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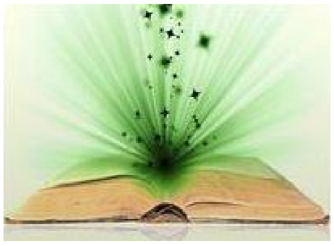

Spectrophotometric Determination of Ziram and Zineb in Commercial Samples and Food-Stuffs Using PAR-Naphthalene as Column Adsorbate for Preconcentration

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ABSTRACT

A procedure has been developed for the determination of zinc(II) bis (dimethyldithiocarbamate) (Ziram) and zinc(II) ethylenebisdithiocarbamate (Zineb) after preconcentration on a column using naphthalene-PAR as adsorbent. Ziram and Zineb are quantitatively retained on the column in the pH range 9.0- 12.5 and at a flow rate of 1-2 ml/min. The solid mass consisting of the Zn-PAR complex along with naphthalene is dissolved from the column with 5 ml of dimethylformamide (DMF). The absorbance is measured at 490 nm with a spectrophotometer against the reagent blank. Beer's law is obeyed over the concentration range 0.1- 15 µg of ziram and 0.1 -13 µg of zineb in 5 ml of the final DMF solution. Ten replicate determinations on a sample solution containing 40 µg of ziram and 36 µg of zineb gave a mean absorbance of 0.30 with a relative standard deviation 0.98%. The interference of various ions has been studied and the method has been employed to the determination of ziram and zineb in commercial samples and in various foodstuffs.

Keywords: Spectrophotometry, Ziram, Zineb, Commercial sample, PAR.

INTRODUCTION

A number of preconcentration techniques are available for the trace determination of metal complexes from aqueous samples. The simple one is the solvent extraction owing to the simplicity and its applications to both trace and macro amounts of the complexes. However solvent extraction is sometimes tedious and the concentration factor is influenced by the miscibility of the two phases. Nowadays, certain materials such as thiol cotton [1] silanized glass beads [2], c1s-bonded silica gel [3], amberlite XAD-4 resin [4], cellulose [5], green tea leaves [6] and polythioether foam [7] have been used as the adsorbent for the metal complexes. Most of these methods involve the tedious method of the column preparation. The desorption of the method takes place by the slow method of elution, thus making the method more time consuming.

Ziram (Zinc(II)bis(dimethyldithiocarbamate) and Zineb (Zinc(II)ethylenebisdithiocarbamate) are a well known dithiocarbamate fungicides, widely used against a variety of plant pathogenic fungicides. Several methods are currently available in the published literature for the determination of dithiocarbamate fungicides. In one such method ziram and zineb are determined on the basis of its decomposition by hot mineral acids to amine and carbon disulphide. This is then absorbed in methanolic potassium hydroxide solution and the potassium methyl xanthate thus formed is titrated iodometrically [8]. In another approach, carbon disulphide is absorbed in an ethanol solution containing copper (II) and an alkyl amine to form copper dialkyldithiocarbamate which can be determined photometrically [9-11]. Dithiocarbamates have also been determined in vegetable food-stuffs using high-performance liquid chromatography [12], extraction voltametry [13] and titrimetry [14]. Zineb is also determined by converting it into molybdenum [15] and copper [16] complexes. The extraction of the molybdenum complex is slow and complexation occurs in acidic medium. Dithiocarbamates can also be determined by other methods such as iodometry in anhydrous solvents [17,18], indirect titration with EDTA [19], polarography [20] and determination of the metallic component of the pesticide using different methods [21,22]. In another method determination of ferbam [23] using bathophenanthroline after adsorption onto microcrystalline naphthalene has a limitation that this was highly specific for ferbam as other dithiocarbamates do not form complex with bathophenanthroline. But this method may be applied for other dithiocarbamates. Mcleod et.al [24] determined dithiocarbamate fungicides by head-space gas chromatography of the carbon disulphide evolved in controlled conditions from foodstuffs and similar methods were also given by the Committee for Analytical Methods [25].

Ziram and Zineb reacts with PAR to form coloured complexes which are suitable for its spectrophotometric determination. Here, we present a relatively simple, rapid, sensitive and selective spectrophotometric method for the determination of ziram and Zineb after its preconcentration onto PAR - naphthalene adsorbate in the column and this can be determined subsequently using spectrophotometry at 490 nm.

