Spectrophotometric Determination of Ferbam [Iron(III) Dimethyl Dithiocarbamate] in Commercial Sample and Wheat Grains after Extraction of Its Bathophenanthroline Tetraphenylborate Complex into Molten Naphthalene

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A procedure has been developed for the determination of iron(III) dimethyldithiocarbamate by converting it into a iron(III)−bathophenanthroline−tetraphenylborate complex, which was then extracted into molten naphthalene, and the absorbance was measured at 534 nm against a reagent blank. Beer's law is obeyed over the concentration range 0.4−20 μg mL^{-1} in final solution. The method is sensitive and highly selective and is applied for the determination of ferbam in a commercial sample, in mixtures with various dithiocarbamates (ziram, zineb, maneb, etc.), and from wheat grains.

Keywords: *Spectrophotometry; ferbam; commercial sample; bathophenanthroline*

INTRODUCTION

Ferbam [iron(III) dimethylditiocarbamate] 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 ferbam is determined on the basis of its decomposition by hot mineral acids to amine and carbon disulfide. This is then absorbed in methanolic potassium hydroxide solution and potassium methyl xanthate thus formed is titrated iodometrically (Clarke et al., 1951). In another approach, carbon disulfide is absorbed in an ethanol solution containing copper(II) and an alkylamine to form copper dialkyldithiocarbamate, which can be determined photometrically (Simpson, 1971; Lowen, 1961; Cullen, 1954). Dithiocarbamates have also been determined in vegetable foodstuffs using high-performance liquid chromatography (HPLC) (Gustafsson and Falhgren, 1983), extraction voltammetry (Ulakhovich et al., 1983), and titrimetry (Verma et al., 1982). Ferbam is also determined by converting it into molybdenum (Rao and Verma, 1985), copper (Rangaswamy et al., 1970), and selenium (Malik et al., 1991) complexes. The extraction of the molybdenum complex is slow and requires ~5 min of shaking; the method using copper involves complexation in acid medium, and with selenium other dithiocarbamates interfere. Ferbam can also be determined by its reaction with diphenylcarbazone (Malik and Rao, 1991), and in this method ziram and zineb interfere. Dithiocarbamates can also be determined by methods that use methods other then acid decomposition, and these include iodometry in anhydrous solvents (Grand and Tamres, 1968; Clyde, 1983), indirect titration with EDTA (Hyman, 1969),

polarography (Halls et al., 1968), and determination of the metallic component of pesticides using different methods (Quintero et al., 1991; Perez-Ruiz et al., 1996). HPLC methods (Brandsteterova et al., 1986) are also reported for the determination of ferbam. McLeod and McCulley (1969) determined dithiocarbamate fungicides by headspace gas chromatography of carbon disulfide evolved in controlled conditions from foodstuffs, and similar methods were also given by the Committee for Analytical Methods (1981). A biosensor (Noguer et al., 1999) is also reported for the determination of dithiocarbamates. However, all of these methods suffer from the following disadvantages:

(a) Methods other than gas chromatography (GC) are indirect and time-consuming, and their sensitivity is low.

(b) GC methods are sensitive but suffer from lack of selectivity because all dithiocarbamate pesticides evolve carbon disulfide on acid hydrolysis.

(c) HPLC methods are less sensitive than GC methods, but they require a longer time for the analysis and use of organic solvents as mobile phase.

Ferbam reacts with bathophenanthroline to form a red complex, which is suitable for its spectrophotometric determination. Here, we present a relatively simple, rapid, sensitive, and selective spectrophotometric method for the determination of ferbam after extraction into molten naphthalene of its iron(II)−bathophenanthroline−tetraphenylborate complex and dissolution into dimethylformamide (DMF).

EXPERIMENTAL PROCEDURES

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 mg/mL) was prepared in acetonitrile. Solutions of 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline, Merck, GR), 1 g/L, tetraphenylborate (Merck, GR), naphthalene (Merck, GR), and hydroxylamine

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Table 1. 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. method	RSD (%)
wheat	10	9.6	2.6	9.5	2.7
	50	49.3	2.2	49.2	2.1
	100	99.4	1.9	99.4	1.8
	150	146.5	1.7	145.1	1.6

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

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 glacial acetic acid (25–30 mL, Merck, GR) and making up the total volume to 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 solutions of the constituents to give the required composition.

Procedures. *Preparation of the Calibration Curve.* To a known volume of the sample solution taken in an Erlenmeyer flask fitted with stopper containing 4.0–200 μg of ferbam were added bathophenanthroline solution (1.5 mL), hydroxylamine hydrochloride (1.0 mL), aqueous acetate buffer solution (1.5 mL, pH 4.5), and tetraphenylborate (2 mL), and the volume was made up to 40 mL with distilled water. To this was added 2 g of naphthalene, and the mixture was heated on a water bath to melt the naphthalene completely, shaken vigorously, and allowed to stand. The naphthalene containing the complex was separated by filtration, air-dried in folds of filter paper, dissolved in DMF, and diluted to 10 mL with DMF; the absorbance was measured at 534 nm against a reagent blank prepared under similar conditions. The calibration curve is shown in Figure 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 a 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 × 10 mL). The extracts were evaporated to 2.0 mL on a water bath (70–90 °C), and remaining solvent was removed in a current of dry air at room temperature. The residue may be dissolved in acetonitrile and determined according to the general procedure. Untreated samples were taken as reference, 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 for the determination of ferbam in a commercial sample (Ferbam 75 WP). The formulated product sample solution was prepared as discussed above and determined according to the general procedure. The results obtained with the present method are compared with those obtained according to the method of Rangaswamy et al. (1970) in which ferbam was determined colorimetrically after reaction with cuprous chloride in 0.3 M hydrochloric acid to form a yellow copper complex and measurement of absorbance at 385 nm. The results of the analysis are given in Table 2.

