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A new method for the determination of dithiocarbamate fungicides using n-bromosuccinimide reagent

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ABSTRACT

A simple and convenient method has been developed for the determination of Dithiocarbamate fungicides e.g. Ziram, Thiram, Ferbam, Zineb and ZDC in technical form and in their formulations. Aliquots containing 1-5 mg of the sample were taken in a 100ml conical flask and 5ml of 0.02 N,N-Bromosuccinimide (NBS), 10ml of glacial acetic acid and 5ml of 4 N HCI were added to it. The contents were shaken well and allowed to react for prescribed time at room temperature. 5 ml of 10% potassium iodide was added to it and kept for a minute. The liberated iodine was titrated against 0.02 N standardised sodium thiosulphate solution using starch as indicator. A blank experiment was also run under identical conditions using all the reagents except the sample. By the calculation of coefficient of variation (C.V.) and standard deviation (SD) values, it becomes evident that the suggested method is reproducible and precise.

Key words: Dithiocarbamate fungicides, n-bromosuccinimide reagent.

INTRODUCTION

Dithiocarbamate fungicides are widely used against a variety of plant pathogenic fungi. Chiefly they are used for foliar sprays, soil treatment and protection of fruits, vegetables, ornamental and turf crops from a variety of fungal diseases. Due to their importance some compounds e.g. Ziram, Thiram, Ferbam, Zineb and ZDC (Zinc Diethyl Dithiocarbamate) have been selected for the present study. Ziram is mainly used in fungicidal control of brown rot, peach leaf curl and short hole in almonds and Peaches, whereas Thiram is mainly used in sprays for control of botrytis, cane spot rusts, scab and tulip, Zineb can be of great use on Zinc deficient soils and Ferbam is mainly used in control of apple scab. cebar apple rust, cranberry diseases, peach leaf curl and tobacco leaf curl. ZDC is used to control rusts, cobweb, potato blight and leaf spot. Because of great agricultural and pathogenic value of these compounds their estimation has widely been studied[1-7]. In the present paper we describe a simple and convenient method for the determination of above Dithiocarbamate fungicides with NBS reagent.

EXPERIMENTAL

N-Bromosuccinimide Solution (NBS, 0.02N) 356 mg. of NBS (CDH) was weighed accurately and dissolved in minimum Volume of warm water and the solution was made up to the mark with distilled water in 100 ml volumetric flask. The solution was standardised iodometrically. Since the reagent decomposes on storage, a fresh solution should be made before use.

Aqueous solution of sodium thiosulphate (0.02 N, BDH) copper sulphate (0.025N, GR,) Potassium iodide (10% Bakar analysed reagent), Hydrochloric acid (4N) and glacial acetic acid were also prepared.

Sample Solution

All the samples are accurately weighed and dissolved in minimum amount of glacial acetic acid in a 100 ml volumetric flask. Thiram was dissolved in dil. H_2SO_4 because it get precipitated in glacial acetic acid. The dissolved samples were then made up to the mark with distilled water to give 1 mg/ml concentration.

Procedure

Aliquots containing 1-5 mg of the sample were taken in 100 ml Erlenmeyer flask followed by the addition of 5ml of 0.02 N NBS reagent and the contents were shaken properly. 10ml of glacial acetic acid and 5ml of 4 N HCl was added to it and the flask was stoppered . The reaction mixture was allowed to stand at room temperature (25^0-30^0C) with occasional shaking for prescribed reaction time. After the reaction was over 5ml of 10% potassium iodide solution was added, contents were shaken properly and allowed to stand for a minute at room temperature. The reaction mixture was titrated against 0.02 N Sodium thiosulphate solution to starch end point. A blank experiment was also run under identical conditions using all the reagents except the sample. In the case of technical preparation the same procedure was applied. It was also observed that the excipients present in formulations do not interfere the determination.

Calculation

The amount of sample was calculated by the following expression.

