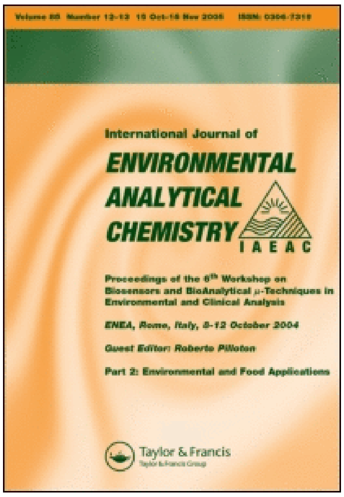

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A NEW SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF MANEB IN COMMERCIAL FORMULATIONS

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A new rapid, selective and sensitive method has been developed for the determination of maneb using pyrocatechol-violet(PV) as chelating reagent in the pH range of 7.5–11.0 in the presence of CTAB producing a complex which shows maximum absorption at 640 nm. Working range of the method is 0.2–3.0 µg ml^{-1} maneb (manganese ethylenebisdithiocarbamate). The molar absorptivity of the color system is 79600 l mol^{-1} cm^{-1} and Sandell's sensitivity is 0.0033 µg cm^{-2}. The reproducibility of the method has been checked by the 10 replicate analysis of 15 µg of maneb in 10 ml of solution. The method is quite sensitive and has been applied for the determination of maneb in various commercial samples, crops, grains and synthetic samples.

Keywords: Maneb, pyrocatechol violet, cetyltrimethyl ammonium bromide, sensitizers, surfactants

INTRODUCTION

Maneb (manganese ethylenebisdithiocarbamate) is a well known dithiocarbamate fungicide widely used against a variety of plant pathogenic fungi. Maneb is not a systematic fungicide rather it is a protective fungicide and, therefore, act upon damaging by surface deposits. So, the residues of undecomposed fungicides are found on fruit, fodder and food. As these items are consumed by man and animals as part of their normal diet, they can create chronic damage to health unless the quantities of such pesticides are kept in close check, their persistent as well as cumulative action could be hazardous. Dithiocarbamates, the derivatives of dithiocarbamic acids are formed as their substituted ammonium salts by the

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reaction of CS_2 with a primary or secondary amine in alcoholic or aqueous solution. Heavy metal salts of dithiocarbamates are prepared by the addition of solution of the heavy metal salt solution to a solution of ammonium or alkali metal salt of the dithiocarbamic acid[1]. Reported values of the oral LD_{50} mg kg^{-1} and ADI mg kg^{-1} of Maneb are 6750 and 0.0005 respectively[2–3]. Although most countries are still at an early stage in the development of residue monitoring, FAO strongly recommends that as many individual countries as possible should provide information on all relevant date to help the joint FAO-WHO meeting of experts on pesticide residues to make recommendations. Methods used for the determination of dithiocarbamate fungicides are reviewed by Malik and Faubel[4]. Most of the methods for the determination of maneb are based on 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[5]. Ahmad et. al.[6] have reported an improved head space gas liquid chromatographic procedure for the determination of dithiocarbamate residues, Capillary electrophoresis was used by Rossi and Rotilio [7] for the qualitative and quantitative analysis of different carbamate, thiocarbamate and dithiocarbamate classes of pesticides. HPLC was used to determine dithiocarbamate fungicides in vegetable food stuffs.

Amongst the spectrophotometric methods which are based on the reaction with the metal part of the pesticide molecule with organic reagents are of considerable importance. Unfortunately, such methods are very few and are not reported in the literature. It is observed that most of the reported methods suffer from the following disadvantages:

a. Methods other than gas chromatography are indirect, time consuming and of low sensitivity.

b. Gas chromatographic methods are sensitive but suffer from lack of the selectivity since all dithiocarbamate pesticides evolve carbon disulphide on acid hydrolysis.

Here we present a simple, less time consuming, sensitive and selective spectrophotometric method for the determination of maneb using pyrocatechol violet (PV) as complexing agent and solubilising the chelate (Mn-PV) in cetyltrimethyl ammonium bromide (CTAB) which act both as solubilising as well as stabilising agent and as sensitizer due to its micellar action.

EXPERIMENTAL

Equipment,

A digital ECIL (Electronic Corporation of India Limited) pH meter and an SP-20 Spectronic spectrophotometer were used for pH and absorbance measurements respectively.

Reagents

All chemicals used were of Anal R grade and double distilled water was used throughout.

Maneb Solution

Maneb was prepared by adding a solution of manganese(II) to a solution of disodium ethylenebisdithiocar-bamte (Wilson Laboratories, Bombay) and its purity was checked by elemental analysis and standardized by complexometric titration.[8] A 0.1% solution of maneb was prepared by dissolving 100 mg in 100 ml of dimethylsulphoxide (Merck, GR). Working solution was prepared by appropriate dilution of the stock solution.

Pyrocatechol Violet

Pyrocatechol violet (PV) (Loba, GR) solution was prepared by dissolving 20 mg of PV in 100 ml of distilled water.