MATERIALS AND METHODS

Equipment and Reagents: A digital pH meter and a Bausch and Lomb SP 20 Spectrophotometer was used. The chromatographic column was a glass tube of 150 mm in length and 7 mm I.D. It was fitted with quartz wool and then filled with the adsorbent to give a height of 1.5-2.0 cm. Ziram and Zineb were obtained from Sigma Aldrich Germany and were used as such. Stock solutions of pure (0.1%) ziram and zineb (1g/L) were prepared by dissolving 100 mg of the samples in 100 ml of 0.1 M sodium hydroxide and 100 ml of dimethyl sulfoxide solution respectively and diluted to 100 ml. PAR solution (0.02%) was prepared by dissolving 20 mg in water and diluted to 100 ml. Boric acid buffer (pH = 9.2) was prepared by mixing the solutions of boric acid (0.2 M) with equal volume of KCI (0.2M) and adjusting the pH of the resulting solution to 9.2 with 0.1 M NaOH.

Preparation of the column: Naphthalene (20 g) was dissolved in 40 ml of acetone and stirred at 35^{o}C and transferred to a beaker containing 1500 ml of distilled water and to this added 100 ml of 0.02% PAR solution and TX-100 10% (50 ml). The resulting solution was stirred continuously for 2 h and allowed to stand for another 2h. The supernatent solution was decanted off and the naphthalene was washed twice with distilled water and packed up to the height 1.5-2.0 c.m. into the column.

Preparation of the calibration curve: To a known volume of the sample solution containing 1-50 µg of ziram or 1-60 µg of zineb taken in a beaker, were added aqueous boric acid buffer solution (1.5 ml, pH = 9.2) and the volume was made upto 40 ml with distilled water. The column was packed upto 1.5-2.0 c.m. with the adsorbate material and preconditioned to pH 9.2 using boric acid buffer solution. Ziram/Zineb solution was passed through the column at the flow rate of 1-2 ml/min. The column material was dissolved in 5 ml of the DMF solution and the absorbance of the solution was measured at 490 nm against a reagent blank prepared under the similar conditions. (Fig.1)

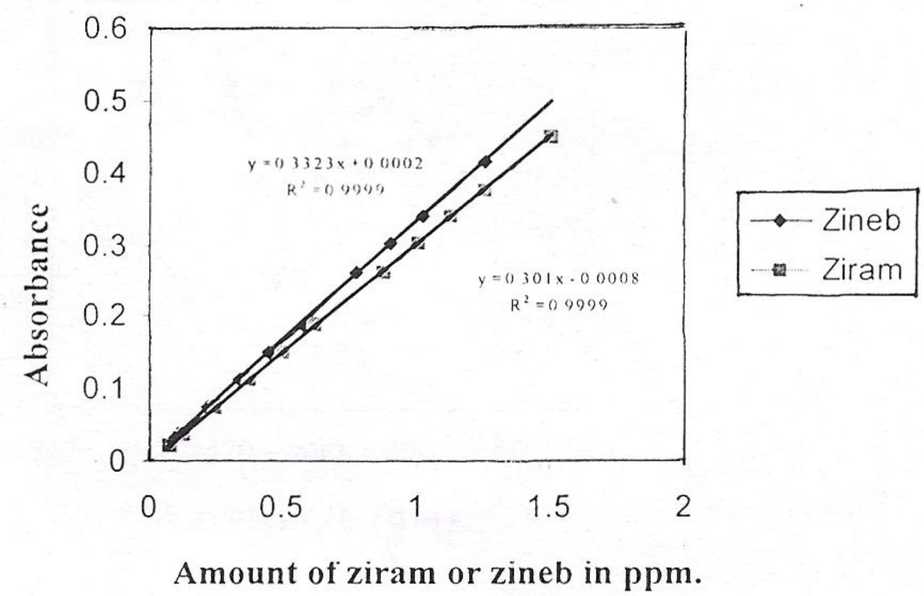

Fig. 1: Calibration curve for the determination of ziram or zineb using PAR

RESULTS AND DISCUSSION

Absorption spectra : The absorption spectra of Zn- PAR complex adsorbed onto the column was recorded against a reagent blank. The complex shows absorption maxima at 490 nm (Figure 2), so it was selected for all further measurements.

