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Chemical Studies of the effect of Fungicides on Water Pollution with Chloramine-T Reagent

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Abstract: *The current study shows that the survey of literature reveals that Chloramine-T In acidic medium has not been used for the determination of dithiocarbamate compounds, either in technical form or in their formulations. In the present work, a quick and convenient method has been developed for the determination of some Dithiocarbomate compounds like Zinc dimethyl dithiocarbamate (Ziram), Tetramethyl thiuram disulphide (Thiram), Zinc ethylene bis dithiocarbamate (Zineb), Ferric dimethyl dithiocarbamate '(Ferbam) and Zinc diethyl dithio carbomate (ZDC) in technical form and in their formulations.*

Background*: The pesticides are group of chemicals intended for preventing/destroying any pest detrimental to man or his interest during production, processing, storage, transportation and distribution of food. These include insecticides, herbicides, fungicides rodenticides, nematicides, chemosterilents, molluscides, plant growth regulators, defoliants, desiccant, attractants, repellents and similarly active compounds.*

Materials and Methods*: Aliquot containing 1-5 mg of the sample were taken in a 100 ml Erlenmeyer flask and 5 ml of 0.1 N Chloramine-T, 5 ml of glacial acetic acid were added to it. The contents were shaken well and allowed to react for 10 minutes at room temperature (27°C). After the reaction was over, 5 ml of 10%potassium iodide solution was added and the contents were allowed to stand for one minute. The liberated iodine was titrated with standard 0.1 N sodium thiosulphate solution using starch as indicator. A blank experiment was also run under the similar conditions using all the reagents except the sample. The amount of Chloramine- T consumed for the sample was calculated with the difference in readings of sodium thiosulphate solution for the blank and sample experiment.*

Results*: For testing quantitative validity of the reaction, Zinc dimethyl dithiocarbamate (Ziram) was taken as the test sample. Aliquots containing different amounts of the sample were taken in 100 ml stoppered conical flasks and a known amount of glacial acetic acid was added. The contents were shaken well and allowed to react with varying concentration of Chloramine- T reagent at room temperature for different intervals of reaction time. After the reaction was over, the unconsumed Chloramine-T was determined iodometrically. A blank experiment was also run under similar conditions using all the reagents except the sample. The stoichiometry of the reaction was established for each sample and a possible course of reaction was suggested. On the basis of reaction conditions developed for Zinc dimethyl dithiocarbamate (Ziram), the estimation of other dithiocarbamate compounds in technical form and in their formulations were carried out.*

Conclusion: *The current study shows that the survey of literature reveals that Chloramine-T In acidic medium has not been used for the determination of dithiocarbamate compounds, either in technical form or in their formulations. In the present work, a quick and convenient method has been developed for the determination of some Dithiocarbomate compounds like Zinc dimethyl dithiocarbamate (Ziram), Tetramethyl thiuram disulphide (Thiram), Zinc ethylene bis dithiocarbamate (Zineb), Ferric dimethyl dithiocarbamate '(Ferbam) and Zinc diethyl dithio carbomate (ZDC) in technical form and in their formulations.*

Key Word*: Chemical Studies, Fungicides, Water Pollution, Chloramine-T Reagent*

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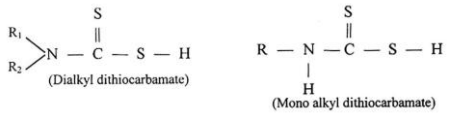
I. Introduction

The pesticides are group of chemicals intended for preventing/destroying any pest detrimental to man or his interest during production, processing, storage, transportation and distribution of food. These include insecticides, herbicides, fungicides rodenticides, nematicides, chemosterilents, molluscides, plant growth regulators, defoliants, desiccant, attractants, repellents and similarly active compounds.

Dithiocarbamates are divided into two mam groups on the basis of evidence for two different machanisms of action, the dialkyl dithiocarbamates and mono alkyl dithiocarbamates.



