

Quantification of Ziram Fungicide Using Rhodamine-B Dye in Agricultural Samples

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ABSTRACT

A Sensitive Spectrophotometric method on the basis of effervesces releases CS_2 gas and decolouration of rhodamine-B dye is illustrated for persistence of Ziram fungicide; it liberates CS_2 in acid medium of hydrolysis. This CS_2 was absorbed in ethanolic solution of sodium hydroxide. The xanthate was thereafter prepared with potassium iodated and N-chlorosuccinimide, during the time free iodine is discharged. Librated iodine selectively oxidized rhodamine-B dye as a result of this pink colour of rhodamine-B dye is decolourise quantitatively. Its maximum absorbance (λ_{max}) obtained at 545nm. Molar absorptivity of Ziram solution $0.175 \text{ l mol}^{-1} \text{ cm}^{-1}$ and Sandal's sensitivity of Ziram solution $1.746 \times 10^{-3} \mu\text{g cm}^{-2}$ were obtained. The analytical parameters were analysis of the experimental results indicates that the proposed method is precise and accurate. The proposed method is freed obstacle of other ions and fungicides. The trust ability of the method was settled by parallel persistence versus reported method. The proposed method has been satisfactory applied to the persistence of Ziram fungicide in several agricultural sampling.

Keyword: Spectrophotometer, Ziram, rhodamine-B dye, potassium iodate, ethanol, sodium hydroxide

Introduction

From time to time being one of the speedily developing worldwide issues is fungicide remains which are present in essential cereals items cause's health issues on human beings¹. Estimation of fungicides to plants and animals hazard can be determined over limits present in the surroundings². It has been reported that causes of pathogenic moulds in radish, carrot, bottle gourd so that cultivator used fungicides practically in frequent for protecting of their crops³. It is appropriate to develop raise awareness to user for certainty that to known how

much quantity of fungicides present in their edible product⁴. Dithiocarbamates having thiocarbonyl group such as Ziram which are frequently used fungicides against wide scope of domestic, vegetable⁵. It was serious that fungicides act as neurotoxin and attack to nervous system of several animals and human beings⁶. The varieties of procedure have been used for the persistence of fungicide⁷. These including HPLC-MS, TLC, GC-MS, AAS, NMR, FTIR, IR, Polarography, Spectrophotometers, and several methods have also been reported for the persistence of fungicide⁸. The aim of proposed work is to develop simple, rapid and precise methods for analysing for the persistence of globally used Ziram fungicide at μg levels⁹. The developed method is based on acidic hydrolysis of Ziram fungicide to carbon disulphide gas, further react with ethanol sodium hydroxide to form xanthate, xanthate further react with potassium iodated to librated free iodine and this librated iodine selective oxidize Rhodamine-B dye pink colour to rhodamine-B colourless¹⁰. The proposed method has been satisfactory applied to the persistence of Ziram fungicide in several agricultural sampling¹¹.

Experimental Section

Apparatus: A Systronics UV-Vis spectrophotometer model no-104 with 2cm cubate and μH meter model no-335 were used for analytical parameters measurements.

Reagents: reagents and distilled water was used throughout the experiment.

Solution of Ziram: $2 \mu\text{g}$ Ziram was dissolved in 100ml of acetonitrile in volumetric flask.

Sodium hydroxide: 5g sodium hydroxide dissolved in 100ml ethanol.

Potassium iodated (Merck): 0.1M of 0.713g potassium iodate dissolved in 100 ml water.

N-chlorosuccinimide solution (Aldrich): 2.5g N-chlorosuccinimide dissolved in 100ml water in 250 ml volumetric flask volume was made up to the mark with water.

Acetate buffer solution prepared: 13.6g (1M) sodium acetate trihydrate dissolved in 80ml of water, solution pH was adjusted 3-6.8 with acetic acid.

Sodium salt of EDTA: 5g EDTA dissolved in 100ml water, 3g Meta phosphoric acid dissolved in 100ml water.

