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Fourth derivative spectrophotometric determination of fungicide thiram (tetramethyldithiocarbamate) using sodium molybdate and its application

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Abstract

A procedure has been developed for the direct fourth derivative spectrophotometric determination of tetramethyldithiocarbamate by converting it into its molybdenum complex, which is then extracted in to methyl isobutyl ketone (MIBK). Beer's law is obeyed over the concentration range 24 μg mL^{-1} in the final solution. The analytical sensitivity is calculated to be 0.004(d^4A/dλ^4) μg^{-1} mL^{-1} from the slope of the calibration curve. The detection limit is 0.3 μg mL^{-1} for thiram (signal to noise ratio = 2). Various parameters, such as effect of acid concentration, interference of a large number of ions in the determination of thiram have been studied in detail. The method is sensitive, highly selective and can be used for the determination of thiram in a commercial sample, in mixtures with various dithiocarbamates (zineb, maneb, etc.) and from wheat grains.

Keywords: Thiram; Spectrophotometeric; Tetramethyl dithiocarbamate

1. Introduction

Thiram (tetramethyldithiocarbamate) (Fig. 1) is a well-known dithiocarbamate fungicide widely used against a variety of plant pathogenic fungi. Thiram (tetramethyldithiocarbamate) is a well known dithiocarbamate fungicide widely used against a variety of plant pathogenic fungi.

Thiram is also used as a seed protectant and to protect fruits, vegetables, ornamentals and turf crops from a variety of fungal diseases. In addition, it is used as an animal repellent to protect fruit trees and ornamentals from damage by rabbits, rodents, and deer. Thiram is available as dust, flowable, wettable powder, water dispersible granules, water suspension formulations, and in mixtures with other fungicides.

It is also used in rubber industry as vulcanization accelerators and anti-oxidants. Thiram has been used in the treatment of human scabies, as a sunscreen, and as a bactericide applied directly to the skin or incorporated into soap. Analytical methods are required for monitoring pesticides in various environmental samples. A number of methods, such as Spectrophotometric [1], chromatography [2], voltammetric [3], polarographic [4], capillary electrophoretic [5], etc. have been reported for the detection and analysis of thiram. Several methods are currently available for the determination of dithiocarbamate fungicides. In one such method thiram is determined on the basis of its decomposition by hot mineral acids to amine and carbon disulphide. This is then absorbed in methanol potassium hydroxide solution and the potassium methyl xanthate thus formed is titrated iodometrically [6]. This method has the drawback with the detection of end point in the thiram with starch, the production of H_2S due to sulphide impurities and the xanthate so formed undergoes hydrolytic decomposition. In another approach, carbon

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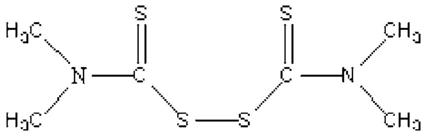

Fig. 1. Structure of thiram.

disulphide is absorbed in an ethanol solution containing copper(II) and an alkyl amine to form copper dialkyldithiocarbamate, which can be determined photometrically [7,8]. The analysis of thiram formulation and technical products has been carried out using high-performance liquid chromatography [2] both qualitatively and quantitatively after extraction with methanol [2], acetonitrile [9], etc by using various column, such as LiChrosorb RP 18 [10], LichroCART RP 18 [11], Bondapak C-18 [12], etc. Methods for the determination of thiram have also been reported using extraction voltammetry [3] and titrimetry [13]. Thiram is also determined by converting it into molbedenum [14], copper(I) [15], and selenium [16] complexes. Dithiocarbamates can also be determined by methods which use methods other then acid decomposition and these include iodometry in anhydrous solvents [17,18] indirect titration with EDTA [19], polarography [20] and determination of the metallic component of the pesticide using different methods [21,22]. McLeod and McCully [23] determined dithiocarbamate fungicides by head-space gas chromatography of the carbon disulphide evolved in controlled conditions from foodstuffs and similar methods were also given by the Committee for Analytical Methods [24]. Dithiocarbamates are also determined by FTIR spectrometry [25], but the method lacks sensitivity. However, all these methods suffer from the following disadvantages:

(a) Methods other then gas chromatography are indirect [6,14,16,17,18,19,21,22] 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 disulphide on acid hydrolysis. Moreover, the dithiocarbamate decomposition [26] are strongly dependent on temperature and on individual dithiocarbamates. The evolution of CS_2 requires more than two hours for the decomposition of dithiocarbamate.
(c) HPLC methods are sensitive and time effective but are costly as well solvent consuming.

