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An Ultraviolet Absorption Method for the Analysis of Maneb Formulations

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The official method for the analysis of ethylene-bis dithiocarbamate formulations is based on evolution of carbon disulfide (CS_2) from hot acid treated samples and iodine titration of the xanthate formed when the CS_2 is absorbed in alcoholic potassium hydroxide solution, (HOROWITZ 1975, RAW 1970, LOWEN & PEASE 1964, LIVITSKY & LOWEN 1954, LOWEN 1953, ZWEIG & SHERMA 1972).

A proposed colorimetric method (RANGASWAMY & VIJAYA-SHANKAR 1975) measures the permanganic acid formed by the periodate oxidation of the manganese component of maneb, but is obviously not suitable for non-manganese containing formulations. Another method utilizes gas chromatography, based on the thermal release of ethylene thiourea from maneb when the sample is introduced into the gas chromatograph (ZIELINSKI & FISHBEIN 1966)

An ultraviolet absorption method has been proposed for the measurement of maneb, which is considerably simpler than the tedious CS_2 procedure (SAWABE, *et al.* 1974). Although preliminary studies of the method in this laboratory produced erratic results, modifications to the original procedure has resulted in a method which gives analytical results which are consistent with and similar to the values obtained by the CS_2 method for maneb and its formulations.

The details of the modifications together with representative analytical results for maneb formulations are presented in this report.

PRINCIPLE: Maneb is converted to nabam, a water soluble ethylenebisdithiocarbamate, by the action of the tetrasodium salt of ethylenedinitrolotetraacetic acid (Na_4 EDTA). Interfering products are removed by extraction with ethyl acetate, chloroform and carbon disulfide. The absorption of the converted maneb is measured at 284 nm. The method is presently also applicable to polyram formulations but not to zineb formulations.

MATERIALS AND METHODS: a. U.V. spectrophotometer with matched 10mm silica cells.
b. An ultrasonic bath.
c. Syringe filtering system: Luerlock syringe (20 ml)

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equipped with a Millipore microsyringe holder, Luer inlet, 25mm, Cat. No. XX30-02500 (Millipore Corp. Bedford, MS, 01730) and a 16 gauge cannula needle about 6 inches long.

d. 0.2 Molar Na_4EDTA: Dissolve 76 g. of Na_4EDTA in distilled water and dilute to 900 ml. Adjust to pH 9.80 with glacial acetic acid and make to 1 liter with distilled water.
e. Mixed solvent: Equal volumes of Reagent Grade, glass distilled, ethylacetate and chloroform.
f. Carbon Disulfide: Reagent Grade, glass distilled.
g. Maneb: Standard reference grade obtained from E.I. duPont de Nemours, & Co., Biochemical Department, Wilmington, DE 19898.
h. Polyram: Standard reference grade obtained from FMC Corp., Agricultural Chemical Div., Middleport, NY 14105.
i. Zineb: Standard refernce grade obtained from FMC Corp. as above.

PROCEDURE:

A. Maneb reference standard solution: Accurately weigh 70 mg maneb into a 100 ml volumetric flask. Add 50 ml of 0.2M Na_4EDTA solution and place the flask in an ultrasonic bath for 10 minutes with occasional swirling. Transfer the contents of the flask to a 250 ml separatory funnel, quantitatively, with the aid of 50 ml mixed solvent. Add 15 ml CS_2, shake vigorously for 1 minute, allow the layers to separate, and drain the solvent layer. Filter the aqueous layer through the syringe filtering unit, transfer 1 ml of filtrate to a 100 ml volumetric flask and make to volume with distilled water.
B. Reference blank solution: Procede as described in A without including the maneb.
C. Sample solution: Weigh sample (equivalent to ca. 70 mg maneb) into a 100 ml volumetric flask. Procede as in A, placing and removing the sample and standard flasks in the ultrasonic bath at the same times. One ml of filtrate is transferred to a 100 ml volumetric flask and diluted to volume with distilled water.

DETERMINATION: Scan the standard and sample solutions between 300 and 250 nm against the reference blank solution. Measure the absorption at 284 nm.
From the above determined absorbances, and the standard solution concentration, calculate the percentage maneb as follows:

$$\% \text{ maneb} = \frac{(\text{absorption of sample}) \times (\text{conc. of standard soln. (mg/ml)})}{(\text{absorption of standard}) \times (\text{conc. of sample(mg/ml)} \times (\% \text{ purity of standard})}$$

RESULTS AND DISCUSSION

The results obtained when maneb formulations were analyzed by CS_2 evolution and the UV method described herein are compared in Table 1. As can be seen the values obtained by the two methods are comparable.

TABLE 1. Analytical Rseults Of Commercial Maneb Formulations by Official AOAC method and U.V. Method

Sample	Guarantee (%)	% maneb found	
		AOAC	UV
Manzate 200	maneb 80%	83.1	84.4
Maneb	maneb 80%	73.9	73.4
Manzeb	maneb 80%	80.5	80.1
Maneb-(1)	maneb 80%	87.2(2)	86.6
Manzate-(1)	maneb 80%	82.9(2)	83.1
Manzate 200	maneb 80%	81.4	81.7
Maneb 6% Dust	maneb 6%	5.7	6.1
Maneb 6% Dust	maneb 6%	5.8	6.0

(1) Sub-sample courtesy,State of California Department of Food & Agriculture, Pesticide Department.
(2) AOAC method, analyzed by the State of California Department of Food & Agriculture, Pesticide Department.