Procedure: Stock solution of Ziram prepared in acetonitrile was introduced in the digestion flask¹². Then $5\text{M H}_2\text{SO}_4$ was added drop wise to the above solution for hydrolysis during which CS_2 gas was librated, sodium hydroxide dissolved in 5ml of ethanol was taken as an absorbing for carbon disulphide gas. Experiment was completed for 4 min, the yellow colour appeared and diluted with water then added 2.5ml of Ziram and 2ml of acetate buffer solution then 2ml of potassium iodated, 1ml of N-chlorosuccinimide were added in above solution then shaken for few min thereafter 2ml of rhodamine-B dye was added pink colour of rhodamine-B dye is disappeared. The reaction mixture was neutralized slightly alkaline with 3% of metaphosphoric acid with sodium salt of EDTA solution, the absorbance was measured at 545nm (Fig.-2).

Citation: Kaushilya Maitry (2025). Quantification of Ziram Fungicide Using Rhodamine-B Dye in Agricultural Samples. Chemical Engineering. DOI: <https://doi.org/10.51470/CHE.2025.06.01.01>

Received on: January 07, 2025

Revised on: February 10, 2025

Accepted on: March 05, 2025

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Result and Discussion

Absorption Spectra of Ziram: Ziram is decomposed by acidic hydrolysis to give carbon disulphide which trapped in methyl potassium hydroxide to give potassium methyl xanthate, which is then titrated iodometrically¹³. The liberated iodine selectively reduced rhodamine-B dye pink colour complex to rhodamine-B dye colourless complex (Scheme-1); rhodamine-B showed maximum absorbance ($\lambda_{\max}$) at 545nm, Value of maximum absorbance ($\lambda_{\max}$) is decreases due to blue shift and intensity of absorbance ($E_{\max}$) is also decreases it is called hypo chromic shift because of colour of rhodamine-B dye is discharged shown in (Fig.-1).

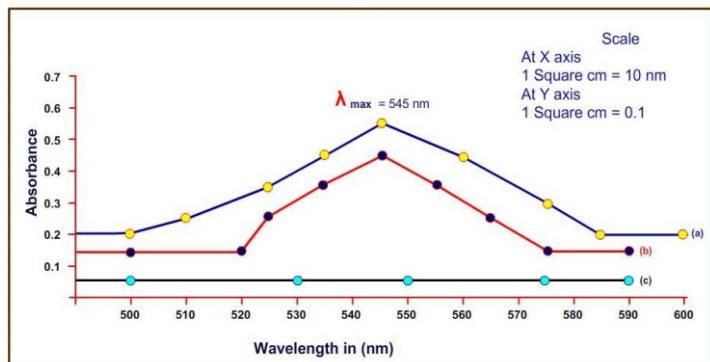


Fig.1-(a) Absorption spectra of Ziram before decolouration of rhodamine-B dye, (b) Absorption spectra of Ziram after decolouration of rhodamine-B dye, (c) Absorption spectra of reagent blank

Colour reaction:- The following steps as described in

(1) Liberation of carbon disulphide from Ziram fungicide by acidic hydrolysis at 25-35 °C temperature. (2) Formation of xanthate with the treatment of CS₂ with alcoholic sodium hydroxide. (3) Iodine is liberated as a result of reaction between potassium iodated act as oxidizing agent and the xanthate in the presence of N-chlorosuccinimide¹⁴. Potassium iodated has +5 oxidation states it changes into zero oxidation state in free iodine in step first. But in step second free iodine has zero oxidation state it changes into +1 oxidation state here iodine is selectively oxidized. (4) Formation of reduced rhodamine-B dye quinine structure through selective reduction reaction of rhodamine-B dye to formed benzenoid structure by liberated iodine (Scheme-1).