CTAB (Loba, GR) solution (0.25%) was prepared by dissolving its 250 mg in 100 ml of water.

Borate buffer solution was prepared by mixing solutions of Boric acid (Glaxo, Anal R) and Potassium chloride (Glaxo, Anal R) (0.2M, 100ml each) and adjusting the pH to 9.2 with 0.2 M sodium hydroxide (Glaxo, Anal R) and diltuing to 500 ml. Stock solutions of various salts were prepared by dissolving them in water.

General Procedure

To an aliquot of maneb solution (2–30 μg), 2 ml of boric acid buffer solution, 0.6 ml of PV and 2.0 ml of CTAB solution were added and the volume was made

10 ml with water. The absorbance of the solution was measured at 640 nm against the reagent blank prepared under the similar conditions.

RESULTS AND DISCUSSION

Absorption Spectra of the pyrocatechol violet and metal-PV complexes were recorded against reagent blank. A bathochromic shift in the Spectrum of the reagent was observed in the presence of cationic surfactant CTAB. The manganese-PV complex shows an absorption maximum at 640 nm and it was selected for further measurements (Figure 1). It was observed that the absorbance was constant and maximum in the pH range 7.5–11.0 with 0.6 ml of 0.02% PV reagent and 2 ml of CTAB (0.25%), (Figure 2). CTAB acts both as solubliser and sensitizer for the metal chelate.

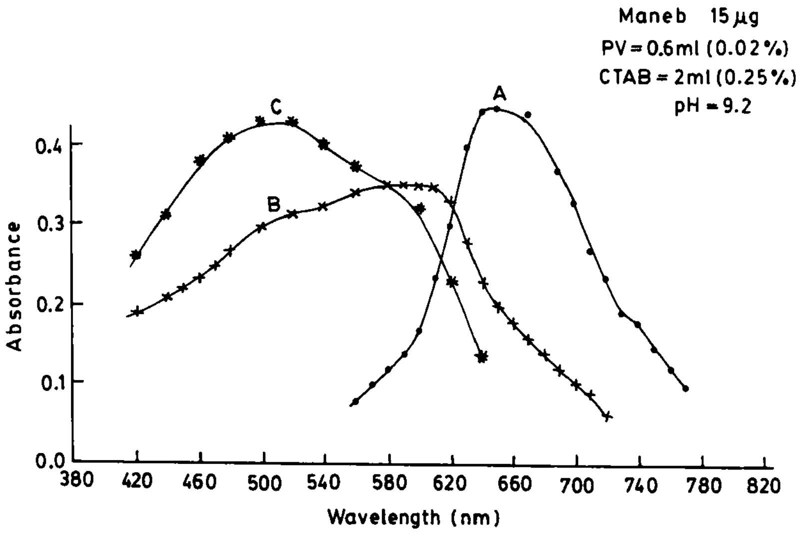

FIGURE 1 Absorption spectra of PV and its manganese complex in aqueous solution, curve A. Mn-PV in the presence of CTAB. curve B:PV in the presence of CTAB. curve C:PV in the absence of CTAB [Maneb 15 µg; PV=0.6 ml (0.02%) CTAB = 2 ml (0.25%) pH = 9.2]

Under the conditions described above a calibration graph for the determination of maneb was linear over the concentration range 0.2–3.0 µg ml^{-1} of the final solution. Aliquots containing 1.5 µg ml^{-1} were taken from the standard reference solution and analysed by the general procedure. Ten replicate determinations on

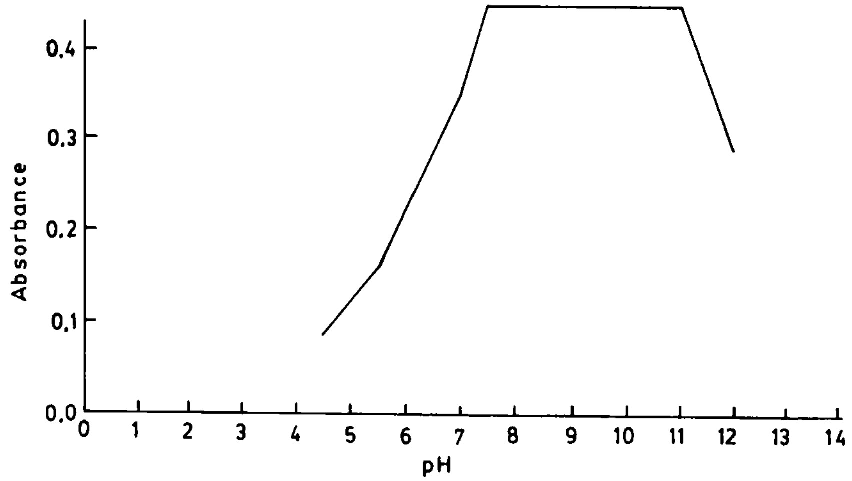

FIGURE 2 Effect of pH on the absorbance of Mn-PV complex (Rest of the conditions same as in Figure 1.)

these sample solutions of maneb gave a mean absorbance of 0.45 with a relative standard deviation 0.6%. The molar absorptivity coefficient was calculated to be 79600 l mol^{-1} cm^{-1} and Sandell's sensitivity[9] which represents the number of the micrograms of the analyte per 10 ml of the final solution having an absorbance of 0.001 for a path length of 1 cm, was found to be 0.0033 µg cm^{-2}.

