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## FOURTH DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF FUNGICIDE ZIRAM (ZINC(II) DIMETHYLDITHIOCARBAMATE) IN COMMERCIAL SAMPLES AND WHEAT GRAINS

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A procedure has been developed for the direct fourth derivative spectrophotometric determination of zinc(II) dimethyldithiocarbamate by converting it into its copper(II) dimethyldithiocarbamate complex, which is then dissolved in Triton X-100. Beer's law is obeyed over the concentration range 0.5–30 µg/mL in the final solution. Various parameters such as the effect of pH and the interference of a number of ions on the determination of Ziram have been studied in detail. The method is sensitive and can be used for the determination of Ziram in commercial samples like Zirax and Ziron containing Ziram and from wheat grains.

*Keywords:* Derivative spectrophotometry; Ziram; Copper(II) sulphate; Commercial samples

### INTRODUCTION

Ziram (zinc(II) dimethyldithiocarbamate, [(CH<sub>3</sub>)<sub>2</sub>NCS<sub>2</sub>]<sub>2</sub>Zn]) (Fig. 1) is an agricultural dithiocarbamate fungicide used on a wide variety of plant fungi and diseases. It may be applied to the foliage of plants, but it is also used as a soil or seed treatment. Ziram is used primarily on almonds and stone fruits. It is also used as an accelerator in rubber manufacturing, packaging materials, adhesives, and textiles. Another use of the compound is as a bird and rodent repellent. Ziram is often marketed as a wettable powder or as granules.

Analytical methods are required for monitoring pesticides in various environmental samples. A number of methods are currently available in the published literature for the determination of dithiocarbamate fungicides. In one such method, Ziram is determined on the basis of its decomposition by hot mineral acids to the corresponding amine and carbon disulphide, which is then absorbed in methanolic potassium hydroxide solution,

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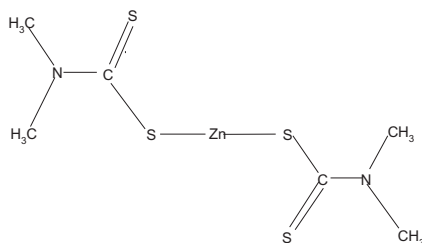


FIGURE 1 Structural formula of Ziram.

and the potassium methyl xanthate thus formed is titrated iodometrically [1]. In another approach, carbon disulphide is absorbed in an ethanolic solution containing copper(II) and an alkyl amine to form copper dialkyldithiocarbamate, which can be determined photometrically [2–4]. Dithiocarbamates have also been determined in vegetable foodstuffs using high-performance liquid chromatography [5,6], extraction voltammetry [7,8], and titrimetry [9]. Ziram is also determined by converting it into molybdenum [10] and copper [11,12] complexes. The extraction of the molybdenum complex is slow, and complexation occurs in acid medium. Other methods for determination of dithiocarbamates than those mentioned above include iodometry in anhydrous solvents [13,14] indirect titration with EDTA [15], polarography [16], and determination of the metallic component of the pesticide using different methods [17]. McLeod and McCulley [18] determined dithiocarbamate fungicides by headspace gas chromatography of the carbon disulphide evolved in controlled conditions from foodstuffs, and similar methods were also given by the Committee for Analytical Methods [19].

Derivative spectrophotometry is a spectral technique in which a slope of the spectrum, that is the rate of change in absorbance with wavelength, is measured as a function of wavelength, which at the same time shows good sensitivity and specificity [20]. In the derivative spectrum, the ability to detect and to measure minor spectral features is considerably enhanced, resulting in increased sensitivity [21]. Thus, the first derivative is a plot of spectral slope against wavelength. The second derivative spectrum is itself the derivative of the first derivative spectrum. In principle, both peak height and peak area measurements are proportional to analyte concentration. The use of the fourth derivative has the additional advantage of a considerably reduced bandwidth (depending on band shape) which leads to improved resolution of overlapping bands with increased sensitivity and offers the possibility of separating two absorption bands, which in fact may merge in zero-order spectra and reduce background interferences. Derivative higher than the fourth are of little use, as bandwidth does not decrease (or is not reduced). Here, we present a relatively simple, rapid, and sensitive fourth derivative spectrophotometric method based on the conversion of Ziram into the copper-dimethyldithiocarbamate complex, which is a golden-yellow-colored complex and is suitable for its spectrophotometric determination after its dissolution into Triton X-100.

## EXPERIMENTAL

### Equipment and Reagents

A digital pH meter (Elico, India) and a Shimadzu UV/visible 160 spectrophotometer were used. Ziram was obtained from Riedel-de Haën (Pestanal®), and its purity was

checked by elemental analysis and by melting point. A stock solution of Ziram (1 g/L) was prepared by dissolving 100 mg of this in NaOH (0.1N) and diluting to 100 mL in a volumetric flask and further dilutions done with 0.1 N NaOH as desired. Copper sulphate (1.0 g/L) was prepared by dissolving 0.1 g in 100 mL of distilled water, which was then acidified, with 0.1 mL of conc. sulphuric acid. Acetate buffer was prepared in distilled water by dissolving sodium acetate trihydrate (68 g; AR grade, Merck) in water (400 mL) and adjusting the pH to 4.5 by adding glacial acetic acid (25–30 mL, AR grade, Merck,) and making up the total volume to 500 mL.