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

where,

M= molecular weight of the sample

N=Normality of sodium thiosulphate solution.

B=Volume of sodium thiosulphate solution for Blank

S =Volume of sodium thiosulphate solution for sample

n=No. of moles of NBS consumed per mole of the sample

On the basis of percentage error of the value of SD and CV were also calculated (Table 1).

RESULTS AND DISCUSSION

The reaction conditions were established after studying the effect of variables such as reaction time, concentration and amount of NBS reagent, hydrochloric acid, glacial acetic acid and reaction temperature. The determination of Ziram, Zineb and ZDC needs 10 minutes time to complete the reaction whereas Ferbam require 15 minutes and Thiram 5 minutes respectively. Much more reaction time (Beyond described timing) does not improve the results. A lower reaction time (other than described) the recovery of the samples is lo because of the incomplete reaction. It was established that the prescribed concentration of the reagent, 0.02N was suitable for accurate results. A more cocentrated reagent, (0.02 N -0.20 N) does not have any effects on accuracy. A lower concentration (0.05 N-0.01N) gives inaccurate results because of incomplete reaction. It was found that recommended (4N) concentration and volume (5ml) of the acid is suitable for the reaction. A higher concentration (4-11N) is not useful. While studying the effect of reaction temperature, it was observed that the reaction was completed at room temperature (25°-30°C). On heating the reaction mixture it gives inaccurate results because of the decomposition of reagent. If the reaction is carried out at lower temperature (0°-3°C) the speed was much more retorted.

Results reported in Table 1 show that the suggested method is accurate, reproducible and precise, It can easily be adopted in an ordinary pharmaceutical laboratory. On the basis of molecularity and available literature, a possible course of reaction may be suggested for each Dithiocorbamate fungicides. Since isolation of the final reaction products and their identification has not been possible, it may be proposed that the compounds get oxidized to suitable corresponding products.

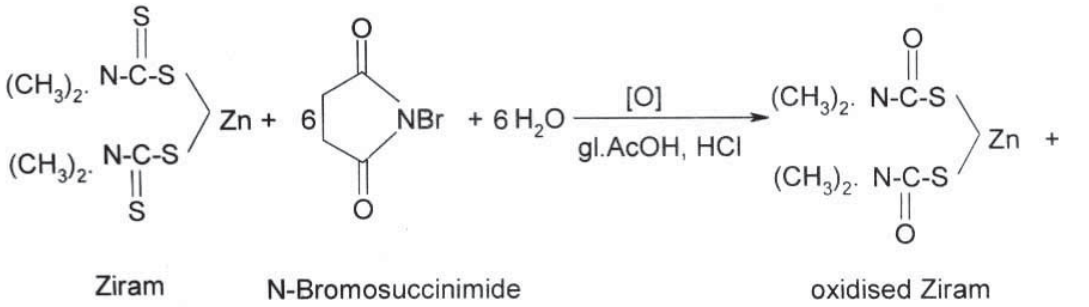
N-Bromosuccinimide has been reported to work as oxidising agent. It involves abstraction of hydrogen from C-H, O-H, N-H, or S-H bonds. Though the reaction involving addition of oxygen have also been observed. The reagent is more active in slightly acidic medium (4.5pH). In such type of reaction to give bromide ion and succinimide as products which do not interfere in the determination of organic

Table 1: Determination of the concentration of some dithiocarbamate fungicides in technical and in their formulation with 0.02 bromosuccinimide reagent in acidic medium

