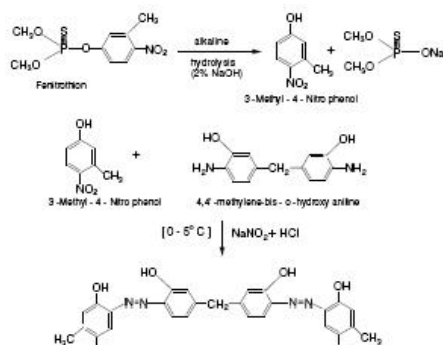
The technical grade samples of fenitrothion pesticide in the form of 50 % emulsifiable concentrate, 40% wettable powder and 5% dust were obtained from Bayer India Ltd., Mumbai, India. The reagents like sodium hydroxide (2%), sodium nitrate (0.2%), 1.5 N HCl were prepared. The solvents like methanol, chloroform, acetone were purified and employed for the present investigation. A stock solution (1 mg ml⁻¹) of fenitrothion (Rallis India Limited, Bangalore, India) was dissolved in methanol and working standard solution (10 µg ml⁻¹) was prepared by appropriate dilution with distilled water.

2% of 4,4'-methylene-bis-o-hydroxy aniline was prepared by dissolving 2 g of 4,4'-methylene-bis-o-hydroxy aniline in 20 ml of 5 M HCl and then made up to 100 ml standard flask with distilled water. An amount of 3.4 ml concentrated sulphuric acid is added to 250 ml distilled water in a 500 ml flask. 25 g of monopotassium dihydrogen phosphate is added to this, shaken until dissolution is complete and diluted to 500 ml for pH 8.0–10.0.

Determination of fenitrothion residues

The colored derivatives of fenitrothion were prepared by azo coupling reaction, 10 ml of fenitrothion standard solution was taken in a clean dry 100 ml beaker, 3 ml of 2% NaOH solution was added and kept for 15 min for complete hydrolysis to yield 3-Methyl-4-nitro phenol. Diazonium salt of 4,4'-methylene-bis-o-hydroxy aniline was prepared using 3 ml of 0.2 % NaNO₂ and 2 ml of 1.5 N HCl for coupling reaction at 0-5°C. The reaction mechanism of the purple colour compound was shown in Scheme 1b. The pH of the reaction was maintained between 8.0 to 10.0. The spectra for the above reaction was recorded in the UV-Vis regions as shown in figure 1 and optical, precision and accuracy data was shown in TABLE 1. Beer's law was obeyed over the range

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Scheme 1(b) : Reaction mechanism of the 4,4' - methylene - bis -o-hydroxyaniline with fenitrothion

from of 0.5-18.0 g ml⁻¹. This data was used for the analysis for water samples.

Determination of fenitrothion in its formulations

Fenitrothion in, 50% EC, 40% wettable powder, 5% dust and 98.7% technical grade were analysed using the aforesaid procedure by coupling with diazotised compound of 4,4'-methylene - bis - o - hydroxy aniline. Percentage recovery of the Fenitrothion in the above formulations was shown in TABLE.2.

Determination of fenitrothion in water samples

The water samples were spiked with concentrations in the ranges from 25.00–150.50 μg ml⁻¹ in methanol in this method under study which was given in the TABLE 3. The spiked water samples were extracted with chloroform. The combined extracts were washed with 0.1M potassium carbonate

TABLE 1: Optical characteristics, precision and accuracy of the diazotisation method

Optical Characteristics	4,4'-Methylene-bis-o-hydroxy aniline
Concentration range (μg ml ⁻¹)	0.5 – 18.0
λ _{max} (nm)	552
Color	Purple
Stability of the color (days)	5
Molar absorptivity (l mol ⁻¹ cm ⁻¹)	1.876 x 10 ⁴
Sandell's sensitivity (μg cm ⁻²)	0.026
Regression equation (Y = bx + a)	
Slope (b)	1.0400
Intercept (a)	0.0129
Standard deviation (S.D.) ^a	0.326
Correlation coefficient	0.9985
Relative error (%)	1.25

^a Calculation for three samples containing same amount of Fenitrothion, Where x is the concentration in mg ml⁻¹.

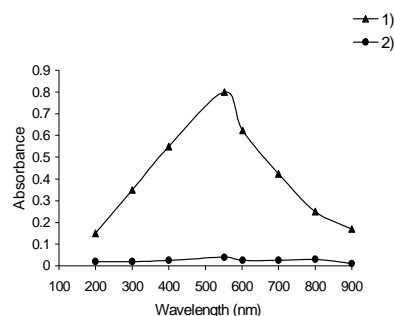


Figure 1: Absorption spectra of the fenitrothion. 1) Fenitrothion + 4,4'-methylene - bis - o - hydroxy aniline, 2) Reagent blank

solution to break any emulsion formed during the extraction and dried over anhydrous sodium sulphate. Finally, chloroform was evaporated to dryness on a steam bath and the residue was dissolved in methanol and the amount was determined using the procedures described earlier.

