



Short Communication

Column Preconcentration and Spectrophotometric Trace Determination of Maneb in Food-Stuffs and Commercial Samples

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ABSTRACT

A new rapid, sensitive and selective method has been developed for the determination of maneb (manganese ethylene bis-dithiocarbamate) present in a large volume of aqueous solution after preconcentration on a column using chitin-4-(2'-pyridylazo)resorcinol (PAR) as adsorbent. Maneb is quantitatively retained on the column as Mn-PAR complex in the pH range 8.0-12.0 and at a flow rate of 1-5 mL min⁻¹. Complex adsorbed on chitin was eluted from the column with 10 mL of dimethylformamide (DMF) and absorbance of the eluate was measured at 500 nm against a reagent blank. Beer's law is obeyed over the concentration range 3.0-41.0 µg of Maneb in 25 mL of the final DMF solution. The reproducibility of the method was checked by ten replicate analysis of 30.0 µg of Maneb in 25 mL of final solution which gave a mean absorbance of 0.40 with a relative standard deviation 1.38%. The interference of various ions has been studied. The method has been employed for the determination of Maneb in crops and commercial samples.

Keywords: Maneb, spectrophotometric, PAR.

INTRODUCTION

Dithiocarbamates are widely used in agriculture as fungicide and in rubber industry as vulcanization accelerators and antioxidants. Maneb (manganese ethylenebisdithiocarbamate) is a common dithio carbamate (DTC) fungicide which is widely used on vegetable crops, in fields, orchards and vines, greenhouses, forestry and also for seed treatment [1]. Various methods [2-8] have been developed for determination of dithiocarbamate pesticides. Chitin is a natural polymer. It and its derivatives have been used for the removal and preconcentration of different metal ions [9-11].

We, present here a simple, sensitive and selective spectrophotometric method for the determination of Maneb after its adsorption on PAR-chitin in the column.

MATERIALS AND METHODS

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 and then dried at 40⁰ C for 24 h before use. Chitin was loaded with PAR by constant stirring with glass rod for 15-20 min and added to the column. 0.1% solution of Maneb was prepared in 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 solutions of boric acid (0.2M) with equal volume of KCl (0.2M) and adjusting the pH of the resulting solution to 9 with 0.1M NaOH. Stock solutions of alkali metal salts and metal salts were prepared by dissolving their suitable amounts in distilled water. All reagents used were of analytical reagent grade.

General Procedure: An aliquot of solution containing 3.0-41.0 µg of Maneb was taken and pH of the solution was adjusted to 9.0 with 3mL of buffer solution. The solution was diluted to 50 mL with distilled water. Column containing 4 g of chitin loaded with PAR (3 ml, 0.01%) was preconditioned to pH 9.0 using boric acid buffer and used for preconcentration process. The sample solution was passed through the column at a flow rate of 3 mL min⁻¹. The Mn-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 500 nm against a reagent blank prepared under the similar conditions.

RESULTS AND DISCUSSION

The Mn-PAR complex eluted from the column shows absorption maxima at 500 nm, against a reagent blank (Fig.1). The adsorption was found to be maximum in the pH range 8.0-12.0 (Fig.2). Therefore, in subsequent studies, 9.0pH was maintained. Manganese was quantitatively adsorbed on the adsorbent over the range 2-5 mL of 0.01% PAR solution of the reagent. Therefore, 3 mL of 0.01% of the reagent was used. The flow rate was varied from 1-5 mL min⁻¹. It was found that the flow rate in this range did not affect adsorption of Mn as Mn-PAR complex. So, a flow rate of 3 ml min⁻¹ was adjusted. 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 optimum conditions described above, calibration graph was linear over the concentration range 3.0-41.0 µg of Maneb in 25 mL of the final DMF solution. Ten replicate determinations on a sample solution containing 30.0 µg of Maneb gave a mean absorbance of 0.40 with a relative standard deviation 1.38%. The Molar absorptivity and Sandell's sensitivity were found to be 8.84 x 10⁴ l mol⁻¹ cm⁻¹ and 0.0030 µg cm⁻² respectively.

