

A SENSITIVE SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF MANEB WITH 1-(2'-PYRIDYLAZO)-2-NAPHTHOL USING CHITIN AS AN ADSORBENT

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ABSTRACT

A sensitive spectrophotometric method has been developed for the determination of Maneb (manganese ethylenedisithiocarbamate) by using a natural polymer chitin loaded with 1-(2'-pyridylazo)-2-naphthol (PAN). Maneb is quantitatively retained on the column and exchange the manganese present in it with PAN in the pH range 7.0-11.0 at a flow rate of 1-5 ml/min. The complex adsorbed on chitin is eluted from the column with 10 ml of dimethylformamide (DMF) and the absorbance of complex was measured at 550 nm against a reagent blank. The molar absorptivity of the complex is $4.1 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity is $0.0064 \mu\text{g cm}^{-2}$, respectively. The reproducibility of the method was checked by five replicate analysis of $56.0 \mu\text{g}$ of mane in 25 ml of final solution which gave a mean absorbance of 0.35 with RSD 1.2%. The method can be applied for the determination of Maneb in synthetic, commercial samples and in various foodstuffs.

Keywords: Maneb, spectrophotometric, DMF, PAN

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INTRODUCTION

Dithiocarbamates are widely used in agriculture as fungicide and in rubber industry as vulcanization accelerators and antioxidants. Many methods¹⁻⁷ have been developed for the determination of dithiocarbamates in various commercial formulations. However, all these methods suffer from the following disadvantages (i) methods other than gas chromatography are indirect, time consuming and sensitivity is low, and (ii) gas chromatographic methods are sensitive, but suffers from a lack of selectivity since all dithiocarbamate pesticides evolve carbon disulfide on acid hydrolysis.

However, spectrophotometric methods have not these disadvantages and are sensitive, selective and no costly instruments are required. PAN as a chelating agent and chitin as an adsorbent have been selected in this work. Metal part of Maneb forms a colored complex with PAN which is the base of its spectrophotometric determination. Chitin, a natural polymer and its derivatives have been used for the removal and preconcentration of different metal ions⁸⁻¹⁰ and pesticides.¹¹⁻¹³

Here, we present a relatively simple, sensitive and selective spectrophotometric method for the determination of Maneb after its adsorption on PAN-chitin in the column as Mn-PAN complex which can be determined subsequently using spectrophotometrically at 550 nm.

EXPERIMENTAL

Reagents

Maneb was obtained from Riedel-de Haën (Pestanal®) and its 0.1% solution was prepared by dissolving 0.1 g in 100 ml of dimethylsulfoxide (DMSO). A 0.01% PAN (Merck, GR) solution in methanol was prepared by dissolving its 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 0.1M NaOH. Stock solutions for interference studies were prepared by dissolving 1% alkali metal salts and 0.1% of metal salts in double distilled water. 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.

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.

Preparation of the column

A glass tube of 12mm 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 1M 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.

Procedure

An aliquot of solution containing 8.0-90.0 µg of Maneb was taken and pH of the solution was maintained to 9.0 with 3 ml of buffer solution. The solution was diluted to 50 ml with distilled water. Column containing 4 g of chitin loaded with PAN (3 ml, 0.01%) was preconditioned to pH 9 with buffer solution. The sample solution was passed through the column at a flow rate of 3 ml min⁻¹. The Mn-PAN 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 550 nm against a reagent blank prepared under the similar conditions.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of Mn-PAN complex in DMF was recorded against a reagent blank prepared under similar conditions. The complex shows absorption maximum at 550 nm (Fig.-1), so it was selected for all further measurements.

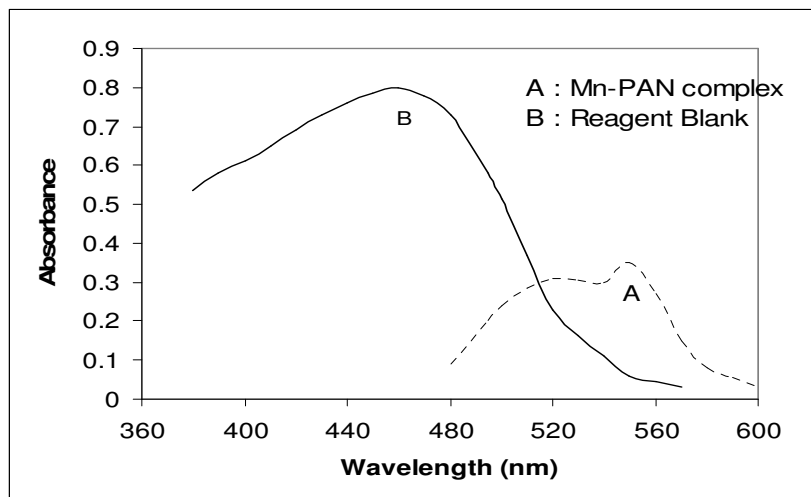


Fig.-1: Absorption spectra of Mn-PAN complex.

(Conditions: maneb = 56.0 µg, pH = 9.0, chitin = 4 gm, PAN (0.01%) = 3.0 ml, Total volume = 25 ml.)