## Procedures

### *Preparation of the Calibration Curve*

To a known volume of the sample solution containing Ziram ( $\geq 300 \mu\text{g}$ ) in a 10 mL standard flask were added copper sulphate solution (1.0 mL), aqueous acetate buffer solution (1.0 mL, pH=4.5), and Triton X-100 (2 mL), and the volume was made up to 10 mL with distilled water. The mixture was shaken vigorously for 2–3 min. The fourth derivative spectrum was recorded in the wavelength range 350–550 nm at a wavelength interval  $\Delta\lambda = 9 \text{ nm}$  against a reagent blank prepared under similar conditions.

### *Determination of Ziram from Fortified Samples of Wheat Grains*

The method was applied for the determination of Ziram from fortified samples of wheat grains. A known amount of Ziram in acetonitrile was crushed with 20 g of wheat grains with pestle and mortar and shaken mechanically with chloroform (100 mL) for 1 h. The mixture was filtered, and the residue in the funnel was washed with chloroform ( $3 \times 10 \text{ mL}$ ). The extracts were evaporated down to 2.0 mL on a water bath (70–90°C), and the remaining solvent was removed in a current of dry air at room temperature. The residue was dissolved in 0.1 N sodium hydroxide and determined by the general procedure. Untreated samples were taken as reference, and the results indicated good recoveries in all cases. The results obtained by the present method are compared with Ziram found by the method of Rao *et al.* [10]. The results of the determinations are given in Table I.

### *Analysis of a Commercial Sample*

For checking the validity of the method, it was applied for the determination of Ziram in commercial samples 'Zirax 75 WP' (India Pesticide Ltd Lucknow, India) and Ziron

TABLE I Determination of Ziram from fortified samples of wheat grains<sup>a</sup>

Crop	Ziram ( $\mu\text{g}$ )	Ziram found by the present method ( $\mu\text{g}$ )	RSD (%)	Ziram found by the method of Rao <i>et al.</i> [10] ( $\mu\text{g}$ )	RSD (%)
Wheat	10	9.8	2.9	9.7	2.7
	50	49.8	2.2	49.2	2.1
	100	99.4	1.9	99.4	1.8
	150	148.8	1.7	148.7	1.6

<sup>a</sup>Amount of crop = 20 g. Each result is the average of 10 experiments.

TABLE II Determination of Ziram in a commercial sample<sup>a</sup>

Ziram	Ziram present ( $\mu\text{g}$ )	Ziram found by the present method ( $\mu\text{g}$ )	RSD (%)	Ziram found by the method of Rao <i>et al.</i> [10] ( $\mu\text{g}$ )	RSD (%)
Zirax (75 W.P.)	20	19.9	2.5	19.7	2.9
	50	49.8	1.6	49.3	2.1
	100	99.5	1.5	99.1	1.9
	150	159.1	1.4	158.1	1.7
Ziron (27% S.C.)	15	14.9	2.8	14.6	3.1
	50	49.0	2.6	49.8	2.7
	100	99.4	2.1	99.1	2.2
	160	158.9	1.6	158.8	1.6

<sup>a</sup>Each result is the mean of 10 experiments.

(27% SC, Ambachem, Baroda, India) under similar conditions. The formulated product sample solution was prepared and determined by the general procedure. The results obtained were compared by the method of Rao *et al.* [10], and the results of the analysis are given in Table II.

## RESULTS AND DISCUSSION

### Absorption Spectra

The absorption spectrum of Ziram as copper(II) dimethyldithiocarbamate complex dissolved into Triton X-100 was recorded against a reagent blank. Figure 2(A) shows the complex shows the absorption maxima at 441 nm, and Fig. 2(B) shows the fourth derivative absorption spectra. The fourth derivative has been used for this study, as derivation leads to sharper zero-order bands and gives higher signals in the resulting spectra. The characteristics of derivative spectra, such as peak height and noise level, depend on the choice of parameters such as the order of the derivative, scan speed, and integration time during the recording of the spectra. To improve the selectivity and sensitivity, these parameters should be optimized to give a well-resolved peak (better resolution). Preliminary observations revealed that the best results were obtained from the fourth derivative with data points registered at a wavelength interval of  $\Delta\lambda = 9$  nm.

### Stability of the Copper(II) Complex

It was found that the absorbance of the solution became constant after 2–3 min, so for all the measurements, a standing time of 5 min was selected. The absorbance of the complex remained practically constant for more than 24 h.