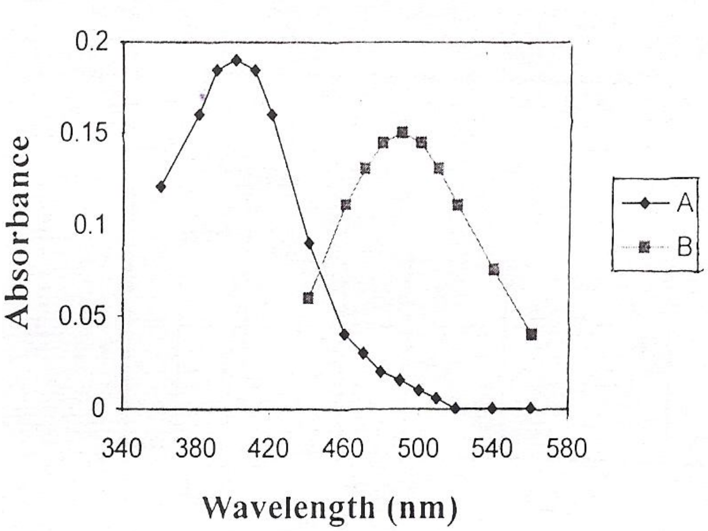

Fig.2: Absorbance curves of (A) PAR and its (B) zinc complex. Conditions: Ziram = 50μg or Zineb = 45μg, pH = 9.2, PAR (0.02%)=0.5 ml, Triton X-100=0.5 ml

Effect of standing time : The absorbance of the solution was measured at different intervals of time and it was observed that the absorbance of the solution remained practically constant for more than 24 h.

Effect of aqueous phase volume : It was observed that the adsorption was quantitative and complete when the aqueous phase volume was less than 1500 ml. More than this volume caused the decrease in absorbance.

Effect of flow rate : The flow rate was varied from 0.5 to 8 ml/min. it was found that the flow rate did not affect adsorption in this range. A flow rate of 1-2 ml/min was recommended in all experiments.

Choice of solvent : The complex is soluble in dimethylformamide, acetonitrile, dimethylsulphoxide and in chloroform, but it was insoluble in benzene, carbon tetrachloride etc. There was a little difference in the absorbance in these solvents and as DMF is cheaper than the other solvents so it was selected for the further study.

Choice of surfactant : CPB, CTAB, SLS and Triton X-100 were used for dissolving the complex. Triton X-100 was found to be most suitable because of providing a high absorbance and stability to the complex (Fig.3). The absorbance shows downward trend in CPB, CTAB and SLS solutions.

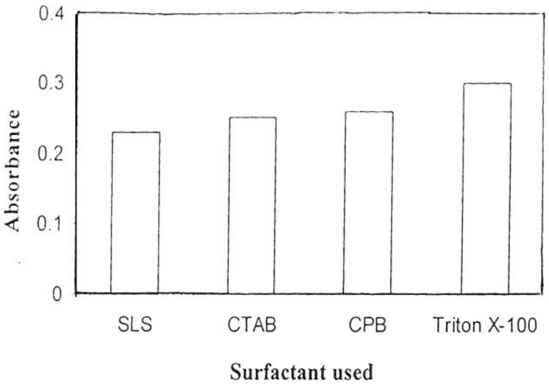

Fig. 3: Effect of surfactant on the absorbance of Zn-PAR complex

Effect of pH: The pH was varied from 5 to 15 , it was found that the absorbance first increases from 6 to 9 after that it remains constant till pH 13 after that it decreases. It did not affect adsorption in the range (10-12) (Fig.4). A pH range of (10-12) is optimum for the determination of Ziram and Zineb by above developed method.