As dialkyl dithiocarbamates are strong chelating agents, they were thought to act by depriving the cell of the needed metal. Recent information however indicates that a heavy metal ion is required for the high toxicity of these fungicides. According to Goksyn", the 1: 1 complex is responsible for the toxicity of dialkyl dithiocarbamates at low concentrations as this presumbly attacks the vital components of the cell and thus prevents growth. The toxicity of dialkyl dithiocarbamates in the cell might involve the mode of action in fungus cells. On the basis of structure-activity relationships, the dialkyl dithiocarbamates and the mono alkyl dithiocarbamates have different modes of action, it is difficult to make any generalizations regarding the effects of structural changes. Mono alkyl dithiocarbamic acid is weaker fungicide than dialkyl dithiocarbamic acid, while m the corresponding ethylene bis dithiocarbamates replacement of the hydrogen atom by the alkyl group greatly decreases the fungicidal activity. Increasing the size of the alkyl groups on the nitrogen atom of dialkyl dithiocarbamates greatly decreases the toxicity. Similarly increasing the number of methylne groups between two thiocarbamyl nitrogens of bisdithiocarbamates also decrease the activity.

The toxicity and mechanism of action of. dialkyl dithiocarbamates and mono alkyl dithiocarbamates are discussed in detail by various workers[5-15]. The toxicological effects like acute toxicity[16], chronic toxicity[17], reproductive effects[18], teratogenic effects[19], organ toxicity[20], mutagenic effects[21], carcinogenic effects[23], ecological effects[24] and environmental fate[24-25] of Dithiocarbamate compounds have also been discussed.

Because of the great insecticidal and fungicidal importance, the analysis of Dithiocarbamate compounds need prime attention. Mckinly and Magarvey[56] reported paper chromatography procedure for the resolution of some dithiocarbamate compounds. Henriet and Co-workers[57] reported a standardised method for analysis of dithiocarbamate residue in lettuces. Sheinina and Co-workers[58] used thin layer chromatography for the determination of thiram in cotton seed with hexane. Strigina and Co-workers[59] reported complexometric determination of TMTD. Butler and Co-workers[60] reported a trace analysis of thiram by microcoulometry. Lukashevich and Co-workers[61] reported a method for determining the working concentrations of TMTD (thiram) and the quality of tuber disinfection. Several other liquid chrornatography[62], titrimetric[63], potentiomertic[64], spectrophotometric[65-66] and high performance liquid chromatographic[67-69] procedures for the determinations of dithiocarbamate compounds are also reported.

Fernandez and Co-workers[70] were estimated some dithiocarbamate compounds by tlow-injection amperometry electrode method. Mathew and Co-workers[71] reported anodic-stripping-voltametric method for the determination of some dithiocarbamate compounds. Gas liquid chromatographic[72-75] procedures are also reported for the determination of dithiocarbamate compounds. Fernandez and Co-workers[76] reported voltametric procedure for the determination of some dithiocarbamate compounds with a cobalt phthalocyanine-modified carbon paste electrode. Perez-Ruiz and Co-workers[77] reported flow-injection-fluorimetric method for the determination of some dithiocarbamate compounds.

Recently, several other spectrophotometry[78] gas chrornatography[79] electrochemical method[80] and spot test method[81] for the determination of dithiocarbamate compounds in soil, vegetation and water have also been reported.

For testing quantitative validity of the reaction, Zinc dimethyl dithiocarbamate (Ziram) was taken as the test sample. Aliquots containing different amounts of the sample were taken in 100 ml stoppered conical flasks and a known amount of glacial acetic acid was added. The contents were shaken well and allowed to react with varying concentration of Chloramine- T reagent at room temperature for different intervals of reaction time. After the reaction was over, the unconsumed Chloramine-T was determined iodometrically. A blank experiment was also run under similar conditions using all the reagents except the sample. The stoichiometry of the reaction was established for each sample and a possible course of reaction was suggested. On the basis of reaction conditions developed for Zinc dimethyl dithiocarbamate (Ziram), the estimation of other dithiocarbamate compounds in technical form and in their formulations were carried out.

II. Material and Methods

Aliquot containing 1-5 mg of the sample were taken in a 100 ml Erlenmeyer flask and 5 ml of 0.1 N Chloramine-T, 5 ml of glacial acetic acid were added to it. The contents were shaken well and allowed to react for 10 minutes at room temperature (27°C). After the reaction was over, 5 ml of 10%potassium iodide solution was added and the contents were allowed to stand for one minute. The liberated iodine was titrated with standard 0.1 N sodium thiosulphate solution using starch as indicator. A blank experiment was also run under the similar conditions using all the reagents except the sample. The amount of Chloramine- T consumed for the sample was calculated with the difference in readings of sodium thiosulphate solution for the blank and sample

experiment. The recovery of the sample was calculated with the amount of Chlorarnine-T consumed for the sample by using following expression;