### Choice of Surfactant

The effects of various surfactants like sodium lauryl sulphate (SLS), Triton X-100 (TX-100), cetyl pyridinium bromide (CPB), and cetyl trimethyl ammonium bromide (CTAB) on absorbance and the solubilization of the Ziram complex were studied. All of these surfactants readily solubilize the Ziram complex, and TX-100 was

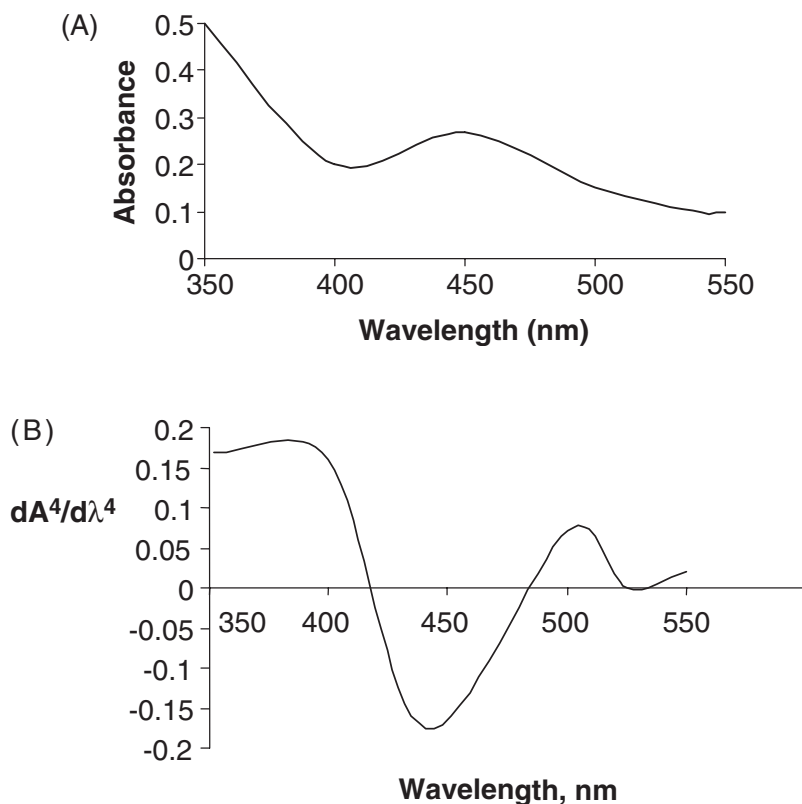


FIGURE 2 (A) Absorption spectrum of Ziram as copper (II) dimethyldithiocarbamate complex in Triton X-100 against the reagent blank. Ziram 100  $\mu\text{g}$ ; copper sulphate 1.0 mL (1 g/L), acetate buffer 1.5 mL (pH 4.5). (B) Fourth derivative absorption spectrum of Ziram as the copper (II) dimethyldithiocarbamate complex in Triton X-100 against the reagent blank. Ziram 100  $\mu\text{g}$ ; copper sulphate 1.0 mL (1 g/L), acetate buffer 1.5 mL (pH 4.5).

preferred, as it showed a maximum increase in absorbance in comparison with other surfactants used.

### Effect of pH

The absorbance of the copper(II)–dimethyldithiocarbamate complex in Triton X-100 solution remained constant in the pH range 4.0–8.0.

### Linear Range and Sensitivity

The spectra were obtained in the range of 330–550 nm. The calibration graph was obtained by measuring the peak height at 441 nm in the spectra of the copper dimethyldithiocarbamate complex of Ziram in the presence of Triton X-100, as recorded against a reagent blank. Under the optimum conditions described above, a calibration graph for the determination of Ziram was linear over the concentration range 0.5–30  $\mu\text{g}/\text{mL}$  of the final solution. The slope of the calibration curve is found to be 0.0162 mL/ $\mu\text{g}$  with a correlation coefficient of 0.9958.

## Interferences

Sample solutions containing 100 µg of Ziram and various amounts of different alkali metal salts or metal ions were prepared, and the general procedure was applied. The following anions did not interfere in the determination of Ziram up to a level of 20 mg: bromide, acetate, chloride, nitrate, sulphate, and oxalate. The following metal ions did not interfere in the determination of Ziram up to a level of 0.20 mg: Pb(II), Zn(II), Bi(III), and Fe(II) or Fe(III).

## CONCLUSIONS

The present method is more sensitive than the earlier spectrophotometric methods, as it allows Ziram to be determined in the presence of various metal ions without any interference, a direct spectrophotometric determination, offering the advantage that no tedious and laborious extraction has to be performed in the clean-up step; this is not possible using the earlier reported methods. FTIR methods [22] require a high temperature for the decomposition of the dithiocarbamates in the presence of a high content of H<sub>2</sub>SO<sub>4</sub>, and during this process, a high volume of water is generated, which interferes in the analysis. The present method is more sensitive than the carbon disulphide evolution methods, as, according to Lowen [3], the minimum of evolved carbon disulphide is 10 µg. According to Cullen [4], a minimum of 20 µg of carbon disulphide evolution is required for the determination, but according to the present method, a minimum of 5 µg of Ziram, equivalent to 3 µg of evolved carbon disulphide, can be determined. The wide applicability, simplicity, and selectivity of this method make it preferable to others.

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