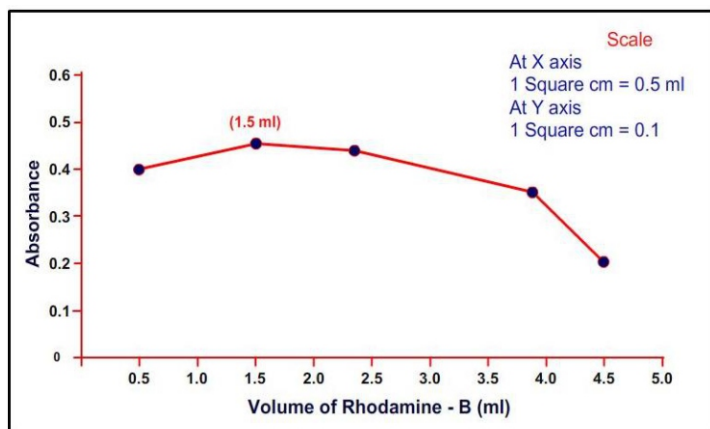
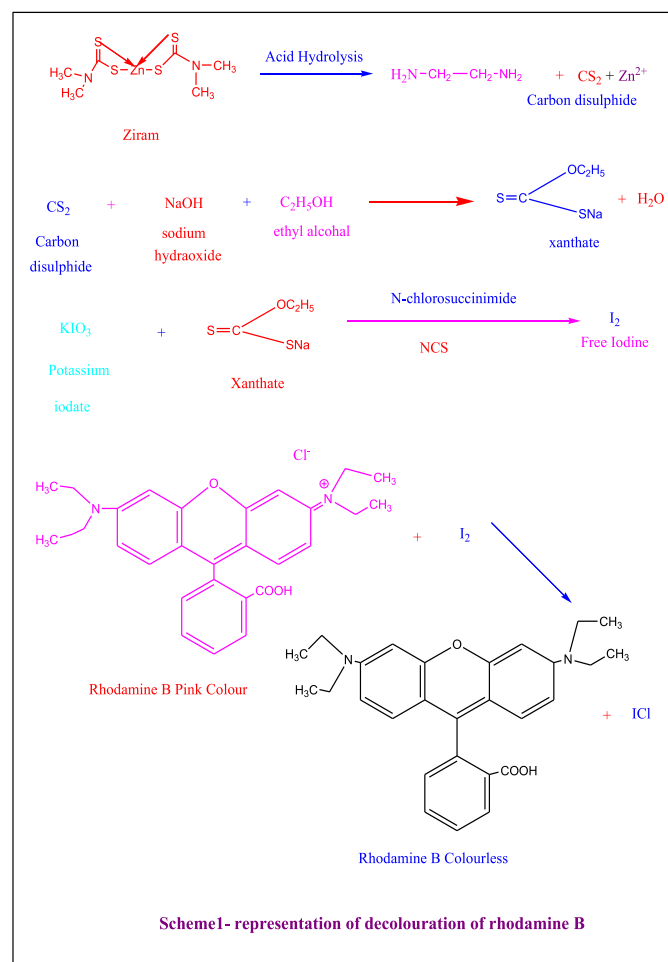


Fig.3-Effect of concentration of rhodamine-B dye 1.5ml (0.1g/1000ml) on absorbance of Ziram 2.4ml (2µg/30ml)



Calibration curve of Ziram fungicide:- This graph is plotted between concentration of Ziram (µg) and absorbance. A straight line is obtained. It follows Beer-Lambert's law at 10-2µg shown in (Fig.-2).

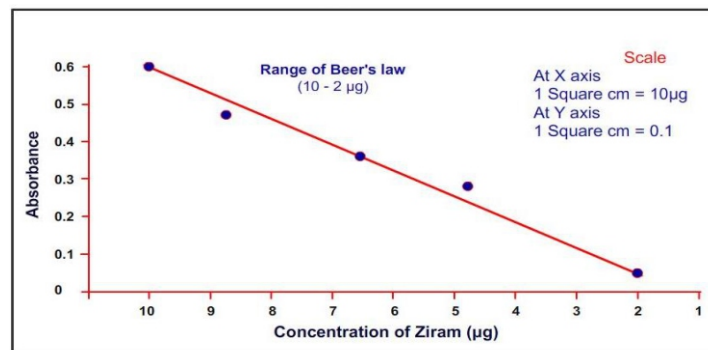


Fig.-2 Calibration curve of Ziram concentration level (2µg/30ml) with rhodamine-B dye (0.1g/1000ml)

Effect of concentration of rhodamine-B dye:- This graph is plotted between volume of rhodamine-B dye and absorbance. 1.5 ml (0.1g/1000ml) of rhodamine-B dye is required for decolourizing itself (Fig.-3).

