

Direct Spectrophotometric Determination of Ferbam (Iron(III) Dimethyldithiocarbamate) in Commercial Sample and Wheat Grains Using 4,7-Diphenyl-1,10-phenanthroline

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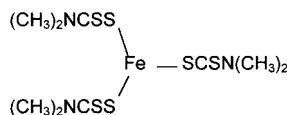
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A procedure has been developed for the determination of iron(III) dimethyldithiocarbamate by converting it into the iron(II)–bathophenanthroline complex, which is then dissolved in acetone–water (1:1), and the absorbance is measured at 534 nm against a reagent blank. Beer's law is obeyed over the concentration range 0.5–20 $\mu\text{g mL}^{-1}$ in the final solution. The method is sensitive and highly selective and is used for the direct determination of ferbam in a commercial sample and in mixtures with various dithiocarbamates (ziram, zineb, maneb, etc.) and from wheat grains.

Keywords: Spectrophotometry; ferbam; commercial sample; bathophenanthroline

1. INTRODUCTION

Iron tris(dimethyldithiocarbamate) (IUPAC name) commonly known as ferbam is a well-known dithiocarbamate fungicide widely used against a variety of plant pathogenic fungi.



Structure of Ferbam

Various characteristics of this compound are summarized in Table 1. Most of the methods for the determination of ferbam are based on its decomposition by hot mineral acids to amine and carbon disulfide. Various approaches are given in the literature to convert these decomposition products into chromophoric structures for the photometric determination of ferbam (Clarke et al., 1951; Simpson, 1971; Lowen, 1961; Cullen, 1954). Ferbam is also determined by converting it into molybdenum (Rao and Verma, 1985;), copper (Rangaswamy et al., 1970), and 1,10-phenanthroline (Malik et al., 1991) complexes. The molybdenum method involves the exchange of the iron(III) present in ferbam in acidic media with molybdenum to form a yellow complex in isobutyl methyl ketone and this requires about 5 min of shaking. The method using copper involves complexation in acid medium; the method with 1,10-phenanthroline involves adsorption onto microcrystalline naphthalene, in which the separation and dissolution of the complex is quite tedious, whereas the present method is direct and does not involve extraction. Ferbam can also be determined by methods which use methods other than acid decomposition based on determination of the metallic component of ferbam using different reagents and techniques (Halls et al., 1968;

Table 1. Physical Characteristics of Ferbam

physical characteristics	value
molecular formula	$\text{C}_9\text{H}_{18}\text{FeN}_3\text{S}_6$
form	black powder
melting point	decomposes above 180 °C
vapor pressure	negligible at 20 °C
density	bulk density 0.6 kg/L
solubility	130 mg/L (room temperature) in water and soluble in organic solvents with high dielectric constant e.g., chloroform, acetonitrile, acetone, pyridine, etc.
stability	stable in closed containers, decomposes on exposure to moisture and prolonged storage
toxicity uses	LD ₅₀ for rabbits > 4000 mg/kg widely used as fungicide for various crops

Quintero et al., 1991; Perez-Ruiz et al., 1996). McLeod and McCulley (1969) determined dithiocarbamate fungicides by headspace gas chromatography of the carbon disulfide evolved in controlled conditions from food-stuffs, and similar methods were also given by the Committee for Analytical Methods (1981). However, all these methods suffer from the following disadvantages: (a) Methods other than gas chromatography are indirect and time-consuming, and sensitivity is low. (b) Gas chromatographic methods are sensitive but suffer from lack of the selectivity since all dithiocarbamate pesticides evolve carbon disulfide on acid hydrolysis. Here we present a relatively simple, rapid, sensitive, and selective spectrophotometric method by converting ferbam into iron(II) bathophenanthroline complex. Ferbam reacts with bathophenanthroline to form a red colored complex which is suitable for its spectrophotometric determination after dissolution into acetone–water (1:1).

2. EXPERIMENTAL PROCEDURES

2.1. Equipment and Reagents. A digital pH meter and a Varian Cary 2400 spectrophotometer were used. Ferbam was obtained from Riedel-de Haën (Pestanal) and used as such. A stock solution of pure (100%) ferbam (1 g/L) was prepared by

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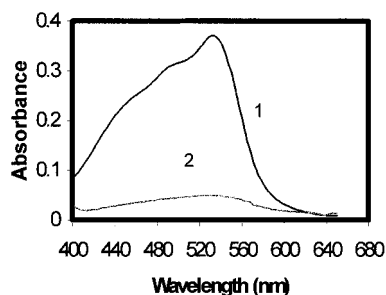


Figure 1. Absorption spectra of (1) ferbam as iron(II)-bathophenanthroline complex in acetone-water (1:1) and (2) ferbam in acetone; reference reagent blank. Ferbam 70 μg ; bathophenanthroline 1.5 mL (1 g L⁻¹), hydroxylamine hydrochloride 1.5 mL (100 g L⁻¹); acetate buffer 1.5 mL (pH = 4.5).

