
SPECTROPHOMETRIC DETERMINATION OF METHYLSOETHIOCYANATE IN ITS COMMERCIAL FORMULATION AND FOUR INDIAN SOILS

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Abstract: Methylisothiocyanate is used as soil fumigant for nematodes, fungi etc. It is volatile, contaminate the non-target areas by diffusion and its exposure can cause various adverse effects to other organisms including human beings. In the present work a simple spectrophotometric method for the determination of methylisothiocyanate is described. The isothiocyanate is treated in acetonitrile medium with known excess of n-butylamine to convert it into a substituted thiourea and the surplus amine can be smoothly quantitatively transformed into bright yellow copper(I) n-butylidithiocarbamate by reaction with carbon disulphide and copper(I) perchlorate. The yellow colour formed is stable for at least 120 min and is measured at 360 nm. The method has been validated for soil adsorption study of methylisothiocyanate on four soils. The adsorption isotherms have been evaluated by Freundlich's adsorption equation and have been found to be S-type. Various adsorption parameters such as (K_d), (K_{oc}), (ΔG°) and (GUS) have also been calculated. The very low values of K_{oc} suggest that methylisothiocyanate is very weakly adsorbed and is highly mobile in soil. The leaching potential of methylisothiocyanate has been evaluated in terms of ground water ubiquity score (GUS) and has been found in the range 1.84-2.02, classifying it as a transient pesticide.

Keywords: Methylisothiocyanate, n-butyl amine, Copper (I) perchlorate, Soil adsorption, Ground water ubiquity score.

Introduction : Methylisothiocyanate (MITC), CH_3CNS , is marketed as Di-trapex and used as soil fumigant for nematodes, fungi etc. It is also released from fumigants such as metam-sodium, metam-potassium and dazomet which undergo decomposition to MITC in moist soils [1]. MITC has a definite environmental advantage over methylbromide in that MITC is much less stable in the troposphere and is not considered to be an ozone-depleting chemical [2,3]. MITC is volatile and diffuse out of the soil into the atmosphere over treated fields and can contaminate the non-target areas by diffusion. Its exposure can cause various adverse effects to other organisms including human beings. At low levels of acute exposure to the vapour, humans may experience irritated or burning eyes and certainly at higher levels, the spectrum of symptoms may expand to include nasal irritation, throat irritation, rash, headache, nausea, salivation, coughing, shortness of breath and may also cause skin allergies [2,3]. Di-trapex is a commercial pesticide formulation containing 235g methyl isothiocyanate and 931g dichloropropane/ dichloropropene per litre of the formulated product.

In the present work a simple spectrophotometric method for the determination of MITC in soil is described. The isothiocyanate is treated in

acetonitrile medium with known excess of n-butylamine to convert it into a substituted thiourea and the surplus amine can be smoothly quantitatively transformed into bright yellow copper(I) n-butylidithiocarbamate through reaction with carbon disulphide and copper(I) perchlorate. The yellow colour which develops immediately is stable for at least 120 min and is measured at 360 nm. It may be mentioned here that the pesticide is not directly involved in its determination but is stoichiometrically related to the concentration of n-butylamine as dithiocarbamate. The method has been successfully applied to the analysis of a commercial insecticide formulation based on MITC - ditrapex and for its soil adsorption studies on four soils of different soil characteristics. The adsorption isotherms have been evaluated by Freundlich's adsorption equation and various adsorption parameters such as (K_d), (K_{oc}), (ΔG°) and (GUS) have also been calculated.

2. Experimental

2.1 Reagents and equipments

Acetonitrile (Merck, AR) was kept over phosphorus pentoxide (5 g L^{-1}) and distilled twice. n-Butylamine, The analytical standard of n-butyl amine (Fluka, Switzerland) was used as received. A standard solution of copper(I)

perchlorate, (0.01 mol L^{-1} in acetonitrile) was used. A 2% solution of carbon disulphide (Merck, AR) in acetonitrile was used. All the spectrophotometric measurements were made with a Spectronic 20 D⁺ spectrophotometer with 1cm matched glass cells.

2.2 Soil samples

The soils used in the adsorption study were collected from Solan District of Himachal Pradesh, India. The soils samples were air-dried, crushed with wooden mortar and sifted through 2 mm sieve. Dried and sieved soil samples were placed in sealed glass jars and stored at room temperature.

2.3 Preparation of calibration graph for pure compound

2.3.1 Preparation of calibration graph for pure n-butylamine:

Aliquots (0.1-2.0 mL) of standard solution (2×10^{-3} M in acetonitrile) of n-butyl amine were taken, diluted to 3 mL with acetonitrile, mixed with 0.5 mL of carbon disulphide solution (2% in acetonitrile) and kept for 5min to ensure the completion of reaction. To each solution was added 1mL of copper(I) perchlorate (0.005 M in acetonitrile) and finally volume made to 5 mL with distilled water. The absorbance of yellowish brown solution so obtained was measured at 360 nm (spectrum illustrated Fig 1), against reagent blank and a calibration graph was also prepared.

