

SPECTROPHOTOMETRIC DETERMINATION OF ZIRAM FUNGICIDE USING MALACHITE GREEN IN AGRICULTURAL SAMPLES

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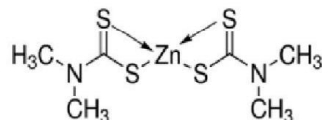
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A spectrophotometric determination of ziram is based on the dissociation of dithiocarbamate complex of zinc react thiocyanate and malachite green to formed wine red colour solution. The reaction medium was maintained at pH 4. Its maximum absorbance (λ_{\max}) at 565 nm, the reaction medium was carried out at 30°C temperatures, the wine red colour solution were stabilized by gelatine powder. The molar absorptivity was found to be $9.74 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$. Sandell's sensitivity was calculated to be $5 \times 10^{-3} \mu\text{g/cm}^2$. The statistical treatment of the experimental results indicates the method is precise and accurate. The method has been successfully applied to the determination of ziram fungicide in various agricultural samples.

KEYWORDS : Spectrophotometric; ziram fungicide, potassium thiocyanate, malachite green, gelatine powder, sodium acetate trihydrate, acetic acid.

INTRODUCTION

Ziram is known as dithiocarbamate fungicide commonly used against plants pathogenic fungi; it is used widely because of high efficiency for the control of fungal and bacterial micro-organism [1]. It has low production cost and mammalian acute toxicity, ziram is not highly toxic, but short-term exposure can cause eye, respiratory and skin irritation, shot-hole, brown rot, scab, downy mildew, Long-term exposure can be caused by physiological changes in the cardiovascular system in human being, non systemic fungicide [2]. Ziram is used as pulp and paper manufacturing; wood preservatives or it is used as clinically for the treatment of chronic alcoholism and anticancer and antitoxic drug agent [3]. Ziram is one of the most commonly used fungicides in agriculture; the ziram fungicides are most frequently detected and monitoring around the world show that are the most and they exhibit the highest frequency is exceeding the maximum residue limits (MRLs) [4].



Structure of ziram

Sources of ziram : The major sources of ziram fungicides is present in various samples like running water, ground water, pond water, soil, agricultural waste water, biological samples like blood, urine, vegetables like tomato, potato, cucumber, spinach, cabbage, problems for public health, cereals, environmental, air, are the application of pesticides and fungicides and increasing the yield of agricultural products [5].

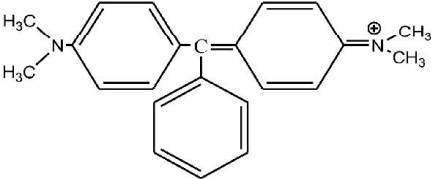
Brief review of the literature : In recent years, pollution of surface waters by such fungicide substances cause's challen-ging agricultural problems. Therefore, the aim of scientists is to face the challenge of protecting clean agricultural field from pollution by these pesticide substances and find new analytical methods for determination of these hazardous materials in agricultural samples [6]. It protected different types of diseases in plants and crops, vegetables cucurbits and early blight of tomatoes and potatoes it applied in agriculture and horticulture as a protectant on fruits, seed treatment on maize, cotton, cereals and a vulcanizing agent in the rubber industry, compound is as a bird and rodents repellent, packaging, adhesives, and textiles, materials ziram is often marketed as a wettable powder or as granules [7].

Toxicity and toxic level of ziram : Eye irritation, irritation of the skin, nose, eyes and throat, reductions in fertility, increase in the number of chromosome changes in bone-marrow, thyroid enlargement, adverse effects on body weight and retarded testicular development etc. [8]. Higher dose 90 mg/kg, moderate doses of ziram (50 mg/kg), lower dose of 10 mg/kg had no effect on reproduction [9].

