Column preconcentration and spectrophotometric trace determination of Ziram and Zineb using chitin as an adsorbate

Sanjiv Kumar Mehta, Ashok Kumar Malik, Usha Gupta & Baldev Singh

Department of Chemistry, Punjabi University, Patiala 147002, Punjab, India
Email: sanjivmehta21@rediffmail.com; malik_chem2002@yahoo.co.uk

A L J Rao*
School of Chemistry & Biochem, Thapar Institute of Engineering & Technology, Patiala 147 004, Punjab, India
Email: aljrao@rediffmail.com

Received 30 September 2004; revised 15 March 2005

A new method has been developed for the determination of Ziram and Zineb present in a large volume of aqueous solution by column preconcentration on a natural polymer, chitin loaded with 4-(2'-pyridylazo)resorcinol. Ziram/Zineb is quantitatively retained on the column and exchange the zinc present in them with PAR. An aliquot of solution containing 2.07-37.70 μg of Ziram or 2.24-31.45 μg of Zineb was taken and conditioned to pH 9.0 with PAR (3 ml 0.01%) and was added to the column. The solution was passed through the column at a flow rate of 5 ml min⁻¹. The Zn-PAR complex adsorbed on the chitin was eluted with 10 ml of DMF and the total volume was made to 25 ml with DMF. The absorbance of the solution was measured at 490 nm against a reagent blank prepared under the similar conditions.

Results and discussion
The Zn-PAR complex eluted from the column shows absorption maxima at 490 nm against a reagent blank. The adsorption was found to be maximum in the pH range 9-12.5. Therefore, in subsequent studies, 9.0 pH was maintained. Zinc was quantitatively adsorbed on the adsorbent over the

Experimental
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. 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 (S.D Fine-Chem Ltd) was used as adsorbent. It was washed successively with 1 M hydrochloric acid, distilled water and acetone, then dried at 40°C for 24 h before use. Chitin was loaded with PAR by constant stirring with glass rod for 15-20 minutes and added to the column. 0.1% Ziram and Zineb solutions were prepared in 100 ml of dimethyl sulfoxide. A solution of 0.01% of 4-(2'-pyridylazo)-resorcinol (PAR) was prepared in distilled water. Boric acid buffer (pH 9) was prepared by mixing the solution 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. Stock solutions of alkali metal salts and metal salts were prepared by dissolving suitable amounts in distilled water. All reagents used were of analytical reagent grade.

General procedure
An aliquot of solution containing 2.07-37.70 μg of Ziram or 2.24-31.45 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 adsorbent chitin (4 g) and PAR (3 ml 0.01%) was taken and conditioned to pH 9. The Ziram or Zineb solution was passed through the column at a flow rate of 5 ml min⁻¹. The Zn-PAR complex adsorbed on the chitin was eluted with 10 ml of DMF solution and the total volume was made to 25 ml with DMF. The absorbance of the solution was measured at 490 nm against a reagent blank prepared under the similar conditions.

IPC Code: Int. Cl. 7 G01N21/00

Ziram (zinc(II) bis(dimethylthiocarbamate) and Zineb (zinc(II) ethylenebis(dithiocarbamate)) are important dithiocarbamate fungicides. Various methods for the analysis of dithiocarbamates have been reviewed by Malik et al.¹. Chitin, a natural polymer and its derivatives have been used for the removal and preconcentration of different metal ions⁵⁻⁷. Chemical reaction between metal part of pesticides with PAR is the basis for their spectrophotometric determination.

Herein, we present a relatively simple, sensitive and selective spectrophotometric method for the determination of Ziram or Zineb after their adsorption on PAR-chitin in the column.
range 2-5 ml of 0.01% PAR solution of the reagent. Therefore, 3 ml of 0.01% of the reagent was recommended in the present study. The flow rate was varied from 1-10 ml min\(^{-1}\). It was found that a flow rate of 1-8 ml min\(^{-1}\) did not affect the retention of the complex. Hence, the flow rate was adjusted to 5 ml min\(^{-1}\). The volume of aqueous phase was varied from 10-150 ml. The retention was almost constant up to 100 ml of aqueous phase and therefore, 50 ml of aqueous phase was maintained for convenience in all experiments. The complex was more soluble and stable in DMF and hence this solvent was used for elution.

Under the conditions described above, calibration graphs for the determination of Ziram and Zineb were linear over the concentration range 2.07-37.7 and 2.24-31.45 \(\mu\)g, respectively, per 25 ml of the final solution. Ten replicate determinations on a sample solution containing 23.2 and 20.96 \(\mu\)g gave a mean absorbance of 0.28 with a relative standard deviation of 2.9% and 3.1% for Ziram and Zineb respectively. The molar absorptivity of the Zn-PAR complex formed was calculated to be 9.2x10\(^4\) \(\text{I} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}\) and Sandell's sensitivity was found to be 0.0033 and 0.0029 \(\mu\)g cm\(^{-2}\) for Ziram and Zineb, respectively.

Interference due to foreign ions

The following foreign anions (20 mg) did not interfere in the determination of Ziram (23.2 \(\mu\)g) and Zineb (20.96 \(\mu\)g): bromide, acetate, chloride, nitrate and sulphate. Oxalate and EDTA interfered strongly. The following metal ions (amount in mg given in parenthesis) did not interfere Mg(II), Ca(II) (40.0); Se(VI) (12.0); Sb(III) (0.87); Th(IV) (0.85); V(V) (0.50); Ni(II) (0.20); Cd(II) (0.018); Co(II) (0.005). Mn(II) interfered but was masked with 1.0 ml of 1 \(M\) KBr solution; while Fe(II) and Fe(III) were successfully masked with 1.0 ml of 5% sodium fluoride solution. Other dithiocarbamates, like dibam, nabam, vapam, sodium N-methylaniline carboxdithioate did not interfere in the determination of Ziram and Zineb. Maneb was masked with 1.0 ml of 1 \(M\) KBr solution.

Determination of Ziram and Zineb in fortified samples of wheat grains

The method was applied for the determination of Ziram and Zineb from fortified wheat grain samples. A known amount of Ziram or Zineb in dimethyl sulphoxide 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 and determined by the general procedure. Untreated samples were taken as reference and the results indicated 99.5±3.6% recovery in all cases.

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 in earlier and determined by the general procedure. The percentage purity of the samples was found 99.7±3.2%. The results obtained by the present method are compared with those obtained by Malik et al.

Acknowledgement

The financial assistance given by UGC, New Delhi, is gratefully acknowledged.

References