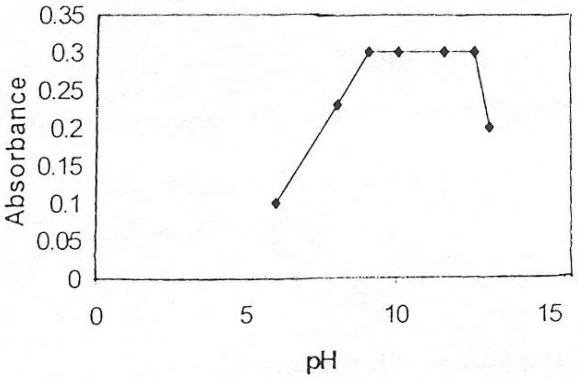

Fig. 4: Effect of pH on the absorbance of Zn-PAR complex.

Beer's law and Sensitivity : Under the conditions described above a calibration graph for the determination of ziram and zineb were linear over the concentration range 1-50 µg and 1-60 µg respectively per 40 ml of the final solution. Aliquots containing 50 µg were taken from the standard reference solution and analysed by the general procedure. Ten replicate determinations on these sample solutions of 40 µg of ziram and 36 µg of zineb gave a mean absorbance 0.30 with a relative standard deviation of 0.85 % and 0.98 % respectively. The molar absorptivity of the Zn – PAR complex formed from ziram or zineb (ε=A/ Lc; where ε is the molar absorptivity coefficient - the value of absorbance for 1 M concentration of a solute and L is the optical path) was calculated to be 9.2×10^4 L $mol^{-1}cm^{-1}$ and Sandells sensitivity [26] which represents the number of the micrograms of the determinand per ml of the final solution having an absorbance of 0.001 for a path length of 1 cm, were found to be 0.0033 and 0.0030 µg cm^{-2} for ziram and zineb respectively.

Interference due to metal ions : Sample solutions containing 40µg of ziram and 36µg of zineb and various amounts of different alkali metal salts or metal ions were prepared and the general procedure was applied. Of the following foriegn anions, (20 mg) did not interfere in the determination of ziram and zineb: bromide, acetate, chloride, nitrate, sulphate and oxalate. Of the following metal ions examined, 0.20 mg did not interfere in the determination of ziram or zineb: Pb(II), Bi(III), Fe(II) and Fe(III) (Table 1).

Table 1
Effect of Diverse Ions on the Determination of Ziram/Zineb

Anion	Tolerance limit (mg/40ml)	Cation	Tolerance limit (mg/40ml)
Fluoride	170	Cd(II)	0.025
Chloride	320	Th(IV)	0.9
Bromide	560	Ni(II)	0.25
Citrate	280	Sb(VI)	0.9
Sulphate	280	Se(VI)	11.8
Acetate	350	Co(II)	0.006
Thiocynate	8	V(V)	0.51
Metabisulphite	170	Pb(II)	I
Tartrate	80	Mn(II)[a]	I
Orthophosphate	0.3		
EDTA	I		

I=Interfered Strongly

a=Masked with 1.0 ml of 1M KBr solution.

Comparison of sensitivity: The present method is more sensitive than the earlier spectrophotometric methods. The present method is more sensitive than the carbon disulphide evolution methods. By this method it is possible to estimate 0.08 µg/ml of ziram and 0.09 µg/ml of zineb equivalent to 0.0398 µg/ml and 0.0497 µg/ml of evolved carbon disulfide of ziram and zineb respectively can be determined which is superior to reported methods (Table 2). The wide applicability and simplicity of this method makes it preferable to others.

Table 2 Comparison of Molar absorptivity with earlier methods

Fungicide	Molar absorptivity 1mol^{-1} cm^{-1}	Method	Remark	Reference
Ferbam	1.33x10^{4}	Molybdenum	Require acidic medium (4M H_2SO_4) and equilibrium time of 5 min.	[15,27,28]
Ziram	0.15x10^{4}			
Zineb	0.62x10^{4}			
Ferbam	1.46x10^{4}	Selenite	Other dithicr bamates interfere	[29]
Ziram	1.59x10^{4}			
Ferbam	5.3x104	Diphenylcar bazone	Maneb, zineb, ziram interference can be avoided using only masking agents	[30]
Ziram/zineb	8.3x10			
Ferbam	5.17x10^{4}	Phenylfluorone+CPB*	Selective and sensitive	[31]
Ziram/zineb	6.9x10^{4}			
Ziram/zineb	9.2x10^{4}	PAR	More sensitive	Present work

*CPB, cetylpyridinium bromide.