Effect of sodium hydroxide:-This graph is plotted between volume of sodium hydroxide and absorbance. Volume of reagent concentration is required for decolourising rhodamine-B dye is 1ml (5g/100ml). It is responsible for maximum hydrolysis shown in (Fig.-4).

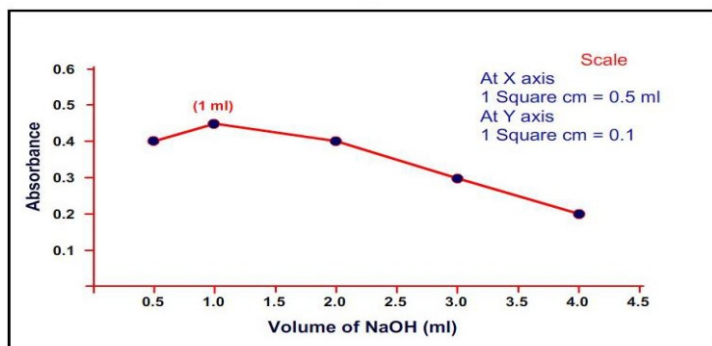


Fig.4-Effect of concentration of sodium hydroxide 1ml(5g/100ml) on absorbance of ziram (2µg/100ml) with rhodamine-B dye (0.1g/1000ml)

Effect of concentration of potassium Iodated:-This graph is plotted between volume of potassium iodated on x-axis and absorbance on y-axis. 1.5 ml (0.713g/100ml) of potassium iodated is sufficient for decolourising rhodamine-B shown in (Fig.-5).

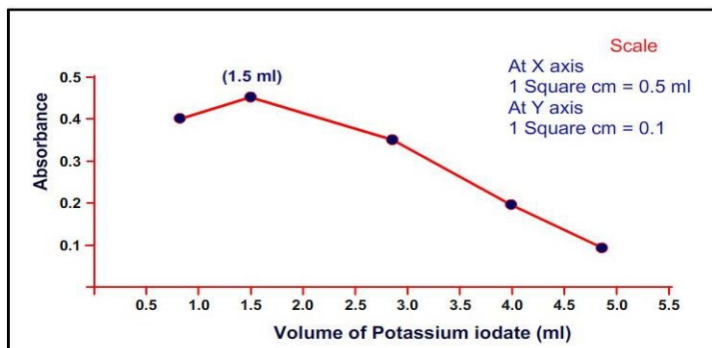


Fig.5- Effect of the concentration of potassium iodate 1.5ml (0.713g/100ml) on absorbance Ziram (2µg/30ml)

Effect of pH :-This graph is plotted between pH on x-axis and absorbance on y-axis. PH 3-6.8 is sufficient for decolourising rhodamine-B dye and acetate buffer solution maintaining the above pH of the system shown in (Fig.-6).

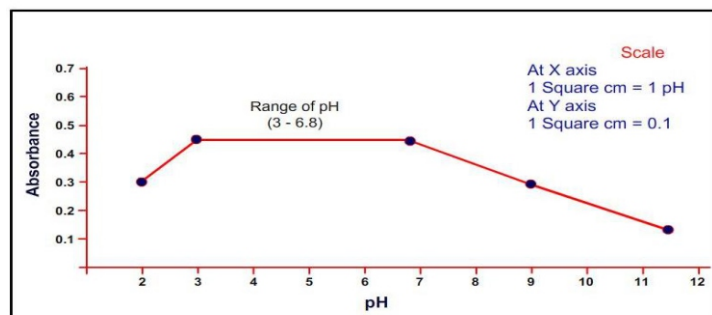


Fig.6-Effect of pH on absorbance of ziram (2µg/30ml) with rhodamine-B dye (0.1g/1000ml)

Effect of time and temperature:-This graph is plotted between temperature and absorbance. It has observed that the hydrolysis of Ziram fungicide was studied at slightly acidic condition. The maximum hydrolysis of the decoloured reaction was observed. The 25-35°C temperature is sufficient for decolourising rhodamine-B dye. It was also found that a required time period is 5min for the complete decolouration of solution after dilution to 10ml water and formed product was stable for several hours shown in (Fig.-7).

