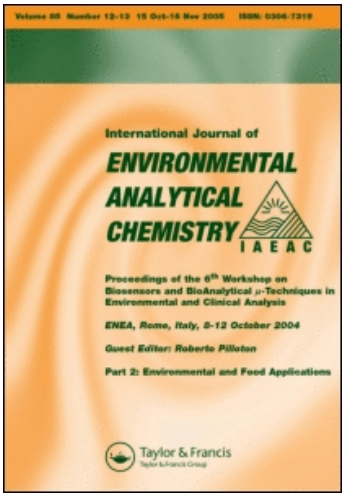

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DETERMINATION OF METHAM AND THIRAM IN SOILS AND VEGETABLES GROWN IN GREENHOUSES

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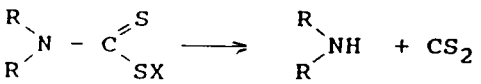
The spectrophotometric method for determining dithiocarbamates based on evolution of carbon disulphide and the formation of coloured complexes with Cu(II) is reviewed and improved for microquantities of Thiram and Metham. The method is applied to the determination of Metham and Thiram in soil samples in order to study the mobility of Metham in soils and the degradation of Thiram in beans and watermelons grown in greenhouses. The $t_{1/2}$ values of Thiram in green beans and watermelons are 10.6 and 12.2 days, respectively.

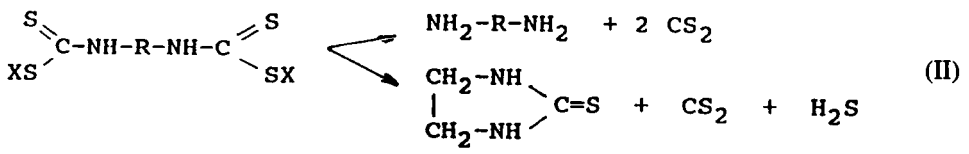
KEY WORDS: Metham, Thiram, spectrophotometric determination, soils mobility, vegetables degradation.

INTRODUCTION

The constantly expanding use of pesticides on food crops and soils accentuates the need to study the characteristic parameters of their presence and degradation in different environmental compartments. Usually, methods for the determination of dithiocarbamates are based on the evolution of carbon disulphide from these fungicides by digestion with dilute mineral acid under reflux conditions. The carbon disulphide formed is removed by a continuous flow of nitrogen or air and it is absorbed in an alcoholic solution, generally containing an amine (diethanolamine, tryethanolamine, diethylamine, etc.) and cupric acetate, to form yellow coloured complexes. The hydrolysis processes can be represented by the following equations depending on the formation of monothio (I) or bisdithio (II) carbamates:

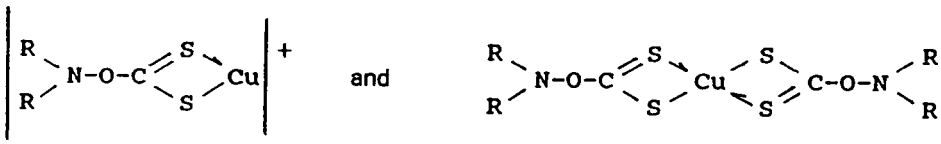


(I)



(II)

The copper complexes formed are:



Colorimetry is carried out at 380 or 435 nm, which are absorption maxima of the 1:1 and 2:1 reagent:Cu(II) complexes, respectively.[1,2]

During the last decades this standard method has been revised and several modifications have been suggested to improve the accuracy of the measurements.[3–7] Three aspects remain as restrictive factors of this method, mainly when the amount of carbon disulphide is small (<40 μg):

– The calibration graphs are generally constructed from standard solutions of carbon disulphide in alcohol; that is, quantitative recovery during hydrolysis, distillation and complexation is assumed.

– Impurities in the sample, which contain sulphur atoms can interfere by reaction with the colouring reagent.

– Two complexes are simultaneously formed (cf. above) and their relative proportion is a function of the carbon disulphide concentration.

This paper describes the additional use of 275 nm (xanthate group of the copper complexes[8]) as an additional wavelength for a more accurate analysis of microquantities of Thiram and Metham and also discusses factors such as possible interferences, trapping of interferences and selection of carrier gas.

EXPERIMENTAL

Reagents

Carbon disulphide standard solution. Add 1.000 g of carbon disulphide via a weighing buret to 50 mL of methanol and dilute to 100 mL in a volumetric flask. One mL of this solution is diluted to 100 mL to make the standard solution.