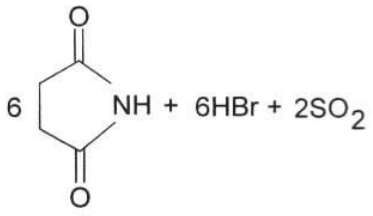
S. No.	Sample	Aliquots Taken (Mg)	Amount Present (Mg)	Reaction Time (Min)	Molecu- (No.)	Amount Obtained Calculation (Mg.)	Error (5)	Standard deviation Variation (SD) (Mg.)	Coeff- of (CV) (%)
1	Ziram	1.0	0.995			0.9854	-0.96	0.0022	0.2232
	teach-	3.0	2.985	10	6	2.9638	-0.71	0.0018	0.0607
	(99.5%)	5.0	4.975			4.9491	-0.52	0.0021	0.0424
	Ziram	2.0	1.60			1.5822	-1.11	0.0021	0.1327
	W,P.	4.0	3.20	10	6	3.1744	-0.80	0.0014	0.4410
	-(80%)	6.0	4.80			4.7760	-0.50	0.0016	0.0335
	Ziram	2.0	1.60			1.5824	-1.10	0.0019	0.1201
	Cuman-L	4.0	3.20	10	6	3.1731	-0.80	0.0021	0.0662
	(80%)	6.0	4.80			4.7722	-0.58	0.0025	0.0524
2.	Zineb	1.0	0.95			0.9406	-0.99	0.0032	0.3402
	tech-	3.0	2.85	10	6	2.8303	-0.69	0.0027	0.0954
	(95%)	5.0	4.75			4.7286	-0.45	0.0021	0.0444
	Zineb	2.0	1.50			1.4827	-1.15	0.0016	0.1079
	W.P.-	4.0	3.00	10	6	2.9763	-0.79	0.0016	0.1079
	(75%)	6.0	4.50			4.4806	-0.43	0.0015	0.0335
3	Ferbam	1.0	0.92			0.9114	-0.94	0.0027	0.2962
	tech	3.0	2.76	15	9	2.7382	0.79	0.0018	0.0657
	(92%)	5.0	4.60			4.5770	-0.50	0.0021	0.0459
	Ferbam	2.0	1.50			1.4832	-1.12	0.0018	0.1214
	W.P.	4.0	3.00	15	9	2.9766	-.078	0.0019	0.0638
	(75%)	6.0	4.50			4.4802	-0.44	0.0016	0.0371
4	Thiram	1.0	0.98			0.9701	-1.01	0.0036	0.3711
	tech	3.0	2.94	5	6	2.9757	-0.70	0.0018	0.0617
	(98%)	5.0	4.90			4.8799	-0.41	0.0021	0.0430
	Thiram	2.0	1.50			1.484	-1.17	0.0029	0.1956
	W.P.	4.0	3.00	5	6	2.9757	-0.81	0.0018	0.0605
	-(75%)	6.0	4.50			4.4797	-0.45	0.0024	0.0536
5.	ZDC	1.0	0.95			9.9406	-0.99	0.0016	0.1701
	Tech	3.0	2.82	10	6	2.7997	-0.72	0.0025	0.0883
	95%	5.0	4.75			4.7310	-0.40	0.0018	0.0380
	ZDC	2.0	1.00			0.9880	-1.20	0.0018	0.1822
	W.P.	4.0	2.00	10	6	1.9836	-0.82	0.0014	0.0706
	75%	6.0	3.00			2.9874	-0.42	0.0015	0.0502

compounds. There is abundant evidence that in polar media the oxidation reactions proceed via a positive halogen which is accepted to be the attacking species.

Possible course of Reaction : In the present paper we have estimated some fungicides and have given their possible reaction. Ziram is a zinc derivative having sulphur atom attached to carbon. On reaction with NBS regent this atom gets oxidised to corresponding oxidised product.