Derivative spectrophotometry is a spectral technique in which a slope of the spectrum i.e., the rate of change of absorbance with wavelength is measured as a function of wavelength, an alternative approach to metal analysis, while at the same time showing good sensitivity and specificity [27]. In the derivative spectrum the ability to detect and to measure minor spectral features is considerably enhanced hence increased sensitivity [28]. Thus, 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 amplitude measurements are proportional to analyte concentration. Fourth derivative used has an additional advantage that in its case considerable reduced bandwidth (depending on band shape), lead 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 not much use as bandwidth do not reduces considerable thereafter. Here, we present a relatively simple, rapid, sensitive and selective fourth derivative spectrophotometric method by converting thiram into its molybdenum complex. Thiram reacts with sodium molybdate to form a green colored complex which is suitable for its spectrophotometric determination after extraction in methyl isobutyl ketone (MIBK).

2. Experimental

2.1. Equipment and reagents

A digital pH meter and a Shimadzu UV–vis 160 spectrophotometer were used. Thiram was obtained from CDH Laboratories, (LR, New Delhi) chemicals and its purity was checked by elemental analysis and by melting point. A stock solution of thiram ($1\,g\,L^{-1}$) was prepared by dissolving 100 mg of this in NaOH and diluting to 100 mL in a standard flask and further dilutions were done with NaOH as desired. Solution of sodium molybdate (Merck, AR) was prepared in distilled water. Stock solution of various salts was prepared by dissolving them in water. Nabam, ziram, maneb and thiram were obtained from Wilson Laboratories, Bombay. Solutions of the dithiocarbamates were prepared by dissolving them in distilled water or in the organic solvents given in the parentheses: thiram (acetonitrile, Merck), zineb and maneb (dimethylsulphoxide, Merck). Synthetic samples were prepared by mixing the solutions of the constituents to give the required composition.

2.2. Procedures

2.2.1. Absorption spectra

The absorption spectrum of the complex of thiram with sodium molybdate after extraction with methyl isobutyl ketone was recorded against a reagent blank. The complex shows absorption maxima at 360 nm (Fig. 2a), first derivative (Fig. 2b), second derivative (Fig. 2c), third derivative (Fig. 2d) and the fourth derivative absorption spectra (Fig. 2e) are given. As derivatization 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 order of derivative; scan speed and integration time during the recording