Established work based on highly sophisticated instruments and Spectrophotometric: 1. Comperison between Three Chromatographic (GC-ECD, GC-PFPD and GC-ITD_MS) Methods and UV-Vis Spectrophotometric Method for the Determination of Dithiocarbamates in Lettuce (Ionara R. Pizzutti, Andre'de kok,^b (2016). 2. Determination of dithiocarbamate pesticides in occupational hygiene sampling devices using the isoctane method and comparison with an automatic thermal desorption (ATD) method Matthew R. Coldwell, Ian Pengelly, (2015). 3 Simple and Excellent Selective Chemiluminescence-Based CS₂ On-Line Detection System for Rapid Analysis of Sulfur-Containing Compounds in Complex Samples (Runkun Zhang, Gongke Li,* and Yufei Hu*2015). 4. Validation of a GC-MS method for the estimation of dithiocarbamate fungicide residues and safety evaluation of mancozeb in fruits and vegetables Sumaiyya Mujawar a, 1, Eddie Fonseca b, 1, Kaushik Banerjee (2014). 5. Comparison Between Three Chromatographic (GC-ECD, GC-PFPD and GC-ITD-MS) Methods and a UV-Vis Spectrophotometric Method for the Determination of Dithiocarbamates in Lettuce *Ionara R. Pizzutti,*, a André de Kok, b Rosselei C. (2016).*

Apparatus : A systronics UV- Vis spectrophotometer 104 with 2 cm matched silica cells was used for all spectral measurements. Systronics pH meter model No. 335 was used for pH measurement.

Table 1. Materials and Chemical Formula

Malachite green	
Potassium thiocyanate	KCNS
Sodium Acetate	CH ₃ COONa
Acetic acid	CH ₃ COOH

Reagents : All reagents were of analytical reagent grade and double distilled deionised water was used throughout the experiment.

Stock solution of ziram : 0.025 gm of solution of ziram in 100 ml distilled water; the required working standard solutions were prepared by appropriate dilution of the stock.

Potassium thiocyanate and malachite green : 5 gm of potassium thiocyanate in 100 ml distilled water, 10 mg malachite green dissolved in 100 ml distilled water.

Gelatine powder : 1 gm gelatine powder dissolved in hot water and makeup 100 ml distilled water.

Sodium acetate and acetic acid : 2M solution was prepared by dissolving 27.2 gm of sodium acetate trihydrate in 100 ml distilled water, 12 ml acetic acid in 100 ml distilled water.

Prepared buffer solution : 2 ml sodium acetate and 2 ml acetic acid are mixed.

Procedure : A known amount of working standard solution of ziram prepared in distilled water was taken in conical flask added 2 ml sodium acetate and 2 ml acetic acid then added 2.5 ml of KCNS then added 5 ml of malachite green then added 1 ml of gelatine solution stirring and shaking. The absorbance of the formed wine red colour solution was measured at 565 nm against the reagent blank. The concentration of ziram content was established from the calibration graph.

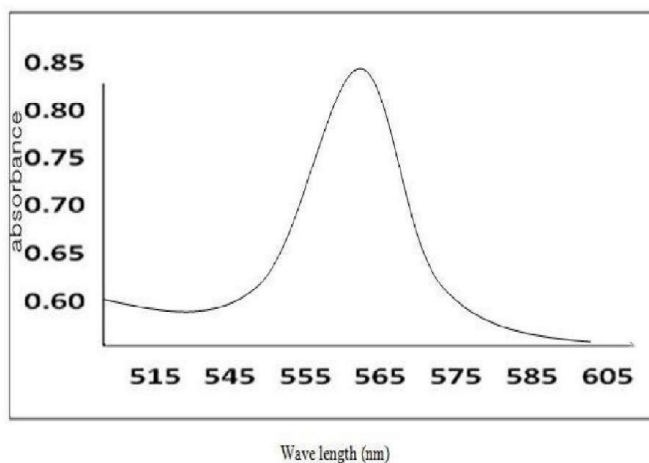


Fig. 1. Absorption spectra of ziram fungicide

RESULTS AND DISCUSSION

Table 2 and fig. 1 Absorbance of ziram fungicide and absorption spectra of ziram fungicide

S. No.	Concentration of ziram	Absorbance
1	1ml	0.600
2	2ml	0.650
3	3ml	0.700

4	4ml	0.750
5	5ml	0.800
6	6ml	0.850
7	7ml	0.870

Effect of pH curve of ziram fungicide: It was found that the complex was obtained at buffer in the pH range 1 to 4. Initially concentration of ziram increases with upto pH 4 after constant. At high pH the absorbance of colour system was decreased [10].