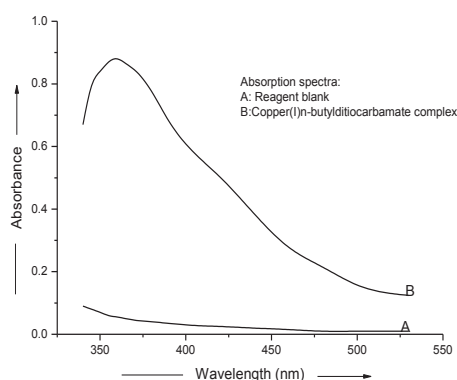


Fig. 1 Absorption spectrum of copper(I)-n-butylthiocarbamate complex

2.3.2 Determination of pure methylisothiocyanate:

Aliquots (0.05-1.0 mL) of standard solution of methylisothiocyanate (2×10^{-3} M in acetonitrile) were taken in 5 mL measuring flasks, diluted to 1.5 mL with acetonitrile, mixed with 1.5 mL of n-butyl amine (0.002 M, in acetonitrile) and kept

for 5 min to ensure the completion of reaction. Each solution was mixed with 0.5 mL of carbon disulphide solution (2% in acetonitrile) and 1 mL of copper(I) perchlorate (0.005 M in acetonitrile) and finally volume made to 5 mL with distilled water. The absorbance of yellow brownish solution so obtained was measured at 360 nm, the wavelength of maximum absorbance of solution against reagent blank. The determination has been made by referring the absorbance values to standard curve obtained with pure n-butylamine.

2.4 Formulation analysis:

One insecticide formulation 'Di-trapex' containing 23.5% active ingredient, emulsifiable concentrate (EC) was used. A single large sample of the formulation was dissolved in fixed volume of acetonitrile. Aliquots of this solution were taken and processed for analysis in the same manner as given above for pure compound. The results of analysis are given in Table 1.

Table I. Assay results of Di-trapex containing 23.5% MITC .

Active ingredient taken, μg	Active ingredient found* %	
	Present method	Comparison method
4.8	98.4 \pm 0.70	97.5 \pm 0.92
9.6	99.0 \pm 0.80	98.7 \pm 0.82
14.4	97.9 \pm 0.82	98.0 \pm 0.80
24.0	98.2 \pm 0.90	97.8 \pm 0.94
28.8	98.6 \pm 0.76	97.4 \pm 0.87

*Values are mean of five determinations with standard deviation (\pm).

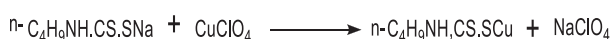
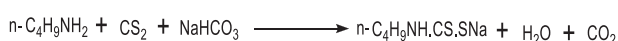
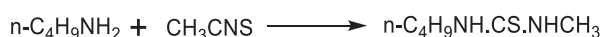
2.5 Soil adsorption study

MITC adsorption isotherms on four Indian soils of different soil characteristics (Table 2) were obtained by the batch equilibration technique using 50 mL conical flask. Triplicate soil samples (2.0 g) were equilibrated with aqueous-acetonitrile MITC solutions in the concentration range from 14.62-43.87 $\mu\text{g mL}^{-1}$ by shaking in Incubator Shaker PT-422 at room temperature ($25 \pm 1^\circ\text{C}$) for 12 hr. equilibrium time. After equilibration, the suspensions were centrifuged and the equilibrium concentrations (C_e) were determined in supernatants by the spectrophotometric procedure described above for the pure compound.

3. Results and discussion : Copper(I) perchlorate in acetonitrile has been found a

suitable reagent for the spectrophotometric determination of primary and secondary amines as dithiocarbamates [5]. That n-butylamine can be smoothly quantitatively transformed into bright yellow copper(I) n-butylthiocarbamate through reaction with carbon disulphide and copper(I) perchlorate has been made the basis of a spectrophotometric method for its determination and consequently to the determination of MITC. It may be mentioned here that the MITC is not directly involved in their determination but is stoichiometrically related to the concentration of n-butylamine as dithiocarbamate. The yellow colour which develops immediately shows λ_{\max} at 360 nm and is stable for at least 120 min.

The most plausible mechanism for the proposed spectrophotometric method is shown below:



Under the optimized experimental conditions, the proposed extractive spectrophotometric method obeys Beer's law in the range 2.43-36.56 $\mu\text{g mL}^{-1}$ of n-butyl amine solution. The molar absorptivity and Sandells sensitivity were found to be $1.27 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0575 \mu\text{g cm}^{-2}$ respectively. The method has successfully been applied to the analysis of a commercial formulation of MITC for its active ingredient content for the purpose of quality control with recoveries of the active ingredient in the range of 97.9-99.0 % of the nominal content with RSDs in the range of 0.70-0.90%. To assess the validity of the proposed method in soil adsorption study the effect of various common ions on the determination of fungicide was studied and it was found that most of the common ions viz. Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{2+} , Pb^{2+} , Cl^- , SO_4^{2-} , CO_3^{2-} , NO_2^- , NO_3^- , SCN^- , PO_4^{3-} and acetate present in the soil do not interfere in the proposed method.