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 dimethylsulphoxide was crushed with 10 gram of vegetable (cabbage and potatoes) were shaken mechanically with dimethylsulphoxide (50 ml) for one hour. The mixture was filtered and the residue in the funnel was washed with dimethylsulphoxide three times taking 10 ml every time. All the washings and filtrate were collected and the maneb content was 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 I.

TABLE I Determination of maneb in crops

Crop	*Maneb* μg	*Maneb found by present method*	*RSD(%)*	*Maneb found by Rao et al[10] method*	*RSD(%)*
Potatoes	10	9.50	2.3	9.4	2.4
	20	19.95	2.1	19.3	22
	30	30.00	1.9	29.5	2.0
Cabbage	10	10.0	2.3	9.4	2.4
	20	18.97	2.1	19.3	2.2
	30	29.99	1.9	29.5	2.0

Amount of crop = 10 g; Each result is average of five experiments.

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 the general procedure. The results obtained by the present method are compared with those obtained by the method of Rao et.al. [10] The results of the determinations are given in Table II.

TABLE II Determination of maneb in commercial samples

Maneb	*Maneb present (μg)*	*Maneb found by present method (μg)*	*RSD (%)*	*Maneb found by Rao et al[10] method (μg)*	*RSD (%)*
Dithane	10	9.99	1.8	9.96	2.2
M-45	20	20.00	1.6	19.80	2.1
	30	30.10	1.4	30.10	1.9
Dithane	10	9.90	1.8	9.80	2.2
M-22	20	19.98	1.6	19.81	2.1
	30	29.99	1.4	29.90	1.9

Each result is a mean of five experiments.

Interferences

Sample soluitons (10 ml) containing 15 μg of maneb and various amounts of different alkali metal salts or metal ions were prepared and the maneb content was determind by the general procedure. The tolerance limit of the diverse ions is given in Table III.

TABLE III Tolerance limit for diverse ions

Anion	*Tolerance limit(mg)*	*Cation*	*Tolerance limit(mg)*
Chloride	11	Co^{2+}	0.53
Bromide	32	Cu^{2+}	0.007
Fluoride	9.0	Mo^{6+}	0.14
Iodide	31	Se^{6+}	2.0
Citrate	0.05	Bi^{3+}	2.0
Acetate	6.0	Mn^{2+}	–
Thiocyanate	9.0	Ni^{2+}	0.05
Sulphate	9.0	$^{a}Fe^{3+}$	5.0
o-Phosphate	0.54	$^{b}Zn^{2+}$	5.0
Tartrate	2.0		
Oxalate	2.0		
EDTA interfered strongly			

a. Masked with 2.0 ml of 5% NaF solution,
b. Masked with 2.0 ml of 5% KCN Solution.

Interference due to other dithiocarbamates such as disodium ethylenebisdithiocarbamate (nabam), zinc ethylenebisdithiocarbamate (zineb), tetramethylthiuramdisulphide (thiram), ferric dimethyldithiocarbamate (ferbam), zinc dimethyldithiocarbamate (ziram), sodium diethyldithiocarbamate and xanthates (n-butyl, isopropyl and ethyl) were studied. Of the above mentioned dithiocarbamtes only zineb and ferbam interfered in the determination of maneb and these were masked with 2.0 ml of 5% KCN and 2.0 ml of 5% NaF respectively.

CONCLUSIONS

The present method is more selective than the earlier reported spectrophotometric methods as it permits safely the determination of maneb in the presence of nabam, zineb, vapam, dibam and sodium diethyldithiocarbamate without any interference, whereas this was not possible by the earlier reported spectrophotometric methods. A comparison of the molar absorptivity with other methods is given in Table IV. The present method is more sensitive than the carbon disulphide evolution methods as reported by Lowen (10 μg of CS_2) and Cullen (20 μg of CS_2) where as in the present method 1.64 μg if CS_2 can be determined. The wide applicability, simplicity and selectivity of this method make it preferable to others.

TABLE IV Comparison of the present method with other spectrophotometric methods

Method	*λ max*	*Detection Range (ppm)*	*ε ($l\ mol^{-1} cm^{-1}$)*	*Remarks*	*Reference*
Molybdenum	670	8–40	$0.384x10^4$	Low senstivity, non-selective and extraction in MIBK is not rapid	10
Diphenyl-carbazone + pyridine	520	0.7–2.65	$6.5x10^4$	Complex is extracted only in the presence of toxic pyridine	13
Pyridylazo naphthol	550	0.66–30.8	$4.1x10^4$	Less sensitive than the present method	14
Pyrocatechol violet	640	0.2–3.0	$7.96x10^4$	Rapid, simple, No extraction more senstive, mole selective	Present method

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