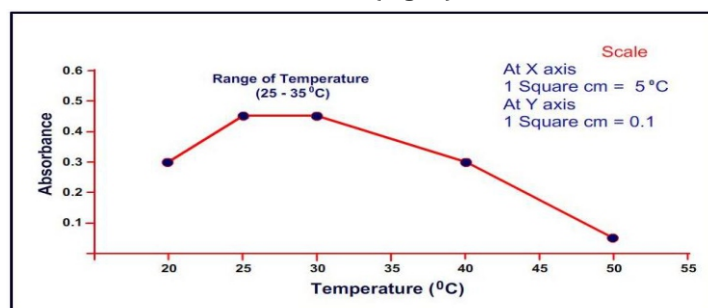


Fig.7-Effect of temperature on absorbance of Ziram (2µg/30ml) with rhodamine-B dye (0.1g/1000ml)

Effect of Ziram Concentration:-This graph is plotted between volume of Ziram and absorbance, the 2.4ml volume of Ziram is enough for decolourising rhodamine-B dye shown in (Fig.-8).

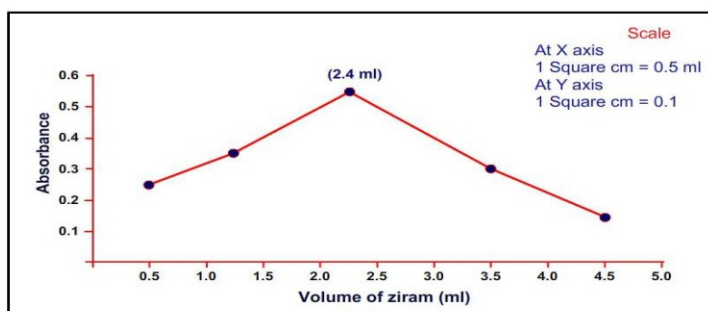


Fig.8-Effect of concentration of Ziram 2.4ml (2µg/30ml) on absorbance with rhodamine-B dye (0.1g/1000ml)

Differentiation with reported methods:-The differentiation between reported method and proposed method, reported method are less sensitive, highly costly, it has extra steps hydrogen sulphide generation but proposed method is highly sensitive, low cost and can be applied to real sampling¹⁵(Table-1).

S. No.	Reported Method	Max (nm)	Beer's Law range	Sensitivity	Reference
	Diphenylcarbazone	520	0.12-0.9	0.08 $\mu\text{g/ml}$	8
	Methylene blue method	655	3-22	6.8 $\times 10^3$	9
	Benzyl mercaptan	430	14-150	-	5
	Quantification of Ziram fungicide by rhodamine B dye method	545	10-2 μg	1.746 $\times 10^{-3}$ μgcm^{-2}	Present method

Effect of foreign species:-The fungicide were evaluated from several agricultural sampling and presence other fungicides, pesticides and commons ions does not interfere in the procedure but hydrogen sulphide and some ions like Cu^{2+} , Hg^{2+} , Fe^{3+} interfere in the persistence of Ziram, interference of other ions is inhibited by absorption in lead acetate¹⁶ (Table -2).

Foreign Species	Tolerance Limit($\mu\text{g/ml}$)	Foreign Species	Tolerance Limit($\mu\text{g/ml}$)
Na^+ , K^+ , Ba^{2+} , Ca^{2+}	2000	Sulphate	380
Zn^{2+} , Fe^{3+} , Al^{3+} , Cu^{2+} , Hg^{2+}	400	Phosphate	20
Thiram, dibam	1100	Oxalate	10
DDT, BHC	950	Citrate	25
Cl^- , Br^- , F^-	500,100,500	Meta bisulphite	30

Analytical parameters characteristics of proposed method (Table-3)