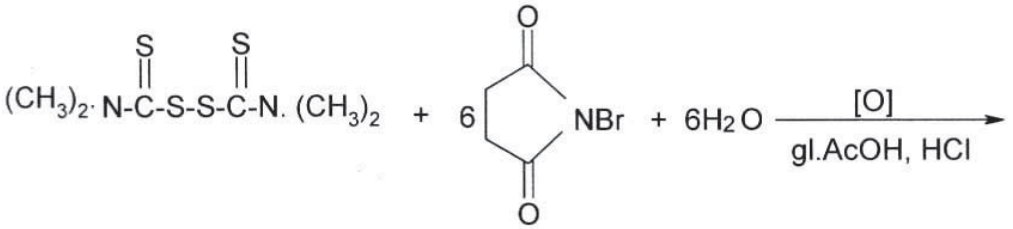


Ziram N-Bromosuccinimide oxidised Ziram

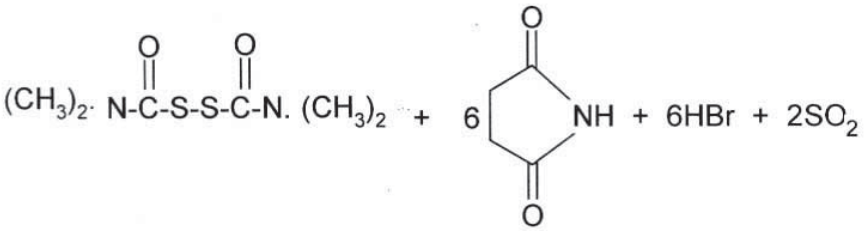


Succinimide

Next compound is Thiram which contains a disulphide linkage, It also gets oxidised to corresponding oxidised product.

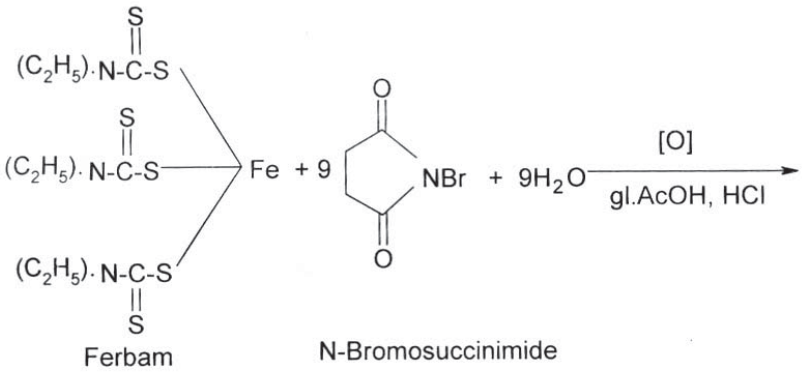


Thiram N-Bromosuccinimide

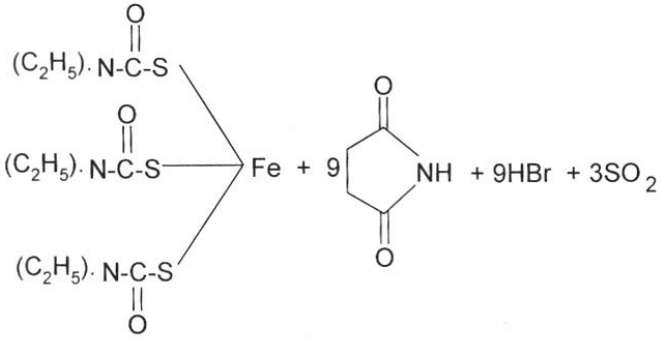


Oxidised Thiram Succinimide

Ferbam is still complex sulphur derivative of Iron. It consumer nine moles of the reagent and get oxidised.

