

Development of new adsorbent chitin for column preconcentration and spectrophotometric trace determination of Ziram and Zineb in synthetic, commercial samples and food-stuffs

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Abstract

A procedure has been developed for the determination of zinc(II) bis(dimethylthiocarbamate) (Ziram) or zinc(II) ethylenebisdithiocarbamate (Zineb) present in a large volume of aqueous solution after preconcentration on a column using chitin–1-(2'pyridylazo)-2-naphthol (PAN) as adsorbent. Ziram/Zineb are quantitatively retained on the column as Zn–PAN complex in the pH range 9.0–11.0 and at a flow rate of 1–8 ml/min. Complex adsorbed on chitin was eluted from the column with dimethylformamide (DMF) and absorbance of the eluate was measured at 550 nm against a reagent blank. Beer's law is obeyed over the concentration range 5.3–55.8 µg of Ziram and 6.8–49.0 µg of Zineb in 25 ml of the final DMF solution. Ten replicate determinations on a sample solution containing 45.22 µg of Ziram or 40.86 µg of Zineb gave a mean absorbance of 0.30 with a relative standard deviation 1.6 and 1.8%, respectively. The interference of various ions has been studied. Many alkali metals and metal salts do not interfere. The method has been employed to the determination of Ziram and Zineb in commercial samples and in various foodstuffs and the results were compared with the earlier reported methods.

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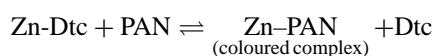
1. Introduction

Zinc(II) bis(dimethylthiocarbamate) (Ziram) and Zinc(II) ethylenebisdithiocarbamate (Zineb) are well known agricultural dithiocarbamate fungicides used on a wide variety of plant fungi and diseases. Various methods for the analysis of dithiocarbamates have been reviewed by Malik et al. [1]. A number of preconcentration techniques are available for the trace determination of metal complexes from aqueous samples. The simplest one is the solvent extraction which is applicable 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 activated carbon [2], green tea leaves [3], thiol cotton [4], selanized glass beads [5], silica gel [6], naphthalene [7,8], cellulose [9] and different resins [10–12] have been used as adsorbents for the determination of metal complexes.

Chitin is a natural polymer. It and its derivatives have been used for the removal and preconcentration of different metal ions [13–18].

Chemical reaction between metal part of pesticides with PAN to form coloured complexes have been reported which is the base for their spectrophotometric determination.



Here, we present a relatively simple, rapid, sensitive and selective spectrophotometric method for the determination of

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Ziram or Zineb after its preconcentration onto chitin–PAN adsorbate in the column as Zn–PAN complex which can be determined subsequently using spectrophotometry at 550 nm.

2. Experimental

2.1. Reagents

Ziram and Zineb solutions (0.1%) (Wilson Laboratories, Bombay) were prepared by dissolving 0.1 g each in 100 ml of dimethyl sulfoxide. A 0.01% PAN (Merck, GR) solution in methanol was prepared by dissolving 10 mg in solvent and diluting to 100 ml. Boric acid buffer (pH 9.0) was prepared by mixing the solutions of boric acid (0.2 M) with equal volume of KCl (0.2 M) and adjusting the pH of the resulting solution to 9 with 0.1 M NaOH. 0.001 M solution of alkali metal salt for anions (bromide, chloride, fluoride, acetate, etc.) and 1×10^{-4} M solution of different metal salts for cations (Pb(II), V(V), Th(IV), Sb(III), Ni(II), Co(II), Mo(VI), Fe(II), Fe(III), Hg(II), Cd(II), Cu(II) and Mn(II)) were used to study the interference of these ions. Solutions of dithiocarbamates were prepared by dissolving them in distilled water or in organic solvents. Synthetic samples were prepared by mixing solutions of the constituents to give the required composition.

2.2. Equipment

A Systronic UV–vis 118 double beam spectrophotometer with 1.0 cm matched quartz cells was used for recording spectra. A digital Century pH meter Cp 901 was used for pH measurement.