Effect of reagent concentration :

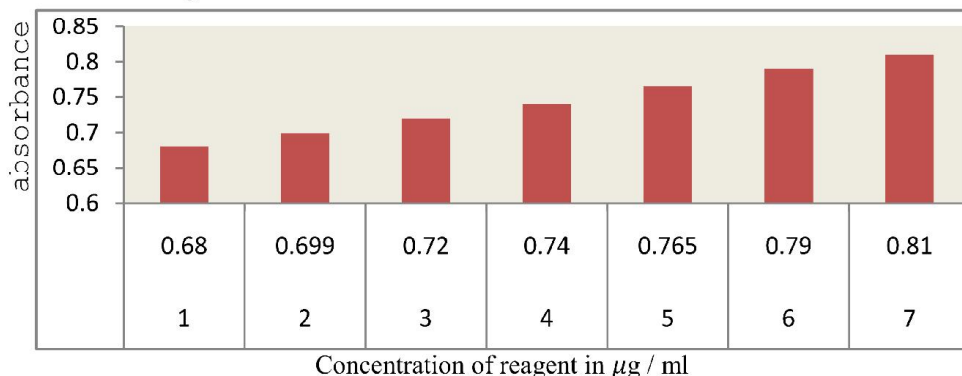


Fig. 2. Effect of reagent concentration

The concentration of reagent increases as well as absorbance also increases [11].

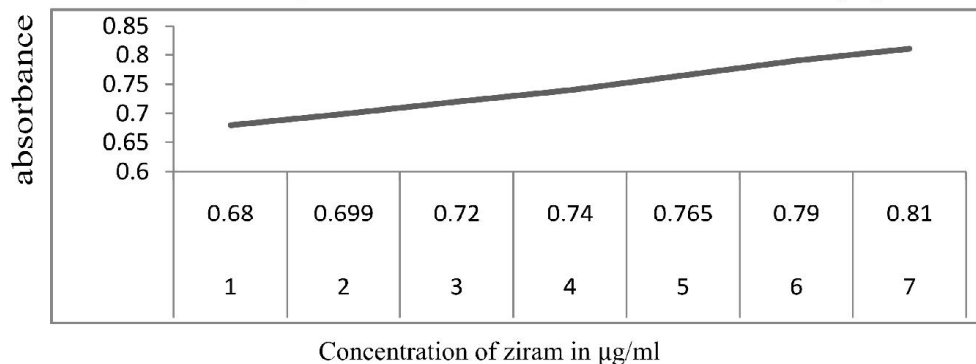


Fig. 3. Calibration curve

Effect of temperature : The reaction medium was carried out at 30°C temperature. The absorbance of ziram solution increases as well as temperature but above 30°C absorbance of ziram solution decreases [11].

Comparison with other methods : The comparison between reported method and developed method the reported method are less sensitive, its required hydrogen sulphide generation by methylene blue and benzyl mercaptan method requires addition extraction step; the present method is highly sensitive and can be applied to real sample in the presence of ziram [12].

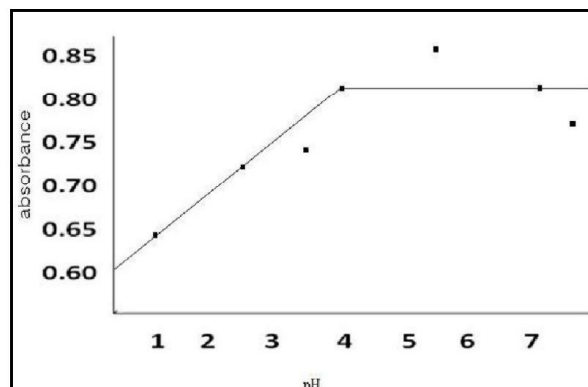


Fig. 4. Effect of pH of ziram fungicide

Table 3. comparison with other methods

S. No.	Method	Max (nm)	Beer's Law range	Sensitivity	Reference
1	Diphenylcarbazone	520	0.12.9	0.08 $\mu\text{g}/\text{ml}$	8
2	Methylene blue method	655	3-22	6.8×10^3	9
3	Benzyl mercaptan	430	14-150	-	5
4.	Malachite green	565	0.68-0.81	$9.74 \times 10^5 \text{ mol}^{-1} \text{ cm}^{-1}$	Present method

Effect of foreign species : The fungicides were evaluated from various samples and presence other commons ions does not interfere in the procedure but hydrogen sulphide and some ions like Cu^{2+} , Hg^{2+} , Fe^{3+} interfere in the determination of ziram; eliminated by its absorption in lead acetate, absorbance interfered in the determination of ziram [13].