Determination of ziram and zineb in synthetic mixtures:

Different synthetic mixture of ziram and zineb in different proportions with other dithiocarbamates were prepared by mixing the solutions to give the required composition. Ziram and zineb in the mixtures was determined by the general procedure (Table 3).

Table 3 Determination of Ziram/Zineb in Synthetic Mixtures

Sample No.	Composition & percentage	Amount of Ziram/Zineb (mg)	
		Taken	Found[a]
Determination of Ziram			
1.	Ziram: 20 NaDDC[b]: 20 Vapam: 20 Maneb: 20 Nabam: 20	7.5 10.5 12.00	7.49 10.3 11.9
2.	Zirazm: 20	10.00	9.76
	Thiram: 15	15.00	14.91
	Nabam: 20	20.00	19.85
	Maneb: 20		
	Vapam: 25		
Determination of Zineb			
3.	Zineb: 25 Nabam: 20 Vapam: 15 Thiram: 10 Maneb: 30	7.5 10.00 12.00	7.48 9.93 12.00
4.	Zineb: 25 NaDDC[b]: 25 Vapam: 20 Thiram: 20 Maneb: 10	10.00 12.00 15.00	9.00 11.89 14.73

[a] Mean of five replicate determinations.
[b] Sodium diethyldithiocarbamate.

Determination of Ziram and zineb from fortified samples of grains (Rice/wheat):
The method was applied for the determination of ziram and zineb from fortified samples grains (rice/wheat). A known amount of ziram in 0.1 M sodium hydroxide and zineb in dimethylsulphoxide was crushed with 20 g of wheat grains with pestle and mortar and shaken mechanically with DMSO (100 ml) for one hour. The mixture was filtered and the residue in the

funnel was washed with DMSO (3x10 ml). The extracts were evaporated down to 2.0 ml on a water bath (70 - 90°C) and the remaining solvent was removed in a current of dry air at room temperature. The residue was dissolved in NaOH solution and determined by the general procedure. Untreated samples were taken as reference and the results indicated good recoveries in all cases. The results of the determinations are given in (Table 4).

Table 4 Determination of Ziram/Zineb from Fortified Samples

Sample	Crop	Ziram/Zineb added (µg)	Ziram/Zineb found (µg)	
			Present method	Rangaswamy et al.[16] method
Ziram	Rice	7.5	7.4	7.3
		10.00	11.10	9.70
		15.00	14.80	14.70
	Wheat	10.00	9.90	9.70
		15.00	14.90	14.90
		20.00	19.90	19.80
Zineb	Rice	10.00	9.80	9.60
		12.00	11.80	11.60
		15.00	14.90	14.80
	Wheat	10.00	9.80	9.60
		15.00	14.80	14.70
		20.00	19.90	19.80

[a] Amount of crop= 20 g. Each result is mean of five experiments.

Determination of Ziram and Zineb in a commercial sample:

The method was applied for the determination of ziram (ziram 27% S.C.) and zineb (Dithane Z-78) in a commercial sample. The formulated product sample solution was prepared as discussed earlier and determined by the general procedure. The results obtained by the present method are compared with those obtained by Rangaswamy et. al (16) method in which ziram and zineb were determined colorimetrically after reaction with cuprous chloride in 0.3 M hydrochloric acid to form a yellow copper complex and measuring the absorbance at 390 nm. The results of the analysis are given in (Table 5).

Table 5 Determination of Ziram/Zineb in Commercial Samples

Commercial Sample	Ziram/Zineb taken (µg)	Ziram/Zineb Found[a] (µg)	
		Present method	Rangaswamy et al.[16] method
Ziram 27% S.C	10.00	9.80	9.70
	15.00	14.90	14.70
Dithane Z-78	10.00	9.90	9.60
	20.00	19.90	19.80

[a] Each result is mean of five experiments.

APPLICATIONS

The method can be applicable for the determination of ziram and zineb in fortified rice and wheat sample grins and in commercial samples.

CONCLUSION

As Ziram (Zinc(II)bis(dimethyldithiocarbamate) and Zineb (Zinc(II)ethylenebisditiocarbamate) are widely used fungicides, there is always a need of a relatively simple, rapid, selective and more applicable method for their determination in different samples which has been achieved in this piece of research work.

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