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Determination of Zineb by Oxidation with Chloramine-T

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A simple volumetric procedure is described for the estimation of zineb in its formulations. This is based on its oxidation in an alkaline medium by chloramine-T after the removal of the oxidizable impurities.

Zineb (or zinc ethylene bis(dithiocarbamate)) is widely used in India as a protective fungicide for the control of plant diseases. It is available as a 78% water-dispersible powder formulation. The analysis of zineb formulation is therefore of great interest.

The most widely used method (Stevenson, 1964; AOAC, 1970) for the analysis of zineb is based on the quantitative evolution of carbon disulfide by digestion with sulfuric acid. The hydrogen sulfide that is evolved simultaneously is removed by passing the mixture of gases through lead acetate. The carbon disulfide is then absorbed in alcoholic potassium hydroxide when the xanthate is formed. The xanthate is determined by titration with iodine. A simple volumetric procedure for the determination of zineb based on its oxidation in an alkaline medium with chloramine-T is described.

It is well known that metallic salts of dithiocarbamic acid undergo degradation during storage and give rise to a variety of products. Thus, it is reported that zineb water-dispersible powder formulations contain (Fishbein and Fawkes, 1965) ethylenethiourea, ethylene thiurammonosulfide, zinc sulfide, and sulfur as decomposition products. Since the degradation products are also susceptible to oxidation with chloramine-T, it is necessary to separate the parent compound from the contaminants. In the method worked out and described below, the organic impurities and sulfur are removed by washing the sample successively with ethyl alcohol, chloroform, and dilute acetic acid. The residue is dissolved in dilute sodium hydroxide when the zineb goes into solution leaving behind the insoluble zinc sulfide. The zineb is determined by taking an aliquot of the alkaline solution.

EXPERIMENTAL PROCEDURE

About 0.4 g of the sample was weighed accurately and transferred into a 100-ml beaker. Alcohol (10 ml) was added and the sample was stirred well. The solid was allowed to settle and the supernatant alcohol was decanted through a dry filter paper. Washing with 10-ml portions of alcohol was continued until the filtrate was colorless. The sample was similarly washed with 10-ml portions of chloroform and then with dilute acetic acid (6 N). With

Table I. Oxidation of Zineb with Chloramine-T

Sample no.	mol of zineb taken $\times 10^4$	equiv of chloramine-T consumed $\times 10^4$	equiv of chloramine-T per mol of zineb
1	0.228	6.845	30.02
2	0.228	6.896	30.25
3	0.230	6.845	29.73
4	0.231	6.896	29.81
5	0.221	6.640	30.05
6	0.230	6.850	29.79
7	0.226	6.780	29.93

each solvent the washing was continued until a colorless filtrate was obtained. Three to four washings with each solvent were sufficient. The solid in the beaker was dissolved in about 50 ml of sodium hydroxide. The solution was poured through the filter paper and collected in a 250-ml volumetric flask. The beaker and the filter paper were washed with further quantities of sodium hydroxide solution so that the sample was quantitatively transferred into the measuring flask. The solution in the flask was then made up to the mark with 1 N sodium hydroxide.

Oxidation with Chloramine-T. The sample solution (5 ml) was pipetted into a 250-ml stoppered conical flask. Sodium hydroxide (20 ml, 1 N) was added, followed by 25 ml of 0.1 N chloramine-T solution. The flask was stoppered, shaken well, and kept aside for 20 min. Then 40 ml of 4 N sulfuric acid was added and the flask shaken and kept aside for 10 min. Potassium iodide (10 ml, 10%) was added followed by 50 ml of water. The liberated iodine was titrated with standard 0.1 N sodium thiosulfate using starch as the indicator near the end point.

Simultaneously, the volume of sodium thiosulfate consumed by 25 ml of the chloramine-T was determined. No blank correction for the reagents is necessary as it amounts to less than 0.05 ml. The zineb content of the sample is calculated from the following formula:

$$\% \text{ zineb content of formulation} = [(a - b) \times N \times 0.919 \times 50 \times 1000] / w$$

where a = milliliters of standard sodium thiosulfate consumed by 25 ml of chloramine-T, b = milliliters of standard sodium thiosulfate consumed by the excess of chloramine-T remaining after reaction with zineb, N =

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Table II. Comparative Results for Zineb Content by the Carbon Disulfide Evolution and Chloramine-T Methods

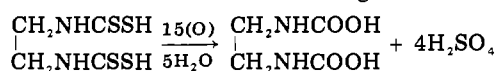
Sample no.	% zineb content	
	CS ₂ evolution	Chloramine-T oxidation
1	78.6	78.7
2	79.2	80.2
3	78.0	77.8
4	78.9	78.7
5	78.7	79.2

normality of sodium thiosulfate, and w = weight of formulation taken in milligrams.

