Pergamon

0039-9140(94)00179-0

Talanta, Vol. 41, No. 12, pp. 2061–2065, 1994

0039-9140/94 $7.00 + 0.00

SPECTROPHOTOMETRIC DETERMINATION OF MANEB BY TERNARY COMPLEX FORMATION WITH PAR AND CTAB

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(*Received* 14 *October* 1993. *Revised* 18 *May* 1994. *Accepted* 19 *May* 1994)

Summary—A rapid, simple, direct, and sensitive method has been developed for the determination of maneb (manganese ethylenebisdithiocarbamate) based on the formation of manganese-4-(2′-pyridylazo) resorcinol complex by a ligand displacement reaction, which is rendered water soluble by a cationic surfactant cetyltrimethylammonium bromide (CTAB) by the formation of an ion association complex. Beer's law is obeyed over the concentration range 0.08–2.4 μg/ml of the final solution at 500 nm in pH range 8–12. The molar absorptivity and Sandell's sensitivity are calculated to be $8.84 \times 10^4 \, l.mol^{-1}.cm^{-1}$ and 0.003 $\mu g/cm^2$, respectively. The developed method has been applied to the determination of maneb in commercial formulations, synthetic mixture, grain samples and vegetables.

Dithiocarbamates are widely used in agriculture as fungicides and in rubber industry as vulcanization accelerators and antioxidants. Most of the methods used to determine dithiocarbamates are based on Clark's method[1] in which dithiocarbamates are decomposed in an acidic medium to yield carbon disulphide (CS_2) which is absorbed in methanolic potassium hydroxide and the potassium methyl xanthate so formed is then titrated iodimetrically. The conditions for acid digestion have been investigated by a number of workers.[2–4] The evolved CS_2 has also been determined[5–9] by spectrophotometric measurement. Dithiocarbamates have also been determined from food products by titrimetry,[10] extraction voltammetry,[11] head space gas chromatography[12] and high performance liquid chromatography.[13] These fungicides have also been determined in air[14] by head space gas chromatography of the CS_2 evolved under controlled conditions from collected air-borne dust and from water samples after acid hydrolysis of the pesticide using a Hall detector.[15] However, most of these methods are non-specific since all dithiocarbamates (ziram, zineb, thiram, ferbam, nabam etc.) yield CS_2 on acid digestion, and other indirect methods are less sensitive, time-consuming, require rigid conditions and give unsatisfactory recoveries. Maneb is also determined by converting it into a molybdenum[16] containing complex in acid medium but the extraction is not rapid. Maneb can be determined by diphenylcarbazone[17] but the method is less sensitive than the method presented here and involves the use of toxic pyridine.

Dithiocarbamates do not belong to systemic fungicides but are protectant fungicides (applied prior to fungus infection) and, therefore, act upon damaging fungi chiefly by surface deposits. Consequently, residues of the undecomposed pesticides are found on fruit, *etc.* Residues of undecomposed dithiocarbamates on field-treated cultures mainly form surface deposits. The dynamics of these residues are largely influenced by exterior factors such as moisture, temperature and atmospheric humidity. Moreover, the substances excreted by leaves of living plants also stimulate degradation. The degradation products of maneb are ethylenebisdiisothiocyanatosulfide, ethylenethiourea and ethylenethiuram disulfide and there are separate methods for the analysis of these degradation products.

We present a simple, sensitive and relatively selective method in which manganese present in maneb is complexed with 4-(2′-pyridylazo) resorcinol (PAR). The manganese–PAR chelate thus formed by ligand exchange reaction is solubilized in water by CTAB by the formation of ternary complex.[18] CTAB acts as solubilizing agent. CTAB and some other surfactants have

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been used as solubilizing agents for many metal chelates.[19,20]

EXPERIMENTAL

Equipment

All absorbances were measured with an SP-20 Spectronic spectrophotometer. The pH measurements were carried out with an ECIL pH meter.

Reagents

All solvents and reagents were of analytical reagent grade.