Dithiocabamate standard mixture. Add 0,500 g of the dithiocarbamate to 49.5000 g of 200 mesh talc and mix. 10 mg of this mixture are equivalent with 10 μg of dithiocarbamate. The content of these solid mixtures was checked by iodometric titration.[9]

Colouring reagent. Add 25 g of diethanolamine to 0.012 g of cupric acetate monohydrate in a 250 mL volumetric flask, and dilute to volume with ethanol.

Stannous chloride solution (40% w/v), sodium hydroxide solution (10% w/v) and 10 M hydrochloric acid solution were also used.

Apparatus

In our study, the decomposition-absorption apparatus of Figure 1 below, a Milton Roy Spectronic 3000 diode array Spectrophotometer and a Perkin Elmer Model 8700 gas chromatograph with FPD detector were used.

For GC-FPD (sulphur mode) a dimethyl-polysiloxane column, 30 m × 0.53 mm × 2.65 mm was used. Carrier Gas: hydrogen, at 10 mL/min.; oven temperature, 80°C; injector temperature, 240°C; detector temperature, 300°C.

Calibration graph for carbon disulphide

Various volumes (0.1–3.0 mL) of carbon disulphide solution in ethanol were slowly added with shaking to 10 mL of the colouring reagent solution. The volume of the solution was made up to 25 mL with colouring reagent solution. The absorbance of the yellow solution was measured at 275 nm against a reagent blank within 30 min.

Calibration graph for Thiram and Metham

Add 10 mL of NaOH solution and 10 mL of n-hexane to the first trap of Figure 1. Add 10 mL of the colouring reagent to the second trap. Add 100 mL of distilled water, 50 mL of hydrochloric acid solution and 5 mL of hydrochloric stannous chloride solution to the

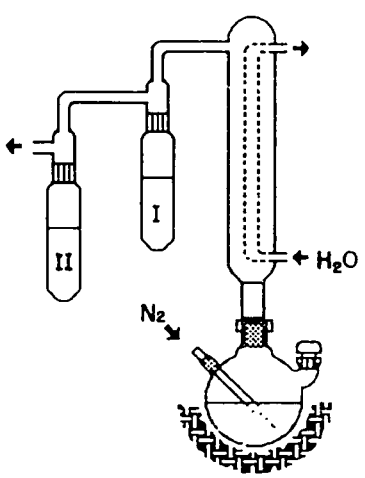


Figure 1 Decomposition-absorption apparatus used for dithiocarbamate determination. (I) Trap volatile absorber. (II) Trap CS_2 absorber.

reaction flask, heat to boiling and apply a gentle nitrogen flow. Transfer between 10 and 500 μg of the appropiate dithiocarbamate standard solid mixture to the 500 mL reaction flask. Reflux for 30–45 min while the carbon disulphide evolved is absorbed by the colour reagent (trap II).

Disconnect the apparatus after digestion and drain the contents of the colouring reagent trap into a 25 mL volumetric flask. Wash the trap column with several 3-mL portions of ethanol and collect the washings in a flask to ensure quantitative transfer. Carefully adjust the volume to the mark with ethanol and mix the contents thoroughly. Determine the absorbance of each standard versus a reference solution with 1 cm cells at 275 nm. Prepare the reference solution by diluting 10 mL of colouring reagent to 25 mL with ethanol. Prepare the standard curve for dithiocarbamate by plotting the absorbance values obtained versus the weight of active ingredient added.

Metham and Thiram in soil samples

Transfer a representative subsample of soil (100 g is about the maximum) containing 10–250 μg of dithiocarbamate to a separatory funnel, add 50 mL of a 10% aqueous methanol solution and shake for 2 min. Separate the extract and repeat the extraction twice by adding two 25-mL portions of the same ethanolic solution. Collect the extracts and adjust the volume to 100 mL with distilled water. Transfer the extracts rapidly to the 500 mL reaction flask and continue as indicated above.

Mobility of Metham in soils

Weigh 30 g of soil, add 30 mL of distilled water and mix to form a homogeneous paste. Fill a 200 mm × 20 mm I.D. chromatographic column with this paste avoiding air bubbles. Add 1 mL of a freshly prepared 1 mg/mL aqueous Metham sodium solution and pass distilled water continuously through the column. Take 30-mL fractions of the eluted liquid and analyze according to the above procedure.