1. Determination of ziram fungicides in polluted water : To check the validity of the method and determination of the ziram fungicide in 20 ml agricultural water sample were taken from the fields where ziram has been sprayed as fungicide [14]. These samples were found to be free from ziram, known amount of ziram is added in agricultural water sample taken in 50 ml beaker 1.5 ml of concentration HCl mixed and pH maintained at 4, these samples were analyzed through recommended procedure [15].

2. Determination of ziram in vegetable and grain samples : Various samples of vegetables, potato tubers, lettuce, green leafy vegetables, and wheat were collected from agricultural field where ziram, has been sprayed [16]. 300 mg of tomato, potato tubers, cabbage, taken and blended in a mixture; known amount of ziram are added and kept some days, sample was digested with 100 ml of 1 : 1 HCl; the mixture was filtered and analysed by recommended procedure [17].

CONCLUSION

The present method for the determination of ziram is a simple sensitive and selective. A spectrophotometric determination of ziram is based on the dissociation of dithiocarbamate complex of zinc react thiocyanate and malachite green to formed wine red colour solution. The reaction medium was maintained at pH 4, its maximum absorbance (λ_{max}) is 565 nm, the molar absorptivity was found to be $9.74 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ Sandell's sensitivity was calculated

to be $5 \times 10^{-3} \mu\text{g}/\text{cm}^2$. The reaction medium was carried out at 30°C temperature. The method is compared with the reported method by V.K. Gupta *et al*, 1998. The method is successfully applied to the determination of ziram fungicides in the agricultural samples.

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REFERENCE

1. Stokholma, Pathogen Michaela S., Wulff, Ednar G., Zidac, Elisabeth P., Thioc, Ibié G., Néyac, James B., Soallac, Romain W., Glazowska, Sylwia E., Andresena, Marianne, Topbjergd, Hcnrik B., Boeltd, Birte, Lunda, Ole S., DNA barcoding and isolation of vertically transmitted ascomycetes in sorghum from Burkina Faso : *Epicoccum sorghinum* is dominant in seedlings and appears as a common root pathogen, **191**, 38–50 (2016).
2. Chatterjee, Sukumar, Pillai, Ajay, Gupta, V.K., *School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, Chhattisgarh* 492010, *India* Spectrophotometric determination of mercury in environmental sample and fungicides based on its complex with *o*-carboxy phenyl diazoamino *p*-azobenzene, *Talanta*, **57**, 461–465 (2002).
3. Yan1, Huiqiong, Chen1, Xiuqiong, Feng2, Yuhong Xiang2, Fei, L., Jiacheng, Shi1, Zaifeng, Wang1, Xianghui, Lin1, Qiang, Yan1, Huiqiong, Chen1, Xiuqiong, Feng2, Yuhong, Xiang2, Fei, Li2, Jiacheng, Shi1, Zaifeng, Wang1, Xianghui, Lin1, Qiang, Modification of montmorillonite by ball-milling method for immobilization and delivery of acetamiprid based on alginate/exfoliated montmorillonite nanocomposite, **73**, 1185–1206 (2016).
4. Kanchi, S., Singh, P., Bisetty, K., Dithiocarbamates as hazardous remediation agent : A critical review on progress in environmental chemistry for inorganic species studies of 20th century Department of Chemistry, Durban University of Technology, P.O. Box 1334, Durban 4000, *South Africa Arabian Journal of Chemistry*, **7**, 11–25 (2014).
5. Singh, Baljit, Sharma, D.K. and Dhiman, Abhishek, Environment friendly agar and alginate-based thiram delivery system, *Toxicological & Environmental Chemistry*, Vol. **95**, No. **4**, 567–578, (2013).
6. European Commission (EC), SEC (2007) 1411, Monitoring of pesticide residues in products of plant origin in the European Union, Norway, Iceland and Lichtenstein (2005) EC, Brussels, Belgium, (2007). Mosby, USA, (1998).
7. Rastegarzadehn, S., Abdali, Sh., Colorimetric determination of thiram based on formation of gold nanoparticles using ascorbic acid, *Talanta*, **104**, 22–26 (2013).
8. European Commission (EC), SEC (2007) 1411, Monitoring of pesticide residues in products of plant origin in the European Union, Norway, Iceland and Lichtenstein (2005) EC, Brussels, Belgium, (2007).
9. Edwards, I.R., Ferry, D.G. and Temple, W.A., Fungicides and Related Compounds, In *Handbook of Pesticide Toxicology*, Volume **3**, Classes of Pesticides. Wayland J. Hayes and Edward R. Laws (eds.) Academic Press, NY (1991).
10. Raman, Jegannathan Kenthorai, Edgard Gnansounou Furfural production from empty fruit bunch – A biorefinery approach *Industrial Crops and Products*, **69**, 371–377 (2015).
11. Hernández-Olmos, M. A., Agüí, L., Sedeño, P. Yáñez, Pingarrón, J. M., *Electrochim. Acta*, **46**, 289–296 (2000).
12. Kesari, R., Gupta, V.K., *Talanta*, **45**, 1097-1103 (1998).
13. Chem, D., Cui, Q. C., Yang, H., Dou, Q.P., *Cancer Res.*, **66** 10425 (2006).
14. Sharma, Vaneet K., Aulakh, Jatinder S., Bansal, Sonam, Malik, Ashok K. and Mahajan, Rakesh K., *Intern. J. Environ. Anal. Chem.*, Vol. **84**, No. **14-15**, pp. 1105-1110 (10-12-2004).
15. López-Fernández, Olalla a, b, Barrosoa, M. Fátima, Fernandes, Diana M. c, Rial-Oterob, Raquel, Simal-Gándara, Jesús b, Morais, Simone a, Nouws, Henri P.A. a, Freire, Cristina c, Delerue-Matos,