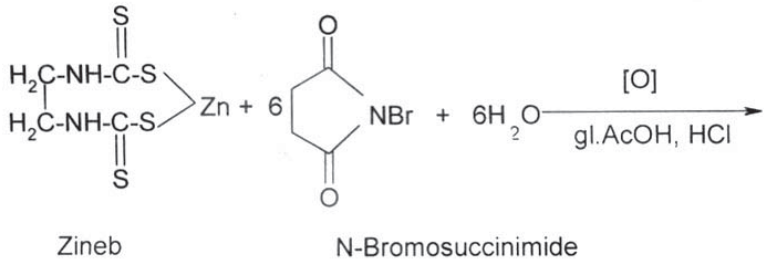


Ferbam N-Bromosuccinimide

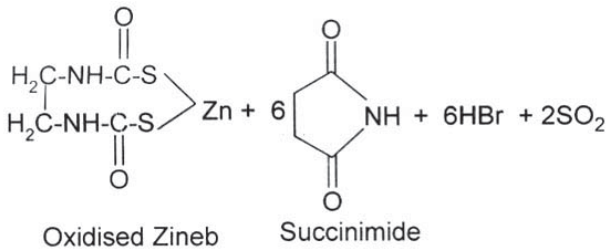


Oxidised Ferbam Succinimide

A similar behaviour is noted in Zineb.

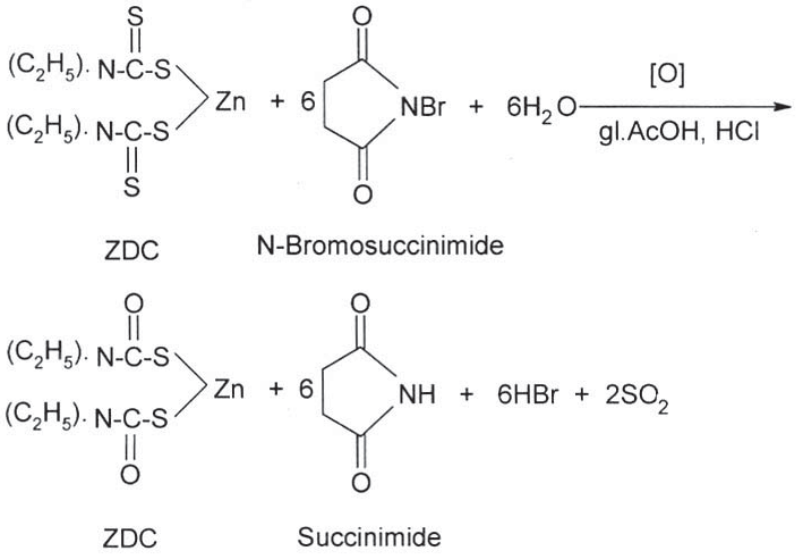


Zineb N-Bromosuccinimide



Oxidised Zineb Succinimide

ZDC is other zinc compound having ethyl substituted nitrogen atom. Without effecting other structure of the compound, it is oxidised at C-S bond.



The detailed mechanism of the oxidation of above compounds has not been studied. All the reactions are on the basis of molecularity oxidation and pattern.

REFERENCES

1. Tirmali, A.M. Pawar, D.R. J. Maharashtra Agricultural University, **5**(3): 248 (2000)
2. Konno, Nobuhiro, Sunoda, Mashi, Nakano. Kyoka, *Environ, Health Prv. Med.* **6**(1): 54 (2001).
3. Galazzi, R, Marucchini, G: Orena M: Zadra, C, Biorganic Medicinal chemistry **10** (4): 1019 (2002).
4. Mary, C.A. Nair, S.K. Saraswathy. P. J. *Tropical Agriculature* **39**(1): 73. (2001).
5. Vryzas, Zisis, Papadakis, Emmanouil N, Papadopoulon Mourkion, Euphemia, *J. Agric Food Chem*, **50**(8): 2220 (2000).
6. Chen, Xiajiao, *Nangyao Kexue Yu Guanli* **22**(4): 16 (2001).
7. Metthieu, C, Herboreteau, B. Anal, *Chim*, *Acta* **402**(1-2): 87 (1999).
8. Knio, K.M. Saad, A Dagher, S. *Food Addit. Contom*. **17**(5): 393 (2000)
9. Alder L, Heise S, Weber H. Fresenius *J. Anal. Chem*. **366**(8): 851 (2000).
10. Malik A.K, Chandra *C.J. Anal. Chem*. **56**(1): 225 (2003).
11. Tiwari, Ashok K. Dubey, B.K. Shukla I.C. *J. Indian Chem. Soc*. **80**: 717 (2003).