Determination of Thiram in vegetables

Weigh 100 g of green beans or watermelon pieces, and introduce these into a 500-mL reaction flask and continue as indicated above for Thiram.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of the copper xanthates formed (Figure 2) show three maxima, viz. at 275 nm (xanthate group), 380 nm (1:1 complex) and 435 nm (2:1 complex) under the

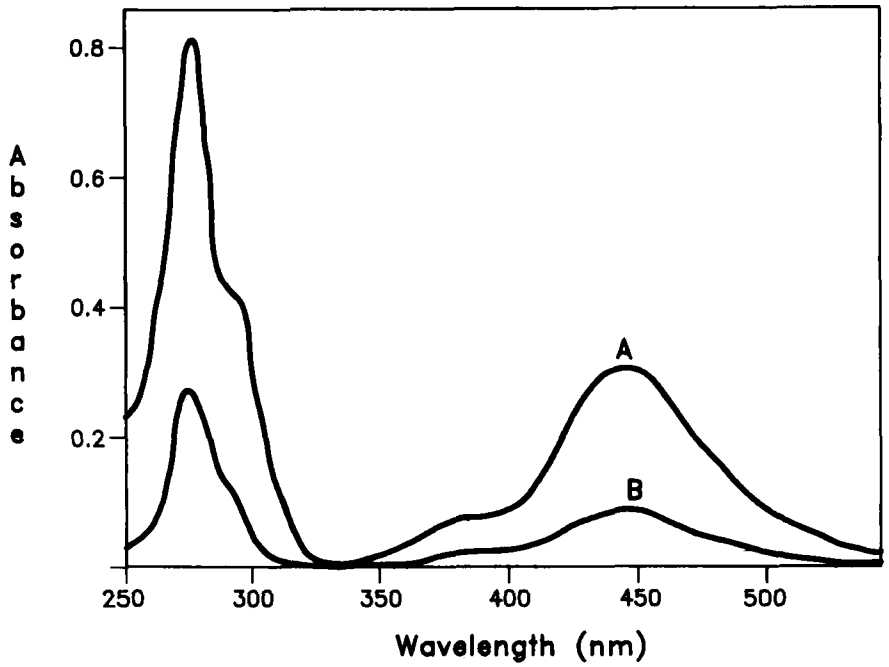


Figure 2 uv-visible absorption spectra of ethanolic solution of copper xanthates under the operational conditions. (A) 100 μg of CS_2; (B) 40 μg of CS_2.

present experimental conditions. It is interesting to note that an equilibrium between the 1:1 and 2:1 complexes takes place even though the equilibrium is greatly shifted. The maximum at 435 nm obeys the Lambert-Beer law between 40 and 500 μg of carbon disulphide. However, for lower amounts there are considerable deviations and the calibration plot does not pass through the origin any more. This problem does not occur when the measurement is performed at 275 nm which is therefore the preferred wavelength for the measurement of low quantities of carbon disulphide (<40 μg) (Figure 3). The regression coefficients are 0.9961 and 0.9996 at 435 nm and 275 nm, respectively.

Calibration

It is better to use a Thiram and Metham standard mixture than a standard carbon disulphide solution to construct calibration plots because slight variations in experimental conditions such as apparatus, temperature, etc. can have a noticeable effect on the percentage yield of CS_2. It was found that the absorbance at 275 nm is linear for amounts of dithiocarbamate from 7 to 250 μg with a minimum error interval between 15 and 150 μg. The relative standard deviation is 1.1 % (for 5 determinations on samples containing 100 μg of dithiocarbamate). The detection limit (LOD) is 1.5 μg of dithiocarbamate. The detection limit and relative

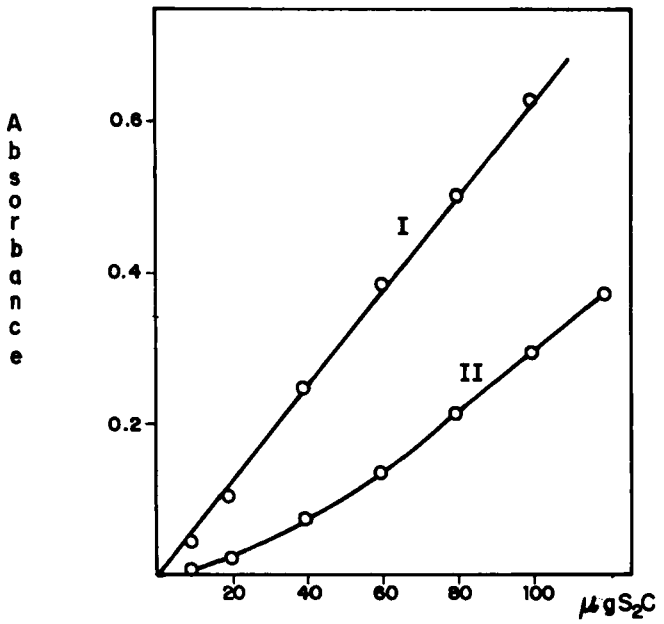


Figure 3 Calibration curves prepared from alcohol solutions of known CS_2 concentration, at (I) 275 nm, and (II) 435 nm.