- Cristina, Voltammetric analysis of mancozeb and its degradation product ethylenethiourea, *Journal of Electroanalytical Chemistry*, **758**, 54–58 (2015).
16. Vettorazzi, G., Almeida, W.F., Burin, G.J., Jaeger, R.B., Puga, F.R., Rahde, A.F., Reyes, F.G., Schwartsman, S., *Teratog. Carcinog. Mutagen*, **15**, 313 (1995).
 17. Abakerli, R.B., Sparrapam, R., Sawaya, A.C.H.F., Luiz, A.J.B., Galvao, T.D.L., Martins, D.S.Y., Yamanishi, O.K., Toledo, H.H.B., *Food Chem.*, **188**, 71 (2015).
 18. Cereser, C., Boger, S., Parvaz, P. and Revol, A., Thiram-induced cytotoxicity is accompanied by a rapid and drastic oxidation of reduced glutathione with consecutive lipid per oxidation and cell death, *Toxicology*, **163**, 153-162 (2001).
 19. Donald, E.H.F., *Chemistry of the Pesticides*, **3rd Ed**, pp 294-297, Van Nostrand, New York, (1955).
 20. Petrascu (S. Petrascu, *et al.* (1986), Rao, A.L.J. *et al* (1989) and Rosentha *et al* (1953).
 21. Rosenthal, J., Carsor, R. L. and Stanley, F.L., *J. Assoc. Off. Agric. Chem.*, **36**, 1170 (1953).
 22. Martin, H., Pesticide Manual, Basic Information on the Chemicals Used as Active Components of Pesticides, firsted, *British Corporation Protection Council*. (2011)
 23. Health & Consumer Protection Directorate-General, Quality control procedures for pesticide residue analysis, document No. SANCO/10232/(2006). European Commission, Brussels (2006).
 24. Malik, A. K., Rao, A. L. J., Spectrophotometric determination of ziram, ferbam and zincb using diphenylcarbazone. *Talanta*, **8**, 941-944 (1991).
 25. Clarke, D. G., Baum, H., Stanley, E.L., Hester, W.E., *Anal. Chem.*, **23**, 1842 (1951).
 26. European commission, Directorate-General for Health and Food Safety; Guidance Document on Analytical Quality Control and Method Validation Procedures for Pesticides residues Analysis in Food and Feed, SANTE (2015).