Effect of pH

The effect of pH for the retention of manganese as Mn-PAN complex on adsorbent was studied by varying the pH of the solution with 1M NaOH and 0.1M HCl solutions. The retention of manganese as Mn-PAN complex was found to be a maximum in the pH range 7-11 (Fig.-2). However, in subsequent studies, pH was maintained to 9.0.

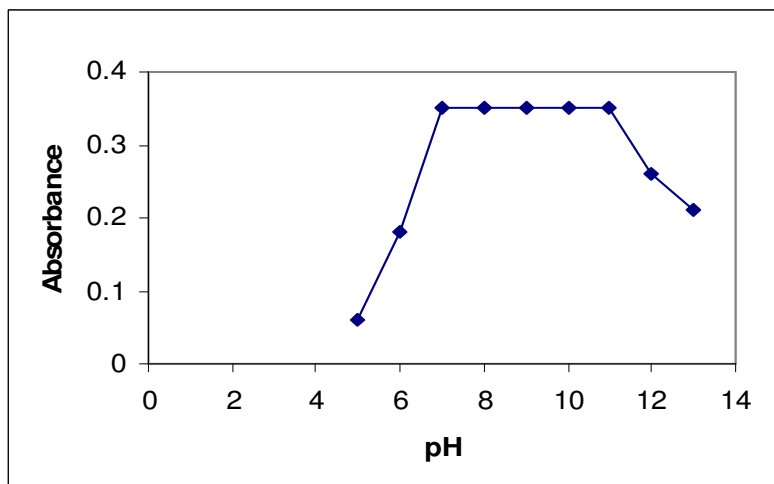


Fig.-2: Effect of pH on absorbance of Mn-PAN complex.

Effect of reagent amount

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

Effect of flow rate

The flow rate was varied from 1 to 10 ml min⁻¹. It was found that absorbance was constant and maximum when the flow rate was 1-5 ml min⁻¹. So, a flow rate of 3 ml min⁻¹ was adjusted.

Selection of eluting reagent

Solvents like acetone, dimethylformamide, acetonitrile, dimethylsulphoxide and chloroform were used to elute the complex from chitin. DMF was found to be better solvent because of higher solubility and stability of complex in it (more than 15 h). Hence it was used for the elution of complex.

Table-1: Determination of dithiocarbamates from crops

Dithiocarbamate	Crop ^a	Amount added(μ g)	Amount found ^b (μ g)	% Recovery
Maneb	Wheat	20.0	19.75	98.75
		30.0	29.50	98.33
	Cabbage	20.0	19.60	98.00
		30.0	29.30	97.66

a. amount of crop-20 g

b. each result is a mean of five replicate determinations.

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.

Beer's law and sensitivity

Under the optimum conditions described above, calibration curve for the determination of maneb was linear over the concentration range 8.0-90.0 μ g, per 25 ml of the final solution. Five replicate determinations on a sample solution containing 56.0 μ g gave a mean absorbance of 0.35 with a relative

standard deviation 1.2%. The molar absorptivity and Sandell's sensitivity were found to be $4.10 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.0064 \mu\text{g cm}^{-2}$.

Table-2: Determination of maneb in commercial samples

Maneb	Maneb added (μg)	Maneb* found (μg)	% Recovery
DithaneM-45	20.0	19.8	99.00
	40.0	39.5	98.75
	80.0	79.5	99.37
DithaneM-22	20.0	19.5	97.5
	30.0	29.8	99.33
	50.0	49.5	99.00

* Each result is a mean of five replicate determinations.

Interference due to foreign ions

To evaluate the interference of diverse ions solutions containing $56.0 \mu\text{g}$ of Maneb and various amounts of different alkali metal salts or metal ions were prepared and the analyzed. The following ions did not interfere in the determination of $56.0 \mu\text{g}$ of Maneb: chloride (50 mg), citrate (45 mg), sulphate (40 mg), fluoride (30 mg), metabisulphite (5 mg) and thiocyanate (3 mg). EDTA interfered strongly.

Of the metal ions examined (amount in μg given in parenthesis) did not interfere V (V) (260), Ni (II) (110), Mo (VI) (25) and Co (II) (20). Zn(II) interfered but was masked with 2.0 ml of 5% sodium citrate solution; and Fe (III) was successfully masked with 1.0 ml of 5% sodium fluoride solution. Other dithiocarbamates, like dibam, nabam, vapam, sodium N-methylaniline carbodithioate did not interfere in the determination of Maneb. Ziram and zineb interfere but could be masked with 2.0 ml of 5% sodium citrate solution. Ferbam was masked with 1.0 ml of 5% sodium fluoride solution.

Applications

The present method has been applied for the determination of maneb in crops and commercial samples.

Determination of maneb in crops

The method was applied for the determination of maneb in fortified samples of crops (potatoes and cabbage). A known amount of maneb in DMSO was crushed with 20 gram of vegetable samples (potatoes and cabbage) and shaken mechanically with DMSO (50 ml) 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 maneb 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.

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.

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