2.3. Preparation of the column

A glass tube of 12 mm i.d. with stopcock fitted with glass wool was used as a column for the preconcentration process. Chitin powder (SD Fine-Chem Ltd.) was used as adsorbent. It was washed successively with 1 M hydrochloric acid, distilled water and acetone, and then dried at 40 °C for 24 h before use. Chitin was loaded with PAN by constant stirring with glass rod for 15–20 min and added to the column.

2.4. Procedure

An aliquot of solution containing 5.3–55.8 μg of Ziram or 6.8–49.0 μg of Zineb was taken and 3 ml of buffer solution of pH 9.0 was added and solution was diluted to 50 ml with distilled water. Column loaded with chitin (4 g) and PAN (3 ml, 0.01%) was taken and conditioned to pH 9.0 with 3 ml of borate buffer with 1 ml min^{-1} . The sample solution was passed through the column at a flow rate of 5 ml min^{-1} . The Zinc–PAN complex adsorbed on the chitin was eluted with subsequent washing of column with dimethylformamide (DMF) solution and the total volume was made to 25 ml with

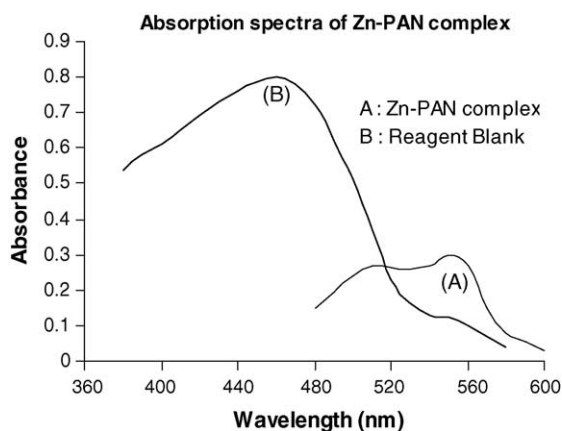


Fig. 1. Absorption spectra of Zinc–PAN complex. Rest of conditions were same as in Fig. 2.

DMF. The absorbance of the solution was measured at 550 nm against a reagent blank prepared under the similar conditions.

3. Results and discussion

3.1. Absorption spectra

The absorption spectrum of Zn–PAN complex in DMF recovered from the column was recorded against a reagent blank. The complex shows absorption maximum at 550 nm (Fig. 1), so it was selected for all further measurements.

3.2. Effect of pH

The effect of pH for the retention of zinc as Zn–PAN complex on adsorbent was studied by varying the pH of the solution with 1 M NaOH and 0.1 M HCl solutions. The retention of zinc as Zn–PAN complex was found to be a maximum in the pH range 9–11 (Fig. 2). In subsequent studies, 9.0 pH was maintained.

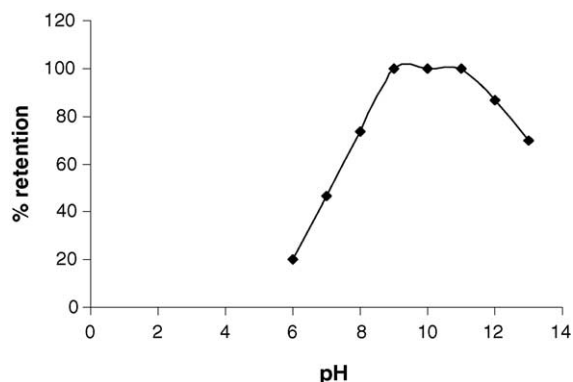


Fig. 2. Effect of pH on the retention of Zn–PAN complex. Preconcentration conditions: 45.22 μg of Ziram or 40.86 μg of Zineb, 3 ml buffer. Total volume of aqueous phase 50 ml, PAN (0.01%) 3 ml; flow rate 5 ml min^{-1} . Complex was eluted with DMF and total volume was made 25 ml with DMF; absorption maxima 550 nm.

3.3. Effect of reagent amount

The amount of reagent was varied for loading of 4 g of chitin. Zinc was quantitatively adsorbed on the adsorbent and absorbance was maximum and constant over the concentration range of 2–5 ml of the reagent. Therefore, 3 ml of 0.01% of the reagent was recommended in the present study.

