Spectrophotometric Determination of Ziram in a Commercial Sample and Wheat by Extraction of Its Copper Dimethyldithiocarbamate Complex into Molten Naphthalene

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A method was developed for the determination of zinc(II) dimethyldithiocarbamate by converting it into the copper(II) dithiocarbamate complex, which is then extracted into molten naphthalene. The absorbance is measured at 430 nm versus a reagent blank. Beer’s law is obeyed for concentrations of 0.63 × 10^{-3} to 17.2 × 10^{-3} g/L in the final solution. The method is sensitive and was applied to the determination of ziram in a commercial sample and in wheat grain.

Ziram, zinc(II) dimethyldithiocarbamate, is a well-known dithiocarbamate fungicide widely used against a variety of plant pathogenic fungi. Several 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 amine and carbon disulfide, which is then absorbed in methanolic potassium hydroxide solution; the potassium methyl xanthate thus formed is titrated iodometrically (1).

In another approach, carbon disulfide is absorbed in an ethanol 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 products by liquid chromatography (5), extraction voltammetry (6), and titrimetry (7). Ziram is also determined by converting it to molybdenum (8) and copper (9) complexes. The extraction of the molybdenum complex is slow, and complexation occurs in acid medium. Dithiocarbamates can also be determined by methods which use procedures other than acid decomposition; these include iodometry in anhydrous solvents (10, 11), indirect titration with ethylenediaminetetraacetic acid (12), polarography (13), and determination of the metallic component of the pesticide by different methods (14, 15). Our earlier method for the determination of ferbam uses bathophenanthroline after adsorption onto microcrystalline naphthalene (16). The limitation of this method is that it is highly specific for ferbam because other dithiocarbamates do not form complexes with bathophenanthroline. However, this method may be applied to other dithiocarbamates. McLeod and McCully (17) determined dithiocarbamate fungicides by head-space gas chromatography of the carbon disulfide evolved from foods under controlled conditions, and similar methods were also reported by the Committee for Analytical Methods (18).

Ziram reacts with copper(II) to form a colored complex, which is suitable for its spectrophotometric determination. In this paper, we present a relatively simple, rapid, sensitive, and selective spectrophotometric method for the determination of ziram after extraction of its copper(II) dithiocarbamate complex into molten naphthalene and dissolution of the complex in dimethylformamide (DMF).

Experimental

Apparatus and Reagents

(a) Digital pH meter.
(b) Spectrophotometer.—Bausch and Lomb SP 20.
(c) Ziram (Pestanal®).—Used as obtained (Hannover, Riedel-de Haën, Germany).
(d) Stock solution of pure (100%) Ziram (1 g/L).—Dissolve 100 mg in 0.1M NaOH and dilute to 100 mL.
(e) Copper sulfate (1.0 g/L solution).—Dissolve 0.1 g in distilled water acidified with 0.1 mL concentrated sulfuric acid and dilute to 100 mL.
(f) Acetate buffer.—Dissolve 68 g sodium acetate trihydrate (Merck GR, Darmstadt, Germany) in 400 mL distilled water, adjust pH to 4.5 by adding 25–30 mL glacial acetic acid (Merck GR), and dilute to a total volume of 500 mL.

Preparation of the Calibration Curve

To a known volume of a solution containing ziram at 0.63 × 10^{-3} to 17.2 × 10^{-3} g/L in an Erlenmeyer flask fitted with a tightly fitting stopper, were added 1.0 mL of a 1.0 g/L solution of copper sulfate and 1.5 mL pH 4.5 aqueous acetate buffer solution, and the volume was diluted to 40 mL with distilled water. A 2 g portion of naphthalene was added to the flask, the mixture was heated in a water bath to melt the naphthalene completely, and the flask was shaken vigorously to extract the complex. The naphthalene containing the complex...
was separated by filtration and air-dried in the folds of the filter paper; the residue was dissolved in DMF, and the solution was diluted to 10 mL with DMF. The absorbance was measured at 430 nm versus a reagent blank prepared under similar conditions.

_Determination of Ziram in Fortified Samples of Wheat Grain_

The method was applied to the determination of ziram in fortified samples of wheat grain. A known amount of ziram in acetonitrile was crushed with 20 g wheat grain with a mortar and pestle, and the mixture was shaken mechanically with 100 mL chloroform for 1 h. The mixture was filtered, and the residue in the funnel was washed with three 10 mL portions of chloroform. The extract was evaporated to 2.0 mL in 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 acetonitrile and determined by the general procedure. Unfortified wheat grain was used as the blank, and the results indicated good recoveries in all cases. The results of the determinations are given in Table 1.