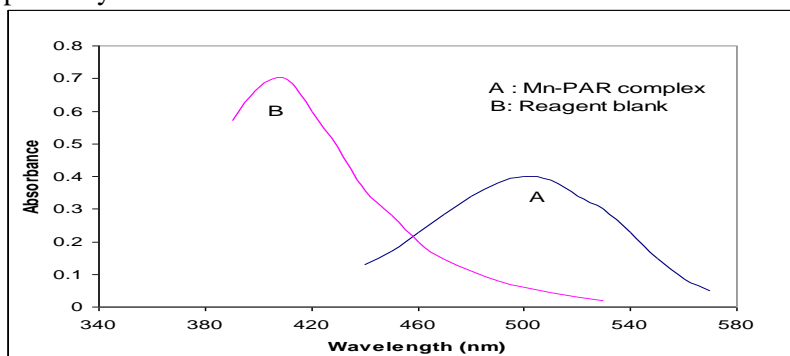


Fig. 1: Absorption spectra of Mn – PAR complex.

Conditions: maneb = 30.0 µg, pH = 9.0, chitin = 4 gm, PAR (0.01%) = 3.0 mL, Total volume = 25 mL.

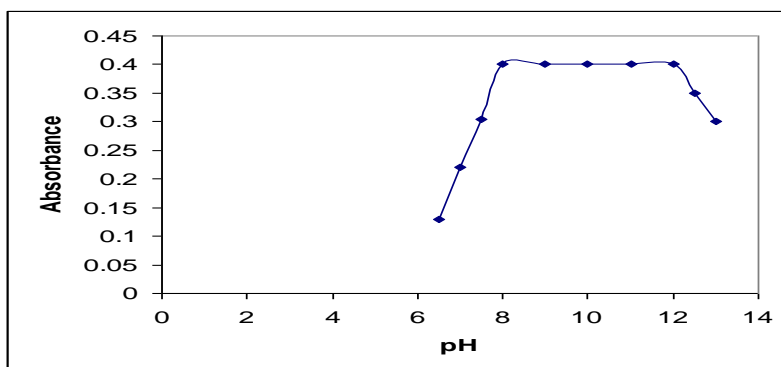


Fig. 2: Effect of pH on absorbance of Mn-PAR complex.

Interferences: Various foreign ions were examined for the interference studies in the determination of Maneb. The following ions did not interfere in the determination of 30.0 μg of Maneb: chloride (30 mg), bromide (10 mg), iodide (15 mg), fluoride (20 mg), citrate (30 mg), sulphate (35 mg), metabisulphite (15 mg) and thiocyanate (12 mg). EDTA interfered in the determination. The following metal ions, amount in mg given in parenthesis did not interfere Se(VI) (7.5 mg), Cd(II) (6.0 mg), Th(IV) (0.5 mg), V(V) (0.28 mg), Ni(II) (0.26 mg), Sb(III) (0.22 mg), Mo(IV) (0.19 mg), Co(II) (0.03 mg). Zn(II) interfered but was masked with 2.0 mL of 5% sodium citrate solution; while Fe(III) was successfully masked with 1.0 mL of 5% sodium fluoride solution.

Dithiocarbamates, e.g., dibam (sodium dimethyldithiocarbamate), nabam (disodium ethylene bisdithio carbamate), vapam (sodium monomethyldithiocarbamate), sodium N-metylaniline carbodithioate did not interfere in the determination. Ziram and Zineb interfere but could be masked with masked with 2.0 ml of 5% sodium citrate solution. Ferbam was masked with 1.0 mL of 5% sodium fluoride solution.

APPLICATIONS

Determination of mane b in crops: The method was applied for the determination of mane b in fortified samples of crops (wheat and potatoes). A known amount of mane b in DMSO was crushed with 20 gram of samples of crops and shaken mechanically with 50 ml of DMSO for one hour. The mixture was filtered and the residue in the funnel was washed with DMSO three times taking 10 ml every time. All the washings and filtrate were collected and the mane b content was determined by 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 1.

Table 1 : Determination of Maneb in crops

Crop	Amount added (μg)	Amount found (μg)	Recovery %
Wheat	20.0	19.70	98.50
	25.0	24.80	99.20
	30.0	29.50	98.33
Potato	20.0	19.70	98.50
	25.0	24.50	98.00
	30.0	29.30	97.66

Determination of maneb in commercial formulations: The method was applied for the determination of maneb in commercial samples (Dithane M-45 and Dithane M-22). The formulated product sample solution (0.1%) was prepared as discussed above and determined by general procedure. The results of the determinations are given in table 2.

Table 2: Determination of maneb in commercial samples

Commercial samples	Maneb amount (μg)		% recovery
	Taken	Found	
Dithane M-45	20.0	19.90	99.50
	25.0	25.0	100.0
	35.0	34.80	99.42
Dithane M-22	15.0	14.80	98.66
	20.0	19.90	99.50
	25.0	24.90	99.60

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