3.4. Effect of flow rate

The flow rate was varied from 1 to 8 ml min⁻¹. It was found that the flow rate in this range did not affect adsorption of Zn as Zn–PAN complex. So, a flow rate of 5 ml min⁻¹ was adjusted.

3.5. Selection of eluting reagent

Solvents like acetone, dimethylformamide, acetonitrile, dimethylsulphoxide and chloroform were tried to elute the complex from chitin. DMF was found to be best, and thus it was used in the present work due to high solubility and stability of the complex in DMF (more than 15 h).

3.6. Effect of aqueous phase volume

The volume of aqueous phase was varied from 10 to 150 ml, keeping other variables constant. The retention was almost constant up to 100 ml of aqueous phase and 50 ml of aqueous phase was maintained for convenience in all experiments.

3.7. Beer's law and sensitivity

Under the conditions described above, calibration graphs for the determination of Ziram and Zineb were linear over the concentration range 5.3–55.8 and 6.8–49.0 µg, respectively, per 25 ml of the final solution. Ten replicate determinations on a sample solution containing 45.22 and 40.86 µg gave a mean absorbance of 0.30 with a relative standard deviation 1.6 and 1.8% for Ziram and Zineb, respectively. The molar absorptivity of the Zn–PAN complex formed was calculated

to be 5.06×10^4 l mol⁻¹ cm⁻¹ and Sandell's sensitivity was found to be 0.006 and 0.005 µg cm⁻² for Ziram and Zineb, respectively.

4. Determination of Ziram and Zineb in crops (rice/potatoes)

The method was applied to the determination of Ziram and Zineb in crops. A known amount of Ziram or Zineb in dimethylsulphoxide was crushed with 20 g of the crop with pestle and mortar and shaken mechanically with 100 ml of DMSO for 1 h. The mixture was filtered and the residue in the funnel was washed with DMSO (3 × 10 ml). The extracts were combined and evaporated 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 and determined by the general procedure. Untreated samples were taken as reference and the results indicated good recoveries in all cases. The results obtained by the present method are compared with those obtained by Malik et al. [19] method. The results of the analysis are given in Table 1.

4.1. Determination of Ziram and Zineb in commercial samples

The method was applied for the determination of Ziram and Zineb in commercial samples Ziram 27% S.C. and Dithane Z-78. The formulated product sample solution was prepared as discussed above and determined by the general procedure. The results obtained by the present method are compared with those obtained by Malik et al. [19] method. The results of the analysis are given in Table 2.

4.2. Determination of Ziram and Zineb in synthetic mixtures

Synthetic mixtures of Ziram and Zineb in different proportions with other dithiocarbamates were prepared by mixing the solutions to give the required composition. Ziram and

Table 1
Determination of Ziram and Zineb in grains and potatoes

Sample	Crop	Ziram/Zineb added (µg)	Ziram/Zineb found ^a (µg)			
			Present method	Recovery (%)	Malik et al. method [24]	Recovery (%)
Ziram	Grain	10.00	9.85	98.5	9.75	97.5
		20.00	19.95	99.75	19.92	99.6
	Potato	15.00	15.08	100.53	15.05	100.33
		20.00	20.00	100.00	20.03	100.15
Zineb	Grain	18.00	18.00	100.00	17.95	99.72
		25.00	24.93	99.72	24.88	99.52
	Potato	25.00	24.80	99.2	24.80	99.20
		30.00	29.60	98.66	29.50	98.33

^a Each result is mean of five experiments.

Table 2
Determination of Ziram and Zineb in commercial samples

Commercial samples	Ziram/Zineb taken (μg)	Ziram/Zineb found ^a (μg)			
		Present method	Recovery (%)	Malik et al. method [24]	Recovery (%)
Ziram 27% S.C	10.00	9.96	99.60	9.91	99.1
	15.00	14.88	99.20	14.95	99.66
	20.00	20.00	100.00	19.97	99.85
Dithane Z-78	10.00	10.01	100.10	10.00	100.00
	18.00	18.02	100.11	17.96	99.77
	22.00	22.12	100.54	22.10	100.45

^a Each result is mean of five experiments.