Maneb solution (0.1%)

Pure maneb was prepared by adding a solution of manganese (II) to a solution of disodium ethylenebisdithiocarbamate (Wilson Laboratories, Bombay) and its purity checked by elemental analysis. The manganese content was checked by decomposing the sample with concentrated nitric acid and complexometric titration.[21] A stock solution (0.1%) of maneb was prepared by dissolving 100 mg in dimethysulphoxide, standardizing and further diluting as required.

Boric acid buffer solution (pH 9.2)

Boric acid and potassium chloride solutions ($0.2M$, 100 ml each) were mixed, the pH adjusted 9.2 with $0.2M$ sodium hydroxide and diluted to 500 ml.

Solutions of diverse ions and other dithiocarbamates

Stock solutions of various salts were prepared by dissolving them in distilled water. Solutions of dithiocarbamates were prepared by dissolving them in suitable solvents (ferbam, ziram and thiram in acetonitrile, zineb in dimethylsulphoxide) or in distilled water (NaDDC, nabam, *etc.*). Synthetic samples were prepared by mixing the appropriate solutions to give the required composition.

General procedure

To a known volume ($\leqslant 1$ ml) of sample containing 1.6–48 μg of maneb taken in a standard flask, 0.6 ml 0.02% of PAR solution, 2 ml of boric acid buffer (pH 9.2) and 5 ml of 0.25% CTAB solutions were added and the volume was made up to 20 ml with distilled water. The absorbance of a part of this solution was measured at 500 nm against a reagent blank.

RESULTS AND DISCUSSION

The absorption spectrum of the manganese–PAR–CTAB complex was recorded against maneb and a reagent blank. The complex absorbed strongly at 500 nm, whereas maneb and the reagent blank absorb negligibly at this wavelength. The absorbance was maximum when the pH of the aqueous phase was 8–12, 0.6 ml of 0.02% PAR, and 5 ml of 0.25% CTAB were used. The absorbance of the complex remained practically constant for more than 12 hr.

The composition of the complex as studied by Job's method of continuous variation and the mole ratio method was 1:3:1 (Mn:PAR:CTAB).

A calibration graph for maneb at 500 nm was linear over the concentration range 0.08–2.4 μg/ml of maneb under the optimum conditions tested above. Ten replicate determinations on sample solutions containing 30 μg of maneb gave a mean absorbance of 0.50 with a RSD of 0.96%. The molar absorptivity and Sandell's sensitivity (for an absorbance of 0.001) were $8.84 \times 10^4 M^{-1}$ cm^{-1} and 0.003 μg/cm^2, respectively.

Interferences

The interference of various ions in the determination of 30 μg of maneb in 20 ml of final solution was studied. The following foreign ions (amounts in parentheses) did not interfere: chloride (18 mg); bromide (16 mg); iodide (5 mg); sulfate (15 mg); fluoride (8 mg); orthophosfate; oxalate and citrate (120 μg); EDTA (50 μg); Ni (II) (200 μg); Cu (II) (150 μg); Mg (II) (300 μg); Cr (III) (100 μg); Pb (II) (50 μg). Zinc interfered strongly but could successfully be masked with 1 ml of 5% potassium cyanide solution.

Dithiocarbamates like nabam (disodium ethylenebisthiocarbamate), vapam (sodium monomethyldithiocarbamate), dibam (sodium dimethyldithiocarbamate), NaDDC (sodium diethyldithiocarbamate), thiram (tetramethylthiuram disulphide) and sodium N-methylanilinecarbodithioate did not interfere in the determination of maneb. Ferbam up to 2 mg did not interfere. Ziram and zineb could be masked with potassium cyanide.

Table 1. Determination of maneb in commercial samples

Maneb	Amount of maneb taken (μg)	Amount of maneb found* (μg) Proposed method	Rangaswamy *et al.* method
Maneb	20.0	19.9	19.7
(pure)	30.0	30.1	29.8
	40.0	39.9	39.8
Dithane M-45	20.0	20.1	19.6
(80% W.P.)	30.0	30.0	29.8
	40.0	39.9	39.8
Dithane M-22	20.0	19.9	19.7
(80% W.P.)	30.0	29.9	29.6
	40.0	40.0	39.8

*RSD, 1.2–2.0% ($N = 10$).