RESULTS AND DISCUSSION

To establish the number of equivalents of chloramine-T consumed by 1 mol of zineb, samples of known zinc ethylene bis(dithiocarbamate) content were analyzed. The results are presented in Table I.

From the results given in Table I, it is evident that each mol of zineb requires 30 equiv of chloramine-T. This is in accordance with the following stoichiometric equation:



Therefore, 1 ml of 0.1 N chloramine-T is equivalent to 0.919 mg of zineb. A few comparative results obtained by the carbon disulfide evolution method and the chloramine-T method are presented in Table II.

Clarke et al. (1951) have pointed out that during digestion of zineb with sulfuric acid in the carbon disulfide procedure, the sample may not decompose to yield the expected 2 mol of carbon disulfide and hydrogen sulfide may be evolved if the digestion is carried out at a lower temperature. The formation of a large amount of hydrogen sulfide may lead one to think that the sample has deteriorated. Therefore, the experimental conditions require careful maintenance. Furthermore, the method also requires special apparatus. The chloramine-T oxidation method described above does not require any special apparatus and it is very simple and rapid. It is also accurate as 30 equiv of chloramine-T is consumed per mol of zineb. It is therefore well suited for routine analysis.

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Crystal and Molecular Structure of Organophosphorus Insecticides. 4. Bromophos

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The crystal and molecular structure of bromophos (*O*-(4-bromo-2,5-dichlorophenyl) *O,O*-dimethyl phosphorothioate, (H₃CO)₂P(S)OC₆H₂Cl₂Br, orthorhombic, $P2_12_12_1$, $a = 7.307$ (5), $b = 27.19$ (3), and $c = 6.440$ (4) Å, $Z = 4$, Mo $K\alpha$ radiation) has been determined by three-dimensional x-ray analysis. The structure was solved by conventional Patterson and Fourier techniques to a final discrepancy index $R = 0.048$ for 1217 observed reflections ($F_o > 2.5\sigma(F_o)$). The structure features an intramolecular hydrogen bond which restricts rotation about the phenolic C-O bond, thus giving a very probable in vivo model. The phosphorus-meta hydrogen distance of 5.52 Å falls well within the range of literature values cited for the intramolecular active site-separation distance for acetylcholinesterase (AChE), yet is well outside that for mammalian AChE.

The crystal-structure investigation of bromophos, a bromine analogue of ronnel, was undertaken as a part of a study of various insecticides being carried on at this laboratory (Gress and Jacobson, 1973; Baughman and Jacobson, 1975; Gifkins and Jacobson, 1976; Rohrbaugh and Jacobson, 1976; Baughman et al., 1976; Takusagawa and Jacobson, 1976). The purpose of such a program is to determine the structural dependence of an insecticide's toxicity/activity and to better understand the mechanism(s) involved.

In the case of acetylcholinesterase (AChE) inhibition, one would ideally like to know the active sites' three-dimensional structure (or that of a small range of possible low-energy conformations). Using organophosphorus (OP)

and/or carbamate insecticides, the problem may be approached indirectly. Such information could lead to the construction of insecticides which would better conform structurally as well as chemically to the most favorable (minimum energy) orientation of AChE.

EXPERIMENTAL SECTION

Crystal Data. A rectangular prismatic crystal (~99% pure) with approximate dimensions 0.15 mm × 0.12 mm × 0.07 mm was selected and mounted on the end of a glass fiber using Elmer's Glue; other glues with an organic solvent base dissolve the OP insecticide crystals. Preliminary oscillation photographs indicated a single crystal with *mmm* (orthorhombic) symmetry. The crystal was then mounted on a four-circle diffractometer and three ω -oscillation photographs were taken at various χ and ϕ settings.

From these photographs 17 independent reflections were

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