The absorption spectra of nabam derived from reference grade maneb, maneb formulations converted to nabam, and reference grade nabam in weak Na_4EDTA solution are shown in Figure 1.

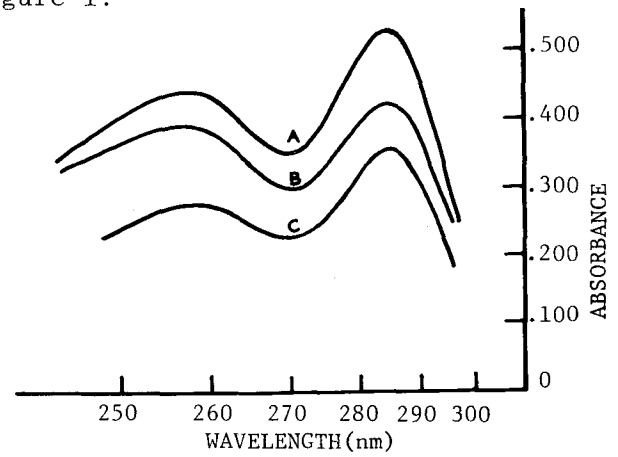

FIG.1. Spectra of nabam (C), maneb formulation (B) and pure maneb (A) in 0.2 M Na_4EDTA.

The absorbance of nabam produced from maneb follows Beer's law over the range 2.0 - 8.0 mg / liter using 10 mm pathlength silica cells. The lower limit of detectability is 0.5 mg/ liter using 50mm cells.

Maneb reacts with a basic solution of Na_4EDTA at pH 9.80 and higher, to form nabam and a manganese chelate. Conversion is incomplete, leading to erratic results at pH less than 9.8. Thus careful control of the pH is essential for the success of the method. Nabam in alkaline solution will decomposed when exposed to oxygen,either pure or as air.(LUDWIG et al. 1955). A time study , the results of which are presented in Figure 2, shows that analytical measurements should be made within on hour of begining the analysis to avoid spurious results caused by air oxidation of nabam.

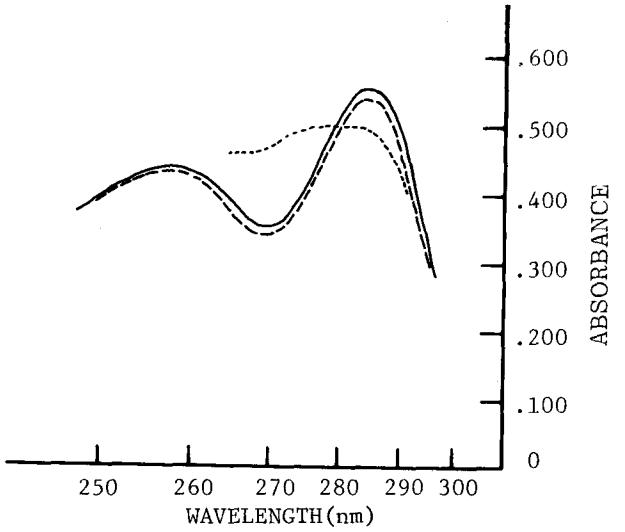

Figure 2.Time study of the decomposition of nabam in pH 9.8 0.2M Na_4EDTA. ——— 30 minutes after start of analysis; -------- 1.5 hrs;····· 2 hrs.

Ethylene thiourea(ETU), ethylene-bis-isothiocyanate (EBIS) and elemental sulfur may be present in ethylene-bis-dithiocarbamate formulations (BONTOYAN et al.1972, CZEGLEDI JANKO 1967,FISHBEIN & FAWKES 1965,HYLIN 1973,VONK & SIJPESTEIN 1970). These must be removed since they interfer in the ultraviolet determination of nabam. The organic impurities are removed by the solvent mixture, while carbon disulfide removes any free sulfur that may be in the formulation. The manganese chelate does not interfer.

The procedure of SAWABE et al. (1974) utilized 1 M sodium carbonate solution to convert maneb to nabam. In our hands, this reagent did not provide complete conversion and lead to erratic analytical results due to the rapid decomposition of nabam in this very alkaline reagent (pH 11.26).

The use of an ultrasonic bath to speed dispersal of the poorly wetted formulations in the EDTA solution is a practical necessity in view of the time constraints of the present method.

Statistical analysis of the results obtained for the analysis of maneb by the AOAC and UV procedures showed no significant difference. On the other hand, the results obtained by applying these methods to zineb, another ethylene-bis-dithiocarbamate fungicide, were consistently higher when the UV method was used.

TABLE 2.
Results Obtained in the Analysis of Zineb Formulations by the AOAC and UV Methods

Zineb Formulation	Guarantee (%)	% Found	
		AOAC	UV
Zineb (FMC)	75	77.5	98.2
Zineb (FMC)	75	88.6	98.8
Zineb 5 yrs old	75	59.1	64.1
Science Products Co. Inc.	75	87.7	99.2
Rohm & Haas Co. 3 yrs old	75	44.6	52.5

Zineb formulations contain ETU, ETM, zinc sulfide and sulfur as principal decomposition products(FISHBEIN & FAWKER 1965) The solvents used for washing the EDTA solution will remove the organic products and sulfur. Zinc sulfide and zinc-EDTA chelate were found not to interfer in the UV analysis. Therfore some other as yet unidentified decomposition product is probably responsible for the high values observed.

The modified UV method for the analysis of ethylene-bis dithiocarbamate formulations appears suitable for maneb and polyram, but as yet not for zineb. It is less time consuming than the AOAC CS_2 evolution procedure and yields comparable results.

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