Determination of Ferbam in Synthetic Mixtures. Aliquots of samples were prepared by mixing solutions of ferbam with other dithiocarbamate solutions which were then analyzed by using the general procedure. The results of determinations are given in Table 3.

Table 2. 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. method (μg)	RSD (%)
75 wt %	10	9.9	1.9	9.7	2.2
	50	49.8	1.6	49.3	2.1
	100	99.5	1.5	99.0	1.9
	160	159.1	1.4	158.1	1.7
	180	179.2	1.0	178.5	1.4

[a] Each result is the mean of 10 experiments.

Table 3. Determination of Ferbam in Synthetic Mixtures[a]

sample	composition and percentage	amount of ferbam (μg)		
		taken	found	RSD (%)
1	ferbam: 50 ziram: 50	40.0	39.6	1.44
2	ferbam: 50 thiram: 50	40.0	39.7	1.53
3	ferbam: 11.76 maneb: 76.48 zineb: 11.76	20.0	19.4	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%).
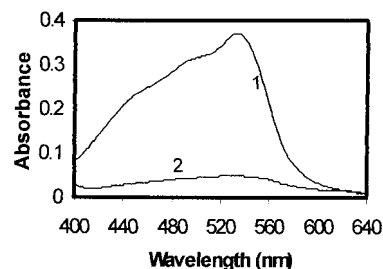

Figure 1. Absorption spectra of complex extracted into molten naphthalene: (1) ferbam as iron(II)−bathophenanthroline−tetraphenylborate complex in DMF; (2) ferbam in acetonitrile; reference reagent blank. Ferbam = 70 μg; bathophenanthroline = 1.5 mL (1 g L^{-1}); hydroxylamine hydrochloride = 1.5 mL (100 g L^{-1}); tetraphenylborate = 2.0 mL (10 g L^{-1}); acetate buffer = 1.5 mL (pH 4.5).

RESULTS AND DISCUSSION

Absorption Spectra. The absorption spectra of the complex extracted into molten naphthalene from ferbam with bathophenanthroline in the presence of tetraphenylborate were recorded against a reagent blank. The complex shows an absorption maximum at 534 nm (Figure 1) so it was selected for all further measurements.

Effect of Standing Time. It was observed that the absorbance of the solution became constant after 2−3 min, so for all measurements 5 min of standing time was selected. The absorbance of the complex remained practically constant for >24 h.

Beer's Law and Sensitivity. Under the conditions described above, a calibration graph for the determination of ferbam was linear over the concentration range 0.4−20 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 using the general procedure. Ten replicate determinations on these sample solutions of ferbam gave a mean absorbance 0.36 with a relative standard deviation of 0.91%.

Table 4. Comparison of Molar Absorptivity with Earlier Methods

molar absorptivity (l mol^{-1} cm^{-1})	method	remarks	reference
1.33×10^4	molybdenum	requires acidic medium (4 N H$_2$SO$_4$) and equilibrium time = 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, ziram interference can be avoided using only masking agents	Malik and Rao (1991)
2.23×10^4	bathophenanthroline + tetraphenylborate	more selective and sensitive	this work
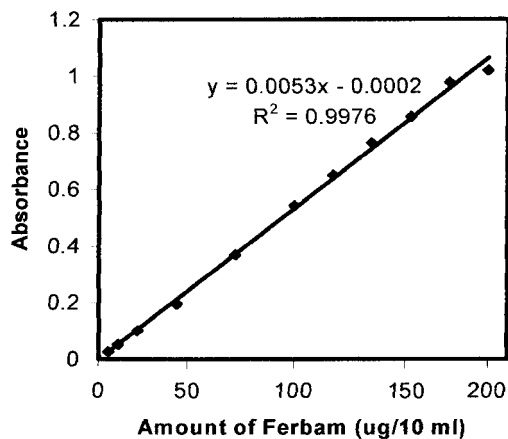
Figure 2. Calibration curve for the determination of ferbam λ_{max} at 534 nm. The rest of the conditions are the same as in Figure 1.

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] was calculated to be 2.23×10^4 L mol^{-1} cm^{-1}, and Sandell sensitivity (Sandell, 1959), which represents the number of the micrograms of the determinand per 10 mL of the final solution having an absorbance of 0.001 for a path length of 1 cm, was found to be 0.0189 μg cm^{-2}.

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. The tolerance limit was considered within ($\pm$2%) of the observed value. 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 interferes in the determination of ferbam. 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 according to 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), tetramethylthi-uramdisulfide (thiram), and sodium diethyldithiocar-bamate was studied, and these do not interfere in the determination of ferbam. Untreated samples are taken for reference; therefore, any interference due to organic iron complexes is eliminated.

COMPARISON OF SENSITIVITY

The present method is more selective than the earlier spectrophotometric methods (Simpson, 1971; Lowen, 1961; Cullen, 1954; Rao and Verma, 1985; Rangaswamy et al., 1970; Malik et al., 1991) as it permits safely 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. A comparison of molar absorptivity with other methods is given in Table 4. The present method is more sensitive than 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 4 μg of ferbam, equivalent to 2.18 μg of evolved carbon disulfide, can be determined. The wide applicability, simplicity, and selectivity of this method make it preferable to others.

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