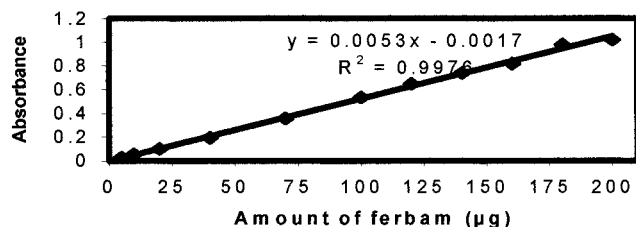


Figure 2. Calibration curve for the determination of ferbam ($\lambda_{\text{max}} = 534 \text{ nm}$). The rest of the conditions are the same as in Figure 1.

dissolving 100 mg of this reference material in 100 mL of acetonitrile and further diluting the resultant solutions with acetonitrile as desired. Solutions of 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline, Merck, GR) (1 g/L) and of hydroxylamine hydrochloride (Merck, GR) (100 g/L) were prepared in distilled water. Acetate buffer was prepared in distilled water by dissolving sodium acetate trihydrate (68 g, Merck GR) in water (400 mL) and adjusting the pH to 4.5 by adding a glacial acetic acid (25–30 mL, Merck, GR) and making the total volume 500 mL.

Stock solutions of various salts were prepared by dissolving them in water. Nabam, ziram, maneb, and thiram were obtained from Riedel-de Haën (Pestanal). Solutions of the dithiocarbamates were prepared by dissolving them in distilled water or in the organic solvents given in parentheses: ziram and thiram (acetonitrile, Merck) and zineb and maneb (dimethylsulfoxide, Merck). Synthetic samples were prepared by mixing the solutions of the constituents to give the required composition.

2.2. Procedures. **2.2.1. Preparation of the Calibration Curve.** To a known volume of the sample solution containing 5.0–200 μg of ferbam in a 10 mL standard flask were added bathophenanthroline solution (1.5 mL), hydroxylamine hydrochloride (1.0 mL), aqueous acetate buffer solution (1.5 mL, pH = 4.5), and 5 mL of acetone, and the volume was made up to 10 mL with distilled water. The mixture was shaken and allowed to stand for 5 min, and the absorbance was measured at 534 nm against a reagent blank prepared under the similar conditions. The calibration curve is shown in Figure 2.

2.2.2. Determination of Ferbam from Fortified Samples of Wheat Grains. The method was applied for the determination of ferbam from fortified samples of wheat grains. A known amount of ferbam 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 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 may be dissolved in acetonitrile and determined by the general procedure. Untreated samples were taken as

Table 2. Determination of Ferbam from Fortified Samples of Wheat Grains^a

crop	ferbam (μg)	ferbam found by present method	RSD (%)	ferbam found by Rangaswamy et al. (1970) method	RSD (%)
wheat	15	14.7	2.3	14.5	2.3
	60	59.5	2.2	59.5	2.1
	120	119.6	1.8	119.4	1.8
	150	146.4	1.4	145.2	1.4

^a Amount of crop = 20 g; each result is the average of 10 experiments.

Table 3. Determination of Ferbam in a Commercial Sample^a

ferbam	ferbam present (μg)	ferbam found by present method (μg)	RSD (%)	ferbam found by Rangaswamy et al. (1970) method (μg)	RSD (%)
ferbam	10	9.9	2.1	9.7	2.2
(75 W.P.)	50	49.6	1.9	49.4	2.1
	100	99.3	1.7	98.0	1.9
	160	158.9	1.4	158.4	1.6
	180	179.4	1.2	178.6	1.3

^a Each result is the mean of 10 experiments.