Analytical Parameters	Ziram fungicide
(λ_{max})	545
Beer's law range (μg)	10-2
Molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$)	0.175
Sandal's sensitivity (μgcm^{-2})	1.746 $\times 10^{-3}$
Standard deviation	7.3086, 0.4020771
Correlation coefficient	-0.986
Slope (m)	-0.06875
Intercept (C)	on the x axis 2.5 , on the y axis 0.670
Limit of detection ($\mu\text{g/mL}$)	-318.920
Limit of quantification ($\mu\text{g/mL}$)	-58.4839
Precision	3.4166 $\pm$ 8
Accuracy	0.004040%
Absolute error	+ 0.004
Relative error	0.004040
Relative standard deviation	1.1244%, 1.20635%

Application of Ziram fungicide in various samples:-To check the credibility of proposed method and persistence of Ziram in 10ml agricultural running water were taken from the region where Ziram has been sprayed such as Pihrid, Kalami¹⁷. These agricultural sampling were found to be freed Ziram, known amount of ziram is added in agricultural running water sample taken in 50ml beaker 1.5ml of concentrated sulphuric acid mixed and pH maintained at 3-6.8; these sampling were analyzed through proposed method¹⁸. Several vegetables, potato, lettuce, green leafy vegetables, wheat were collected from agricultural region where Ziram has been sprayed. 300g of tomato, potato, cabbage, taken and blended in a mixture; known amount of ziram is added and kept some days; the sample was digested with 100ml of sulphuric acid. The mixture was filtered and analysed by proposed method¹⁹ (Table-4).

Samples	Fungicide Added (μg) A	Fungicide Found (μg) B	Recovery % $(\text{B/A}) \times 100$
Ziram	4	3.02	$(3.02/4) \times 100 = 75.5$
Rice	7	6.04	$(6.04/7) \times 100 = 86.28$
Wheat	4	2.89	$(2.89/4) \times 100 = 72.25$
	7	5.20	$(5.20/7) \times 100 = 74.28$
Lettuce	4	3.07	$(3.07/4) \times 100 = 76.75$
	7	5.09	$(5.09/7) \times 100 = 72.71$
Radish	4	2.97	$(2.97/4) \times 100 = 74.25$
	7	5.43	$(5.43/7) \times 100 = 77.57$
Carrot	4	3.01	$(3.01/4) \times 100 = 75.25$
	7	5.05	$(5.05/7) \times 100 = 72.14$
Cabbage	4	2.78	$(2.78/4) \times 100 = 69.5$
	7	5.26	$(5.26/7) \times 100 = 75.14$
Brinjal	4	2.45	$(2.45/4) \times 100 = 61.25$
	7	5.33	$(5.33/7) \times 100 = 76.14$
Papaya	4	2.79	$(2.79/4) \times 100 = 69.75$
	7	5.34	$(5.34/7) \times 100 = 76.28$
Agricultural	4	2.81	$(2.81/4) \times 100 = 70.25$
Polluted water	7	5.62	$(5.62/7) \times 100 = 80.28$
Drinking water	4	3.03	$(3.03/4) \times 100 = 75.75$
	7	5.07	$(5.07/7) \times 100 = 72.42$

Conclusion

The proposed method is on the basis of use of reagent rhodamine-B dye for the persistence of ziram. Proposed method offers simple sensitive, selective and affordable. This developed method is much better than other sophisticated equip mental methods. Impact on community to spread awareness, amongst community, that have this fungicide of harmful to human health and environment. To give suggestion to the local farmers for tempted used for this fungicide. In present scenario development of method for analysis of any harmful chemical is important technique, through many sophisticated instrumental methods are available but this classical method have their own importance forever. Significance of method was many analytical parameters have been studied, results as approved by statics analysis accuracy and precision are determined. Results of application reflect the reliability to the method. In the development method no any harmful, chemicals were used; the proposed method is reliable, precise, affordable and easily available in small laboratory then other sophisticated instrumental reported method.

Acknowledgement

I express my gratitude to Principal Dr. B. D. Jangade Govt. Vedram College Malkharoda, District-Sakti (C.G.), and India. I am also thankful to University Grant Commission, New Delhi for providing laboratory facilities and financial assistance to carry out this experiment.

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