standard deviation are similar to those observed with other analytical techniques. For example, procedures for dithiocarbamate determination by hydrolysis to liberate carbon disulphide with GC determination[10] have an LOD of 0.5 $\mu g.L^{-1}$ of CS_2. HPLC procedures[11] allow the determination of Thiram with an LOD of 1 $\mu g.L^{-1}$. The indirect determination by AAS after complexation with e.g. Cu(II)[12] has an LOD of 40 $\mu g.L^{-1}$ and a relative standard deviation of 2.6%. Titrimetric methods[13] give higher LODs.

Analytical parameters

Interferences are mainly due to impurities containing sulphur atoms. Obviously, the most important is the H_2S generated during hydrolysis. Therefore it is necessary to insert a trap (I) which should contain a 10% w/v NaOH solution. However, H_2S is not the only interference and therefore it is necessary to add an organic solvent to trap I.

For further testing, different organic solvents plus the NaOH solution were added to the trap. Then, the recommended procedure was carried out putting sulphur-containing impurities in the reaction flask. Trap II contained toluene to recover the gases. After each experiment, the toluene solution was analyzed by GC-FPD (Table 1). n-Hexane was selected in order to retain interferences and also to avoid water vapour reaching trap II. Besides this solvent is transparent at the chosen detection wavelengths.

Table 1 Study of intereferences in the determination of Metham and Thiram.

Interferences	*Trap I (solvent)**	*GC analysis of trap II*	
		peak (tr)	*peak height*
Organic matter (10 g)	-	1.47	225
	benzene	1.47	30
	toluene	1.47	30
	n-hexane	1.47	40
	-	-	-
Ethylenethiourea	benzene	-	-
(15 mg)	toluene	-	-
	n-hexane	-	-
	-	1.05	1350
Thiosulphate/sulphite	benzene	1.05	125
(10 mg)	toluene	1.05	120
	n-hexane	1.05	110

*10 mL of solvent indicated added to trap I which always contains 10 mL of 40% (w/v) NaOH solution.

It is preferable to use nitrogen rather than air as carrier gas in order to avoid any oxidation of the reaction products during decomposition and distillation. The flow rate of nitrogen had no noticeable effect on the analytical result between 10 and 15 mL/min. The use of acetic acid in the hydrolysis reaction produced more interferences than hydrochloric acid, so the latter one was chosen in the recommended procedure.

Applications

The method was applied to the determination of Metham and Thiram in soil samples fortified with these fungicides; the results are summarized in Table 2. The method was also applied to a study of the mobility of Metham in these soil samples. The results are shown in Figure 4. The retention volumes (eluate volume containing carbon disulphide concentration maximum) of soils 1 and 2 are 32 and 85 mL, respectively under the operational conditions used. This strong interaction between Metham and soil 2 compared to soil 1 is notably related to

Table 2 Determination of Metham and Thiram in soil samples*.

Active ingredient	*Matrix*	*Spike (μg/kg)*	*Found (μg/kg)*
Metham	soil 1	-	<LOD
		200	200 (0.2)
	soil 2	-	<LOD
		200	180 (0.3)
Thiram	soil 1	-	<LOD
		200	210 (0.3)
	soil 2	-	<LOD
		200	18 0(0.4)

*n = 5; RSD in brackets. Soil 1: 0.60% organic matter; soil 2: 3.20 % organic matter.

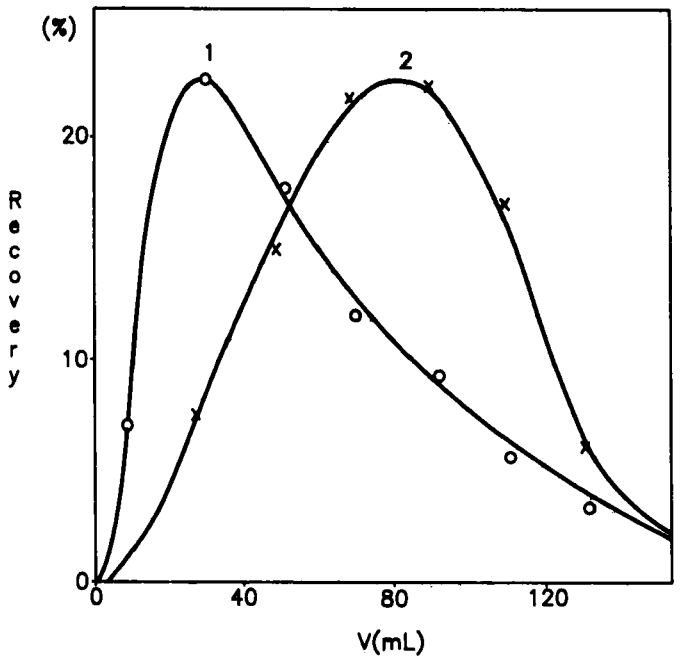


Figure 4 Study of mobility of Metham in soils. (1) soil 1: 0.60% of organic matter; (2) soil 2: 3.20% of organic matter.

the higher organic matter content of soil 2. The band tailing seen in the case of soil 1 may be due to the very low retention capacity of this soil column.