Table 4. Determination of Ferbam in Synthetic Mixtures^a

sample no.	composition and percentage	amt of ferbam (μg)		RSD (%)
		taken	found	
1	ferbam: 50 ziram: 50	50.0	49.6	1.47
2	ferbam: 50 thiram: 50	50.0	49.7	1.39
3	ferbam: 11.76 maneb: 76.48 zineb: 11.76	60.0	59.4	1.62

^a Each result is the average of 10 experiments. This composition is identical to the active ingredient ratio in the Pennwalt product (ferbam 10%, maneb 65%, and zineb 10%).

reference, and the results indicated good recoveries in all cases. The results of the determinations are given in Table 2.

2.2.3. Analysis of a Commercial Sample. The method was applied for the determination of ferbam in a commercial sample "ferbam 75 WP". The formulated product sample solution was prepared as discussed in section 2 and determined by the general procedure. The results obtained by the present method are compared with those obtained by the Rangaswamy et al. (1970) method in which ferbam was determined colorimetrically after a reaction with cuprous chloride in 0.3 M hydrochloric acid to form a yellow copper complex and measuring the absorbance at 385 nm. The results of the determinations are given in Table 3.

2.2.4. Determination of Ferbam in Synthetic Mixtures. Aliquots of the samples were prepared by mixing solutions of ferbam with other dithiocarbamate solutions which were then analyzed by the general procedure. The results of the determinations are given in Table 4.

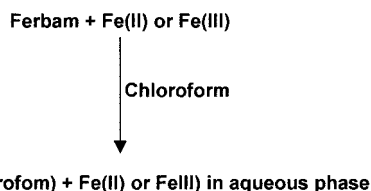
3. RESULTS AND DISCUSSION

3.1. Absorption Spectra. The absorption spectra of the complex of ferbam with bathophenanthroline was recorded against a reagent blank. The complex shows absorption maxima at 534 nm (Figure 1), so it was selected for all further measurements.

3.2. Effect of Standing Time. It was observed that the absorbance of the solution became constant after

Table 5. Comparison of Molar Absorptivity with Earlier Methods

molar absorptivity (L mol ⁻¹ cm ⁻¹)	method	remark	reference
1.33 × 10 ⁴	molybdenum	requires acidic medium (4 N H ₂ SO ₄) and an equilibrium time of 5 min	Rao and Verma (1985)
1.46 × 10 ⁴	selenite	other dithiocarbamates interfere	Malik et al. (1991)
5.3 × 10 ⁴	diphenylcarbazone	maneb, zineb, and ziram interference can be avoided by using only masking agents	Malik et al. (1991)
1.2 × 10 ⁴	phenanthroline	requires adsorption of the complex onto naphthalene, which is quite tedious and time consuming	Malik et al. (1997)
2.24 × 10 ⁴	bathophenanthroline	direct, more selective, and sensitive	this work

**Figure 3.** Scheme for the removal of Fe(II) or Fe(III) from ferbam in aqueous phase.

2–3 min, so for all the measurements 5 min of standing time was selected. The absorbance of the complex remained practically constant for more than 48 h.

3.3. Beer's Law and Sensitivity. Under the conditions described above a calibration graph for the determination of ferbam was linear over the concentration range 0.5–20 μg mL⁻¹ (Figure 2) of the final solution. Aliquots containing 70 μg (7 μg/mL) were taken from the standard reference solution and analyzed by the general procedure. Ten replicate determinations on these sample solutions of ferbam gave a mean absorbance of 0.36 with a relative standard deviation 0.83%. The molar absorptivity ($\epsilon = A/Lc$; where ϵ is the molar absorptivity coefficient—the value of absorbance for 1 M concentration of a solute and L is the optical path length) was calculated to be 2.24×10^4 L mol⁻¹ cm⁻¹ and Sandells sensitivity (Sandell, 1959), which represents the number of the micrograms of the determinant per 10 mL of the final solution having an absorbance of 0.001 for a path length of 1 cm, was found to be 0.0187 μg cm⁻².

3.4. Interferences. Sample solutions (10 mL) containing 70 μg of ferbam and various amounts of different alkali metal salts or metal ions were prepared, and the general procedure was applied. For the following foreign anions 20 mg did not interfere in the determination of ferbam: bromide, acetate, chloride, nitrate, sulfate, and oxalate. Of the following metal ions examined, 0.20 mg did not interfere in the determination of ferbam: Pb(II), Zn(II), Cu(II), and Bi(III). Fe(II) or Fe(III) if present with ferbam interfere in the determination of ferbam (Figure 3). However, their interference can be avoided by the pre-extraction of ferbam into chloroform; Fe(II) and Fe(III) will remain in the aqueous phase, and ferbam can be determined by the general procedure after evaporation of the chloroform to dryness. Interference due to other dithiocarbamates such as disodium ethylenebisdithiocarbamate (nabam), manganese ethylenebisdithiocarbamate (maneb), zinc ethylenebisdithiocarbamate (zineb), tetramethylthiuramdisulfide (thiram), and sodium diethyldithiocarbamate were studied, and these do not interfere in the determination of ferbam. As untreated samples are taken for reference, if there is any interference due to organic iron complexes it is eliminated.