Determination of maneb in commercial samples and synthetic mixtures

The developed method was applied for the determination of maneb in commercial formulations 'Dithane M-45' and 'Dithane M-22' both containing 80% as active ingredient. Table 1 shows the results of five dilutions of stock solutions prepared from a pure and commercial samples. The results are compared with those obtained by Rangaswamy *et al.*[22] and the recoveries are seen to be fully satisfactory.

Determination of maneb in synthetic mixtures

Mixtures of maneb with nabam, vapam, thiram, NaDDC, ziram and zineb in various proportions were prepared and determined by general procedure. The results are given in Table 2. As compared to the method based on the formation of a molybdenum containing complex in which the other dithiocarbamates like zineb, ziram, thiram, nabam, vapam and NaDDC form their molybdenum complex under specified conditions, the method presented here is relatively selective. Nabam, vapam, NaDDC, thiram did not interfere with this method. Ziram and zineb did interfere but could be masked with potassium cyanide solution.

Though the sensitivity of gas chromatographic methods is greater, in terms of selectivity the present method possesses some distinct advantages over the determination of dithiocarbamates by gas chromatography which involves the acidification of the samples to hydrolyse the dithiocarbamates to form CS_2, extraction of CS_2 and determination of CS_2 by gas chromatography.[14,15] The varying conditions of acid hydrolysis are reported.[15] All the dithiocarbamates evolve CS_2 on acid hydrolysis. Whereas the present method is direct and simple, and is made relatively selective for maneb since it is based on the complexation of manganese present in maneb with PAR, other dithiocarbamates do not interfere with this method.

Table 2. Determination of maneb in synthetic mixtures

No.	Composition and percentage	Amount of maneb (μg) Taken	Found	Rel. error (%)
1.	Maneb:50 Thiram:20 Vapam:20 NaDDC*:10	20.0	20.1	0.5
2.	Maneb:40 Ferbam:40 Ziram:20	30.0	30.2	0.6
3.	Maneb:50 NaDDC:20 Nabam:20 Ziram:10	40.0	40.1	0.6
4.	Maneb:40 Ferbam:30 Vapam:20 Zineb:10	50.0	50.2	0.5

*Sodium diethyldithiocarbamate.

Determination of maneb in crops

The procedure was applied for the determination of maneb in grain, tomato and cabbage. A known amount of maneb was sprayed on

Table 3. Determination of maneb in crops

Crop	Amount of maneb (μg)* Taken	Found
Grain	30.0	29.9
	40.0	40.1
Tomato	30.0	29.8
	40.0	39.6
Cabbage	30.0	30.0
	40.0	39.5

*$N = 3$; 20 g of crops taken.

Table 4. Comparison of proposed method with other spectrophotometric methods

Method	Max (*nm*)	Detection range (*ppm*)	Molar absorptivity (M^{-1} cm^{-1})	Remarks	Reference
Rangaswamy *et al.* method	540	1.2–20	—	Low sensitivity, long tedious procedure	22
Complex formation with molybdenum	670	8–40	0.384×10^4	Low sensitivity and selectivity. Extraction not rapid.	16
Complex formation with diphenylcarbazone and pyridine	520	0.7–2.65	6.5×10^4	Completely extractable in the presence of toxic pyridine	17
Complex formation with PAN	550	0.66–3.8	4.1×10^4	Less sensitive than present method	25
Complex formation with PAR	500	0.125–4.8	8.84×10^4	Rapid, simple, more sensitive, does not involve the extraction step and also selective.	Present method

crops and after 15–20 min the crop was crushed finely, homogenized in a mixer and shaken mechanically for 1 hr. The mixture was filtered and the residue in the funnel was washed with three 10 ml portions of dimethylsulphoxide. The extracts were evaporated down to 2 ml and the remaining solvent removed by blowing a current of dry air at room temperature. The residue was dissolved in dimethylsulphoxide and maneb was determined by the general procedure. The results are given in Table 3.