RESULTS AND DISCUSSIONS

TABLE 1. shows that the formation of colored product to the coupling reaction of the pesticide sample with the reagents under study are instantaneous and stable for a reasonable period of time indicates its advantage over reported method^[22]. Beer's law was obeyed in the concentration range from 0.5 to 18.0 μg ml⁻¹ indicating low Sandell son's sensitive values. The results obtained for Fenitrothion (TABLE.1) was reproducible with low relative standard deviations ranges from 0.326. The correlation coefficient values obtained for this reaction was very close to unity suggesting that the absorbance depend upon the concentration of the fenitrothion. The values obtained for the relative standard deviation and percentage error suggest that these new procedures offer a good precision and accuracy.

The data included in TABLE 2 shows that the active ingredient present in the formulations of fenitrothion can be successfully determined spec-

TABLE 2: Determination of fenitrothion in it's formulations

Formulation	4,4'-methylene-bis-o-hydroxy aniline
5 % dust	4.89 ± 0.02
40 % Wettable Powder	39.91 ± 0.06
50 % EC	49.95 ± 0.03

TABLE 3: Recovery of Fenitrothion residue from spiked water samples

Sample No.	4,4'-Methylene-bis-o-hydroxy aniline			Reported method ^[22]		
	Taken($\mu\text{g ml}^{-1}$)	Found($\mu\text{g l}^{-1}$)	Recovery \pm S.D ^a (%)	F-test	t-test	Recovery \pm S.D ^a (%)
1.	25.00	24.88	99.52 \pm 0.05	0.18	0.39	99.10 \pm 0.09
2.	50.25	50.15	99.80 \pm 0.09	0.88	0.54	99.60 \pm 0.08
3.	75.50	75.39	99.85 \pm 0.13	0.32	0.21	99.50 \pm 0.09
4.	100.00	99.89	99.89 \pm 0.03	0.35	0.29	99.70 \pm 0.06
5.	125.25	125.17	99.92 \pm 0.02	1.0	0.22	99.67 \pm 0.05
6.	150.50	150.37	99.87 \pm 0.10	0.11	0.17	99.80 \pm 0.08

^an = 7

trophotometrically using the new reagent. The results of these recoveries reveal that the amounts close to the manufacturer's specifications and these are favourably compared with the method reported in the literature^[22] were shown in TABLE 4. These observations suggested that the other ingredients present in these formulations do not interfere. Hence, the methods can be adopted as an additional method for a routine control of the purity of the commercial insecticide formulations. The data presented in TABLE 3 suggested that the percentage of pesticide recovery from fortified water sample range from 99.2–99.92%.

Analytical Application

The proposed method was applied to the determination of fenitrothion in spiked water samples. The results obtained was in good agreement with the reported method^[22] were given in TABLE 4.

CONCLUSION

The present method describes simple analytical procedure for the determination of fenitrothion in its formulations, fortified water samples. The

comparison of the proposed method with the other method was given in TABLE 4. The preparation of the coupling reagent 4,4'-methylene-bis-o-hydroxy aniline is simple and convenient to synthesis in any ordinary laboratory. The colour derivatives of the fenitrothion are more stable than the other reported method^[22].

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TABLE 4 : Comparison of fenitrothion in its formulations and water samples.

Samples	Fenitrothion added($\mu\text{g ml}^{-1}$)	Proposed method			Reported method ^[22]	
		Found($\mu\text{g ml}^{-1}$)	Recovery \pm S.D ^a (%)	F-test	t-test	Recovery \pm S.D ^a (%)
Formulation						
5 % dust	-	4.89	98.94 \pm 0.09	0.31	0.54	98.90 \pm 0.14
40 % wettable powder	-	39.91	99.32 \pm 0.16	0.16	0.62	99.28 \pm 0.13
50 % EC	-	49.95	98.81 \pm 0.15	0.25	0.83	98.77 \pm 0.07
Water samples ^b						
Spiked water	5.0	4.88	98.0 \pm 0.21	0.34	0.62	97.62 \pm 0.07
Natural water	5.0	4.96	99.2 \pm 0.15	0.20	0.36	97.50 \pm 0.182

Recovery in %, amounts of insecticide in μg ^a Avarage values for n=6.

^bAgricultural samples collected from S.V. Agricultural Research Institute, Tirupati, A.P.,India.

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