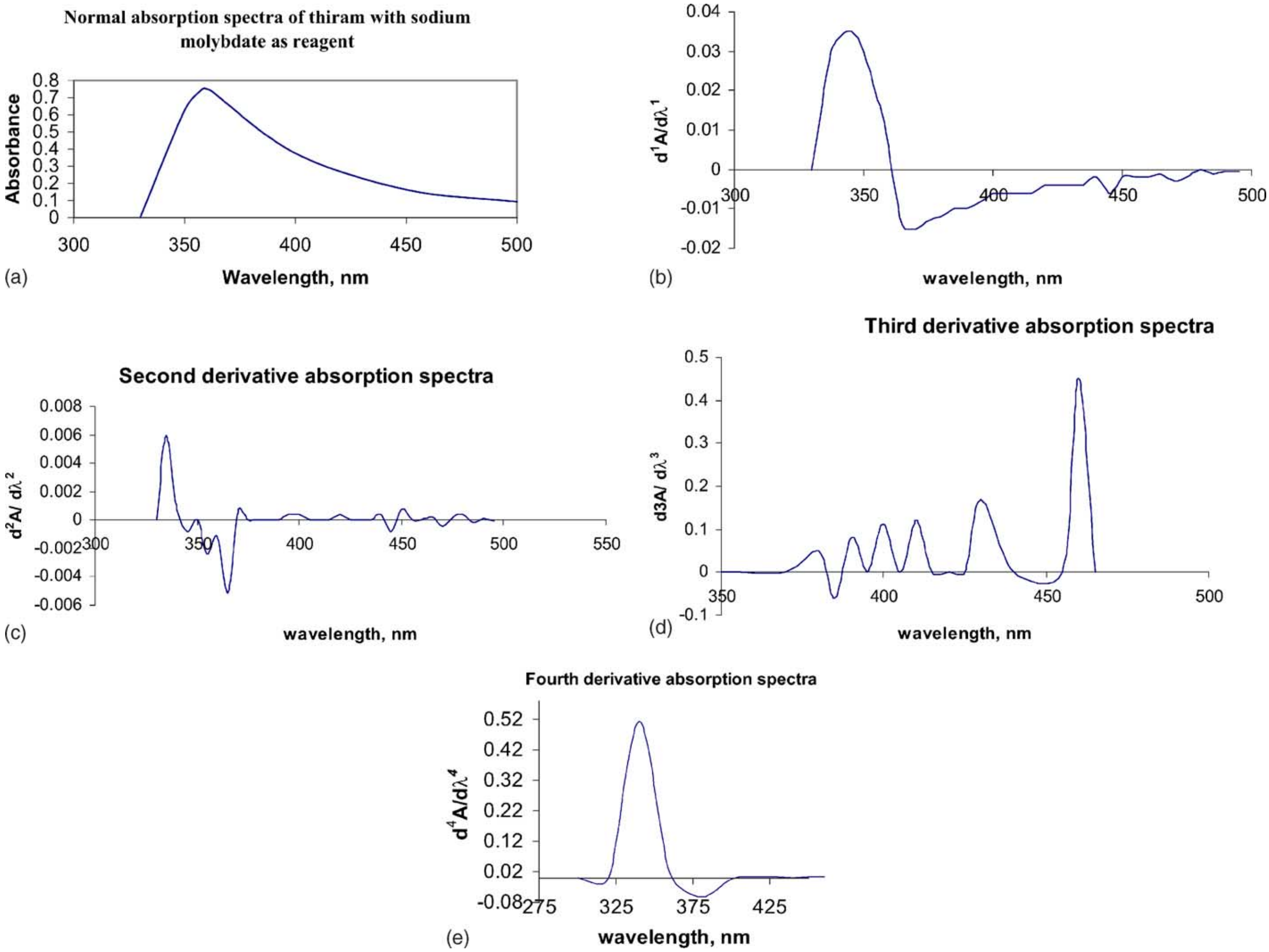

Fig. 2. (a) Normal absorption spectra of thiram complex with sodium molybdate as reagent against reagent blank: thiram 200 μg; sodium molybdate 1.0 mL (1 g L^{-1}), (b) First derivative absorption spectra of thiram complex with sodium molybdate as reagent against reagent blank: thiram 200 μg; sodium molybdate 1.0 mL (1 g L^{-1}), (c) Second absorption spectra of thiram complex with sodium molybdate as reagent against reagent blank: thiram 200 μg; sodium molybdate 1.0 mL (1 g L^{-1}), (d) Third absorption spectra of thiram complex with sodium molybdate as reagent against reagent blank: thiram 200 μg; sodium molybdate 1.0 mL (1 g L^{-1}), (e) Fourth derivative absorption spectra of thiram complex with sodium molybdate as reagent against reagent blank: thiram 200 μg; sodium molybdate 1.0 mL (1 g L^{-1}).

of the spectra. These parameters should be optimized to give a well resolved peak (better resolution) i.e., to good selectivity and higher sensitivity in a determination. Preliminary observations revealed that the best result were obtained from the fourth derivative with wavelength interval $\Delta\lambda$ = 9 nm.

2.2.2. *Preparation of the calibration curve*

To a known volume of the sample solution containing 20.0–400.0 μg of thiram in a 10 mL standard flask were added 0.5% sodium molybdate (2.0 mL), 4N H_2SO_4.(0.2 ml) 0.1 N NaOH (1.0 mL) and solution made to 5 ML. The mixture was shaken and then extracted into methyl isobutyl ketone (5 mL) and the fourth derivative spectrum was recorded at a wavelength interval $\Delta\lambda$ = 9 nm against a reagent blank prepared under the similar conditions.

3. Results and discussion

3.1. *Beer's law and sensitivity*

The various parameters affecting the shape of the spectra were studied. The analytical objective was to get the highest possible sensitivity at the maximum possible signal to noise ratio. A wavelength interval of 9 nm was found to be optional for best resolution and sensitivity. The spectra were obtained in the range from 300 to 450 nm. The calibration graph was obtained by measuring the peak height between wavelengths of 345 and 360 nm spectra of the sodium molybdate complex with thiram recorded against a reagent blank, was linear over the concentration range 24 μg mL^{-1} of the final solution. The analytical sensitivity is calculated to be 0.004($d^4A/d\lambda^4$) μg^{-1} mL^{-1} from the slope of the calibration

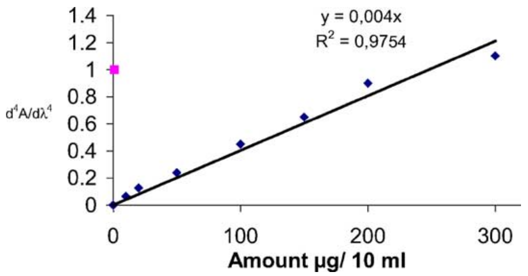

Fig. 3. calibration curve for the determination of thiram using sodium molybdate as a reagent.