CONCLUSIONS

The present method is selective for the determination of maneb in the presence of other dithiocarbamates such as nabam, vapam, thiram, ziram, zineb, *etc.* The sensitivity of the present method is better than those reported by Lowen,[9] Cullen[23] and Chmiel.[24] According to Lowen a minimum of 10 μg of CS_2, and according to others a minimum of 20 μg of CS_2 evolved can be determined. According to Rangaswamy *et al.*,[22] 6 μg of the dithiocarbamate equivalent to 3.43 μg of CS_2 can be determined. However, with the present method a minimum of 4 μg of maneb equivalent to 2.29 μg of CS_2 can be determined. Although the gas chromatographic methods are more sensitive than the present one, they lack selectively since all dithiocarbamates pesticides liberate CS_2 on acid hydrolysis. As compared to the method of Rao *et al.* based on the formation of manganese-1-(2′-pyridylazo)-2-naphthol (Mn-PAN) complex,[25] the sensitivity of the present method is double (Table 4). Moreover, the present method does not involve an extraction step, thus making it easier to perform. The simplicity, sensitivity, selectivity and wide applicability of this method make it a choice amongst the others.

Acknowledgement—One of the authors (J.K.) thanks the Council of Scientific and Industrial Research, New Delhi, for providing a Senior Research Fellowship.

REFERENCES

1. D. G. Clarke, H. Baum, E. L. Stanley an W. E. Hester, *Anal. Chem.*, 1951, **23**, 1842.
2. J. Rosenthal, R. L. Carlsen and E. L. Stanley, *J. Assoc. Off. Agric. Chem.*, 1953, **36**, 1170.
3. H. Roth and W. Beck, *Mikrochim. Acta*, 1957, 845.
4. R. Warren and J. Bontoyan, *J. Assoc. Off. Agric. Chem.*, 1965, **48**, 562.
5. C. H. Hall, *J. Assoc. Off. Agric. Chem.*, 1960, **43**, 37.
6. C. Reinhard, *Fachgruppe Lebensmittelchim. Gerichuil. Chem.*, 1971, **25**, 1.
7. C. L. Hilton and J. E. Newell, Paper presented at Pittsburgh Conf. Anal. Chem. & Appl. Spectroscopy; abstr. in *Anal. Chem.*, 1953, **25**, 530.
8. J. Piechocka, *Rocz. Panstow. Zakl. Hig.*, 1984, **35**, 83.
9. W. K. Lowen, *J. Assoc. Off. Agric. Chem.*, 1953, **36**, 484.
10. B. C. Verma, H. S. Sidhu and R. K. Sood, *Talanta*, 1982, **29**, 703.
11. N. A. Ulaknovich, E. D. Medyantseva, V. F. Frolova and O. N. Romanova, *Zh. Anal. Khim.*, 1983, **38**, 1963.
12. H. McLeod, K. A. McCully, *J. Assoc. Off. Anal. Chem.*, 1969, **6**, 52.
13. K. H. Gustafsson and C. H. Falhgren, *J. Agric. Food Chem.*, 1983, **31**, 461.
14. M. Palov and B. Renzo, *Bull. Environ. Contam. Toxicol.*, 1986, **37**, 931.
15. T. M. Engel, J. S. Warner and W. M. Cooke, *EPA-600/4-85/072*, 1985; *Chem. Abstr.*, 1986, **105**, 196862m.
16. N. Verma and A. L. J. Rao, *Rev. Roum. Chim.*, 1990, **35**, 625.
17. A. K. Malik, J. Kapoor and A. L. J. Rao, *Chem. Environ. Res.*, 1992, **1**, 29.
18. R. G. Anderson and G. Nickless, *Analyst*, 1967, **92**, 207.
19. Y. Shijyo and T. Takeuchi, *Bunseki Kagaku*, 1967, **16**, 51.
20. Y. Horiuchi and H. Nishida, *Bunseki Kagaku*, 1968, **17**, 1325.

21. A. L. Vogel, *A Textbook of Quantitative Inorganic Analysis*, 3rd ed. Longman, Essex, 1969.
22. J. R. Rangaswamy and Y. N. Vijayashankar, *J. Assoc. Off. Anal. Chem.*, 1975, **58**, 1232.
23. T. E. Cullen, *Anal. Chem.*, 1964, **36**, 221.
24. Z. Chimiel, *Chem. Anal. (Warsaw)*, 1978, **24**, 505.
25. A. L. J. Rao, A. K. Malik and J. Kapoor, *Talanta*, 1993, **40**, 201.