

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 into methyl isobutyl ketone (MIBK). Beer's law is obeyed over the concentration range $24 \mu\text{g mL}^{-1}$ in the final solution. The analytical sensitivity is calculated to be $0.004(d^4A/d\lambda^4) \mu\text{g}^{-1} \text{mL}^{-1}$ from the slope of the calibration curve. The detection limit is $0.3 \mu\text{g mL}^{-1}$ 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.

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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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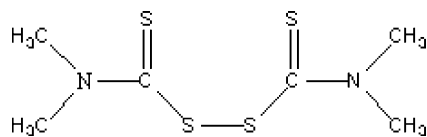


Fig. 1. Structure of thiram.

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 molybdenum [14], copper(I) [15], and selenium [16] complexes. Dithiocarbamates can also be determined by methods which use methods other than 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:

- Methods other than gas chromatography are indirect [6,14,16,17,18,19,21,22] time consuming and sensitivity is low.
- 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.
- 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 deriva-

tive 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 reduce considerably 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

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