Table 1
Determination of thiram from fortified samples of wheat grains

Crop	Thiram (µg)	Thiram found by present R.S.D. method	R.S.D. (%)	Thiram found by Rangaswamy et al. [15] R.S.D. method	R.S.D. (%)
Wheat	10	9.5	2.4	9.4	2.6
	60	59.6	2.3	59.4	2.5
	120	118.7	1.7	118.6	1.8
	180	179.7	1.4	178.2	1.4

Amount of crop = 20 g. Each result is average of 10 experiments.

curve. The detection limit is 0.3 µg mL^{-1} for thiram at the minimum instrumental setting (signal to noise ratio = 2). Under the conditions described above a calibration graph for the determination of thiram is given in (Fig. 3).

3.2. *Effect of standing time*

It was observed that the absorbance of the solution became constant after 2–3 min, so for all the measurements 5 min standing time was selected. The absorbance of the complex remained practically constant for nearly 25–30 min.

4. Determination of thiram from fortified samples of wheat grains

The method was applied to the determination of thiram from fortified samples of wheat grains. A known amount of thiram in NaOH was crushed with 20 g of wheat grains with pestle and mortar and shaken mechanically with chloroform (100 mL) for 1 hour. The mixture was filtered and the residue in the funnel was washed with chloroform (3 × 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 was dissolved in acetonitrile and determined by 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.

4.1. *Analysis of a commercial sample*

The method was applied for the determination of thiram in a commercial sample Thiram 75 DS. The formulated product sample solution was prepared as discussed above and determined by the general procedure. The results obtained by the present method are compared with those obtained by Rangaswamy et al. [15] method in which thiram was determined colorimetrically after 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 2.

4.2. *Determination of thiram in synthetic mixtures*

Aliquots of the samples were prepared by mixing solutions of thiram with other dithiocarbamate solutions, which were then analyzed by the general procedure. The results of the determinations are given in Table 3.

5. Interferences

Sample solutions (1.0 mL) containing 100 µg of thiram 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 thiram: bromide, acetate, chloride, nitrate, sulfate and oxalate. Of the following metal ions examined, 0.20 mg did not interfere in the determination of thiram: Pb(II), Zn(II), Bi(III) and Fe(II) or Fe(III) if present with thiram interfere in the determination of thiram. However, their interference can also be avoided by pre-extraction of thiram into chloroform. Of the dithiocarbamates examined like disodium ethylenebisdithiocarbamate (nabam), manganese ethylenebisdithiocarbamate (maneb) and zinc ethylenebisdithiocarbamate (zineb-) form blue coloured

Table 2
Determination of thiram in a commercial sample

Thiram	Thiram present (µg)	Thiram found by present R.S.D. method (µg)	R.S.D. (%)	Thiram found by Rangaswamy et al. [15] R.S.D. method (µg)	R.S.D. (%)
Thiram (75 DS)	10	9.9	1.9	9.9	2.2
	50	49.8	1.7	49.8	2.1
	100	99.5	1.5	96.2	1.9
	160	158.9	1.4	157.9	1.6
	180	179.6	1.0	178.6	1.3

Each result is a mean of 10 experiments.

Table 3
Determination of thiram in synthetic mixtures

Sample no.	Composition and percentage	Amount of Thiram (μg)		R.S.D. (%)
		Taken	Found	
1.	Thiram: 50, zineb: 50	60	59.8	1.4
2.	Thiram: 50, maneb: 50	60.0	59.6	1.9
3	Thiram: 11.76, maneb: 76.48, zineb: 11.76	70.0	69.7	1.9

Each result is average of 10 experiments.

complexes on heating with sodium molybdate so this offer a distict major advantage over the existing method.

6. Comparison of sensitivity

The present method is more selective than the earlier spectrophotometric methods as it permits safely the determination of thiram in the presence of nabam, maneb and zineb, without any interference, whereas this is not possible using the earlier reported methods. In contrast to spectrophotometric methods [16,28,29,30], voltammetric [31], and chromatographic methods [26]. FTIR methods [25] require high temperature values and a high content of H_2SO_4 involves generation of high volume of water. By this method a 0.055 mg of Ziram equivalent to 27 μg CS_2 and equivalent to 49 μg of ferbam can be determined. The present method is more sensitive than the carbon disulphide evolution methods, as according to Lowen [32] the minimum of evolved carbon disulphide is 10 μg. According to Cullen [8] and many others 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 thiram, equivalent to 2.73 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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