_Analysis of a Commercial Sample_

The method was applied to the determination of ziram in a commercial sample, Ziram 75 WP. The sample solution of the formulated product was prepared as described above, and ziram was determined by the general procedure. The results obtained by the present method were compared with those obtained by the method of Rangaswamy et al. (9), in which ziram is determined colorimetrically, after reaction with cuprous chloride in 0.3M HCl to form a yellow copper complex, by measuring the absorbance at 385 nm. The results of the analysis are given in Table 2.

**Results and Discussion**

_Absorption Spectrum_

The absorption spectrum of the copper(II) dimethylthiocarbamate complex extracted into molten naphthalene by the reaction of ziram with copper was recorded versus a reagent blank. The complex shows an absorption maximum at 430 nm (Figure 1), which was selected for all further measurements.

_Effect of Standing Time_

The absorbance of the solution was measured at different time intervals, and it was observed that the absorbance of the solution remained practically constant for >24 h.

_Effect of Naphthalene and Shaking Time_

The complex formed by the reaction of copper with ziram was readily extractable into molten naphthalene. The amount of the naphthalene was varied between 0.5 and 2.5 g. It was observed that, with >2.0 g naphthalene, it was difficult to collect and separate the naphthalene and to dissolve the residue in DMF. Therefore, for convenience, 2 g naphthalene was used.

<table>
<thead>
<tr>
<th>Ziram present, g</th>
<th>Ziram found by present method, g</th>
<th>RSD, %&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Ziram found by method of Rangaswamy et al. (9), g</th>
<th>RSD, %&lt;sup&gt;c&lt;/sup&gt;</th>
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<tr>
<td>10</td>
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<td>2.5</td>
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<tr>
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<tr>
<td>160</td>
<td>159.1</td>
<td>1.4</td>
<td>158.1</td>
<td>1.7</td>
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</table>

<sup>a</sup> Ziram 75 WP.<br>
<sup>b</sup> Each value is the average of 10 determinations.<br>
<sup>c</sup> RSD = relative standard deviation.
It was observed that the extraction was quantitative and complete when the volume of the aqueous phase was between 30 and 100 mL. A greater volume caused a decrease in absorbance.

**Choice of Solvent**

The complex is soluble in DMF, acetonitrile, dimethyl sulfoxide, and chloroform, but it is insoluble in benzene, carbon tetrachloride, etc. There was little difference in the absorbance in the former solvents but, because DMF is less expensive than the other solvents, it was selected for further study.

**Beer’s Law and Sensitivity**

Under the conditions described above, a calibration graph for the determination of ziram was linear over the concentration range of \(0.63 \times 10^{-3}\) to \(17.2 \times 10^{-3}\) g/L of the final solution. Aliquots containing 64 g ziram were taken from the standard reference solution and analyzed by the general procedure. Ten replicate determinations of ziram in these solutions gave a mean absorbance of 0.30 with a relative standard deviation of 1.31%. The molar absorptivity \((\varepsilon = \text{A/CL})\), where \(\varepsilon\) is the molar absorptivity coefficient, \(A\) is the value of absorbance for a 1M concentration, \(C\), of a solute, and \(L\) is the optical pathlength) was calculated to be \(1.6 \times 10^4\)L/moL·cm; Sandell’s sensitivity (19), which represents the number of micrograms of analyte per 10 mL final solution having an absorbance of 0.001 for a pathlength of 1 cm, was 0.021 g/cm².

**Interference Due to Metal Ions**

Sample solutions containing ziram at \(6.4 \times 10^{-3}\) g/L and various amounts of different alkali metal salts or metal ions were prepared, and the general procedure was applied. The following foreign anions (20 mg) did not interfere in the determination of ziram: bromide, acetate, chloride, nitrate, sulfate, and oxalate. The following metal ions examined (0.20 mg) did not interfere in the determination of ziram: Pb(II), Zn(II), Bi(III), and Fe(II) or Fe(III).

**Comparison of Sensitivity**

The present method is more sensitive than earlier spectrophotometric methods and the carbon disulfide evolution methods. By this method, it is possible to estimate ziram at \(0.63 \times 10^{-3}\) g/L, which is equivalent to evolved carbon disulfide at \(0.3 \times 10^{-3}\) g/L and is superior to results for previously reported methods. The wide applicability and simplicity of this method make it preferable to other methods.

**References**