4. COMPARISON OF SENSITIVITY

The present method is more selective than the earlier spectrophotometric methods as it safely permits the determination of ferbam in the presence of nabam, ziram, maneb, zineb, vapam, dibam, and sodium diethyldithiocarbamate without any interference, whereas this is not possible using the earlier reported methods (Simpson, 1971; Lown, 1961; Cullen, 1954; Rao and Verma, 1985; Rangaswamy et al., 1970). A comparison of the molar absorptivity with other methods is given in Table 5. The present method is more sensitive than the carbon disulfide evolution methods, as according to Lowen the minimum of evolved carbon disulfide is 10 μg. According to Cullen and many others a minimum of 20 μg of carbon disulfide evolution is required for the determination, but according to the present method a minimum of 5 μg of ferbam, equivalent to 2.73 μg of evolved carbon disulfide, can be determined. The wide applicability, simplicity, and selectivity of this method makes it preferable to others.

LITERATURE CITED

- Clarke, D. G.; Baum, H.; Stanley, E. L.; Hester, W. E. Determination of dithiocarbamates. *Anal. Chem.* **1951**, *23*, 1842–1846.
- Committee for Analytical Methods for Residues of Pesticides and Veterinary Products in Foodstuffs of the Ministry Agriculture, Fisheries and Foods. Determination of residues of dithiocarbamate pesticides in foodstuffs by a headspace method. *Analyst* **1981**, *106*, 782–787.
- Cullen, T. E. Spectrophotometric determination of dithiocarbamate residues on food crops. *Anal. Chem.* **1964**, *36*, 221–224.
- Halls, D. J.; Townshend, A.; Zumen, P. The polarographic determination of trace dithiocarbamates and their heavy metal complexes. *Analyst* **1968**, *93*, 219–223.
- Lowen, W. K. Determination of dithiocarbamate residues on food crops. *Anal. Chem.* **1961**, *23*, 1846–1850.
- Malik, A. K.; Rao, A. L. J.; Puri, B. K. Spectrophotometric determination of ferbam using sodium selenite. *Int. J. Environ. Anal. Chem.* **1991**, *44*, 159–166.
- Malik, A. K.; Rao, A. L. J. Spectrophotometric determination of ziram, ferbam and zineb using diphenylcarbazone. *Talanta* **1991**, *8*, 941–944.
- Malik, A. K.; Rao, A. L. J. Spectrophotometric determination of iron(III) dimethyldithiocarbamate. *Talanta* **1997**, *44*, 177–183.
- McLeod, H. A.; McCully, K. A. Headspace gas procedure for screening food samples for dithiocarbamate pesticide residues. *J. Assoc. Off. Anal. Chem.* **1969**, *52*, 1226–1230.
- Perez-Ruiz, T.; Martinez-Lozano, C.; Tomás, V.; Casajús, R. Flow injection fluorimetric determination of nabam and metham. *Talanta* **1996**, *43*, 193–98.
- Quintero, M. C.; Silva, M.; Perez-Bendito, D. Kinetic determination of zineb in agricultural samples by continuous addition of reagent. *Talanta* **1991**, *38*, 359–363.

- Rao, A. L. J.; Verma, N. Determination of ferbam (ferric dimethyldithiocarbamates) residues in apples by a spectrophotometric method. *J. Indian Acad. For. Sci.* **1985**, *24*, 1–5.
- Rangaswamy, J. R.; Poornima, P.; Majumder, S. K. Rapid colorimetric method for estimation of ferbam and ziram residues on grains. *J. Assoc. Off. Anal. Chem.* **1970**, *53*, 1043–1044.
- Sandell, E. B. *Colorimetric determination of traces of metals*, 3rd ed.; Interscience publishers: New York, 1959; p 82.

- Simpson, B. W. Determination of dithiocarbamates in carbonate-based formulations of maneb and zineb. *Pestic. Sci.* **1971**, *2*, 127–128.

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