The proposed method was also applied to determine residue levels of Thiram in green beans and watermelons. The results for spiked samples shown in Table 3 indicate recovery percentages of over 90%.

A study of Thiram degradation in watermelons and beans was carried out in an experimental greenhouse from Almería (Spain) on four blocks of 100 m^2 each in the greenhouse. Two of them were treated with a normal dose and the others with a double dose. The spray concentrations were 3 and 6 g/L, respectively; the quantity applied was 30 L in both cases. The harvest was carried out 21 days after application. The mean temperature was 32°C and

Table 3 Determination of Thiram in vegetables.

Sample	Spike (μg/kg)	Found (μg/kg)*
Green beans	-	<LOD
	500	474
Watermelons	-	<LOD
	500	458

*n = 4

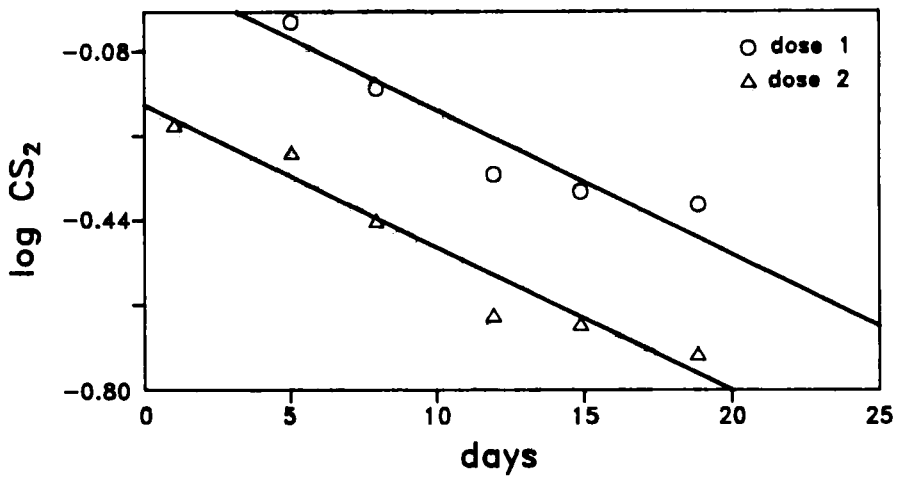


Figure 5 Degradation curves of thiram in green beans using doses of (1) 3 g/L, and (2) 6 g/L.

the mean relative humidity 82%. Figure 5 shows the pertinent degradation curve in green beans. Relevant parameters are summarized in Table IV. The degradation kinetics are first order. In Table IV the $t_{1/2}$ and $t_{1/10}$ values (time necessary for 50% resp. 90% reduction of initial residue level), as well as R_{15} (residue level after 15 days) are summarized. The R_{15} values with a double dose of application are higher than the RMLs (Residue Maximum Levels) established used in the U.K. and by CODEX (0.5 ppm of dithiocarbamate) or Italy (0.2 ppm) for green beans; those for watermelons are slightly higher than the RMLs used in Italy (0.2 ppm), but lower than those used in other EC countries or by CODEX (>1 ppm).

Table 4 Thiram degradation curves in green beans and watermelons.

Parameter	*Green beans*		*Watermelons*	
	Dose 1	*Dose 2*	*Dose 1*	*Dose 2*
r*	0.941	0.937	0.973	0.969
Slope	−0.018	−0.023	−0.030	−0.030
Stand. dev.	0.16	0.20	0.20	0.204
$t_{1/2}$	10.6	4.5	12.2	9.6
$t_{1/10}$	>21	>21	>19	>19
R_{15}	0.59	0.88	0.22	0.42

*r: regression coefficient

CONCLUSIONS

The CS_2/spectrophotometric method for determining microquantities of dithiocarbamates such as Thiram and Metham has been improved, primarily by using 275 nm as the detection wavelength. The method has been applied to the determination of these dithiocarbamates in soils and vegetables grown in greenhouses.

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