$$\text{mg of sample} = \frac{M \times N \times (B-S)}{n \times 2}$$

III. Result and Discussion

Study of Variables is discussed as follows. Effect of following variables were studied to develop a reaction conditions for the determination of the concentration of some fungicidal dithiocarbamate compounds. Taking Ziram (tech.) as a test sample. Effect of Reaction Time is as follows. Keeping the amount of Ziram (tech.), concentration of Chloramine-T and acetic acid as constant, reaction time was varied from 1-30 minutes. Aliquots (5 ml) containing 4.975 mg of Ziram (tech.) was taken in 100 ml Erlenmeyer flask and 5 ml of 0.1 N Chloramine- T, 5 ml of glacial acetic acid was added to it. Now the reaction mixture was shaken well and allowed to react at room temperature (27°) for 1, 3, 5, 10, 15, 20, 25, and 30 minutes respectively. The unconsumed Chloramine-T was determined by titrating the reaction mixture against standardised (0.1 N) sodium thiosulphate solution using potassium iodide and starch as indicator. It was observed that the recovery of Ziram (tech.) becomes constant within 10 minutes. The value does not change significantly by allowing more reaction time. By increasing reaction time, the tendency of positive error increases. It may be due to loss of the reagent in long standing. Similar experiments were performed with other samples of dithiocarbamate compounds. It was observed that Thrarn, Zineb and ZDe compounds require 10 minutes, while F erbam require 15 minutes for complete the reaction.

Keeping reaction time, amount of Ziram (tech.) and glacial acetic acid as constant, the effect of varying concentration of Chloramine-Twas studied. 4.975 mg of the sample was allowed to react with 5 ml of varying concentration (0.01 to 0.50N) of Chloramine-T reagent. The unreacted Chloramine-Twas determined iodometrically and the recovery of the sample was calculated. It was found that the best recovery was obtained at 0.1 N concentration of Chloramine- T reagent. A lower and higher concentration tends to give inaccurate results (Table-2). Even by increasing the concentration upto 0.50N, the recovery does not change to a considerable extent. Thus, to avoid the wastage of the reagent and to get accurate results, 0.1 N concentration of Chloramine- Twas recommended for further estimation. Experiments with the same concentration were carried out with other dithiocarbamate compounds. Variation in volume of 0.1 N Chloramine-T reagent was also observed in the determination of Ziram (tech.) (Table-3). It was found that 5 ml of 0.1 N Chloramine-T reagent gives accurate results. Same result was also obtained in the determination of other fungicidal samples.

Effect of Concentration Of Acetic Acid is as follows. Keeping reaction time, amount of Ziram (tech.) and concentration of Chloramine-T as constant, the concentration of acetic acid 5% to glacial was varied and the results were noted (Table-4). The dilute solutions of acetic acid were obtained by mixing distilled water in glacial acetic acid. As indicated in the table, glacial acetic acid gives quantitative and stoichiometric results with Ziram. The same results were obtained in case of other dithiocarbamate compounds. Reaction was also carried out in the absence of glacial acetic acid; the results are inaccurate and concordant values were not obtained.Effect of recovery due to the change in the volume of glacial acetic acid was also studied in the determination of Ziram (tech.) (Table-5). It was observed that 5 ml of glacial acetic acid gives best recovery. Same effect was also noted in the estimation of other fungicidal samples. This amount of glacial acetic acid was recommended for further estimations.

Effect of Temperature is discussed here. Keeping all other conditions constant, the reaction temperature was varied from 0°C to 100°C and the recovery of Ziram (tech.) was calculated (Table-6). It was observed that the reaction was completed within 10 minutes at room temperature (27°C). The heating of the reaction mixture gives inaccurate results. Since the reagent decomposes on heating, the reaction is carried out at room temperature. However, if the reaction temperature is lowered to freezing point (DOC) the reactivity of the reagent is retarded. At the lowest temperature there is no reaction.

IV. Conclusion

The current study shows that the survey of literature reveals that Chloramine-T In acidic medium has not been used for the determination of dithiocarbamate compounds, either in technical form or in their formulations. In the present work, a quick and convenient method has been developed for the determination of some Dithiocarbomate compounds like Zinc dimethyl dithiocarbamate (Ziram), Tetramethyl thiuram disulphide (Thiram), Zinc ethylene bis dithiocarbamate (Zineb), Ferric dimethyl dithiocarbamate '(Ferbam) and Zinc diethyl dithio carbomate (ZDC) in technical form and in their formulations.

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