Table 3
Determination of Ziram or Zineb in synthetic mixtures

Composition and percentage of individual compounds in the synthetic mixture	Ziram/Zineb found ^a		Recovery (%)
	Taken (μg)	Found (μg)	
Ziram: 20	20.00	20.14	100.70
Thiram: 15			
NaDDC ^b :10			
Ferbam ^c : 10			
Zineb: 20	22.00	22.00	100.00
Ferbam ^c : 10			
Vapam: 10			
NaDDC ^b : 15			
Ziram: 15	25.00	25.10	100.40
Thiram: 10			
Vapam: 12			
Dibam: 10			

^a Each result is mean of five experiments.

^b Sodium dimethyldithiocarbamate.

^c Ferbam was masked with masked with 1.0 ml of 5% sodium fluoride solution.

Zineb in the mixture were determined by the general procedure and the results are given in Table 3.

5. Interferences

To evaluate the interference of diverse ions solutions containing 45.22 μg of Ziram or 40.86 μg of Zineb and various amounts of different alkali metal salts or metal ions were prepared and the analysed. The following ions did not interfere in the determination of 45.22 μg of Ziram or 40.86 μg of Zineb: acetate (15 mg), bromide (11 mg), chloride (3.5 mg), fluoride

(2 mg), citrate (20 mg), metabisulphite (8 mg), thiocyanate (0.2 mg), tartrate (20 mg) and EDTA (0.06 mg).

Of the metal ions examined, V(V) (0.047 mg), Sb(III) (0.15 mg), Th(IV) (0.35 mg), Mo(VI) (0.14 mg), Ni(II) (0.30 mg), Co(II) (0.009 mg) did not interfere. Fe(II), Fe(III) were masked with 1.0 ml of 5% sodium fluoride solution; Hg(II), Cu(II) were masked with 2.0 ml of 5% sodium citrate solution; and Mn(II) was successfully masked with 1.5 ml of 1% potassium bromide solution. Because the masking ion forms the stronger complex as compared to the PAN complex. Therefore, these were used as masking agents. It was also observed that there is no effect of the masking agent on the absorbance at these levels.

Dithiocarbamates, e.g., dibam (sodium dimethyldithiocarbamate), nabam (disodium ethylenebis(dithiocarbamate), vapam (sodium monomethyldithiocarbamate), sodium *N*-metylaniline carbodithioate did not interfere in the determination of Ziram and Zineb. Maneb was masked with 1.5 ml of 1% potassium bromide solution.

6. Conclusions

By this method, 0.0527 $\mu\text{g ml}^{-1}$ of Ziram or 0.0681 $\mu\text{g ml}^{-1}$ of Zineb can be preconcentrated. The present method is more sensitive than the carbon disulphide evolution methods [20–23]. According to the present method, a minimum of 0.0527 μg of Ziram and 0.0681 μg of Zineb, equivalent to 0.013 and 0.018 μg of evolved carbon disulphide, can be determined. The sensitivity of the present method is comparable to spectrophotometric methods [24]. As summarized in Table 4, the wide applicability and

Table 4
Comparison of molar absorptivity with earlier methods

Fungicide	Molar absorptivity ($1\text{ mol}^{-1}\text{ cm}^{-1}$)	Method	Remark	Reference
Ziram	0.15×10^4	Molybdenum	Require acidic medium ($4\text{MH}_2\text{SO}_4$) and equilibrium time of 5 min	[24]
Zineb	0.62×10^4			
Ziram	1.59×10^4	Selenite	Other dithiocarbamates interfere	[20]
Ziram/Zineb	8.3×10^4	Diphenylcarbazone	Maneb, Zineb Ziram interference can be avoided using masking agents	[25]
Ziram/Zineb	6.9×10^4	Phenylfluorone +CPB ^a	Selective and sensitive	[19]
Ziram/Zineb	5.06×10^4	PAN	Column concentration factor is quite high	Present work

^a CPB, cetylpyridinium bromide.

simplicity of this method makes it an excellent choice among available methods.

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