Soil adsorption study

The adsorption isotherms of MITC on four soils of different soil characteristics (Table 2) were evaluated by Freundlich's adsorption equation which is written as

$$X = K_f C_e^{n_f} \quad (1)$$

Where X is the amount of pesticide adsorbed mg kg^{-1} of the adsorbent; C_e is the equilibrium concentration in solution (mg L^{-1}); K_f and n_f are adsorption coefficients which are calculated by using equation (2).

$$\log X = \log K_f + n_f \log C_e \quad (2)$$

The various adsorption parameters viz. soil-adsorption coefficient (K_d), soil organic carbon partition coefficient (K_{oc}), Gibb's free energy (ΔG°) and Groundwater Ubiquity Score (GUS) have been calculated by using equations 3-6 respectively [6-8] and are presented in Table 3.

$$K_d = \frac{X}{C_e} \quad (3)$$

$$\Delta G^\circ = -RT \ln K_d \quad (4)$$

$$K_{oc} = K_d \times \left(\frac{100}{\%O.C.} \right) \quad (5)$$

$$GUS = \log t_{1/2} [4 - \log(K_{oc})] \quad (6)$$

Where R = gas constant, T = absolute temperature, $t_{1/2}$ = pesticide persistence (half life), OC = organic carbon content of soil. Based on the Giles classification [9] the isotherms obtained for MITC are almost S-type depending on the initial slope of the curve which is further supported by n_f ($n_f > 1$) which infer that there is competition between MITC and solvent molecules for adsorption sites on the surface of soil (Fig 2).

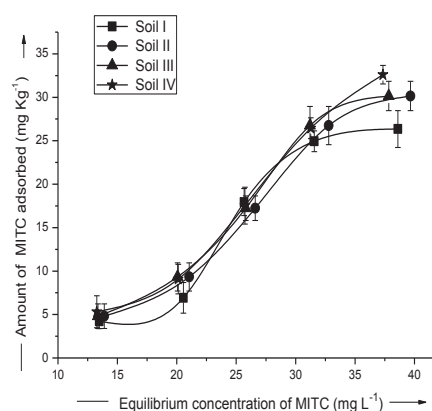


Fig 2. Adsorption isotherm of MITC on four different soils.

The low K_f value and higher n_f value of MITC may due to its less hydrophobic nature and greater solubility in water. The cation exchange capacity (CEC) of soil is directly proportional to hydrophobic nature of adsorbent and higher the value of CEC, more will be the adsorption of hydrophobic pesticides [10]. The K_d and K_{oc} are

important adsorption parameters which represent the extent of adsorption. The K_{oc} is less soil specific and is calculated by normalizing K_d with the organic carbon (OC) content of the soil [11]. The very low values of K_d and K_{oc} suggest that MITC is very poorly adsorbed to soils and it is highly mobile in the soils.

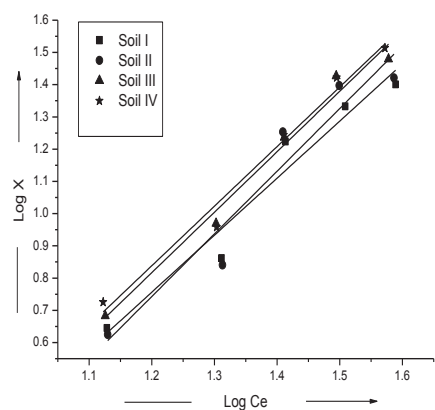


Fig 3 Plot of log X versus log Ce for the evaluation of Freundlich's adsorption coefficients K_f and n_f for MITC.

The leaching potential of MITC was evaluated in terms of GUS index which has been determined by using experimentally observed K_{oc} value for each soil sample and literature reported half life of MITC. The GUS values for MITC ranged from 1.84-2.02 which classifies it as a transient pesticide. GUS score is used for predicting the leaching behaviour of compounds. Generally they can be classified as leacher ($GUS > 2.8$), transition ($2.8 > GUS < 1.8$) and non-leacher ($GUS < 1.8$) [12].

4. Conclusion

The proposed method for the determination of MITC is simple, rapid and reliable and is of wide applicability. Adsorption studies indicates that adsorption isotherms of MITC are almost of S-type which are further supported by n_f values ($n_f > 1$). The very low values of K_d and K_{oc} suggest that MITC is very poorly adsorbed and is highly mobile in the soils. The GUS further indicates that MITC is a transition pesticide and can leach to groundwater sources.

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Table 2. Characteristics of the four Indian soils used in the adsorption study of MITC.

Soil Sample	Soil Texture	pH	Clay (%)	Organic carbon (%)	C E C (meq/100g)
I	Clay Loam	7.2	32.6	0.80	13.11
II	Silt loam	7.6	18.2	0.90	12.91
III	Sandy Loam	6.5	20.0	1.50	11.0
IV	Gravelly Sandy Loam	6.8	23.4	1.60	12.80

Table 3. Adsorption parameters for the adsorption of MITC on four Indian soils.

Soil	k_f	n_f	K_d	K_{OC}	ΔG°	GUS
I	0.043	1.77	0.53	66	-1.578	1.84
II	0.025	1.94	0.56	63	-1.417	1.86
III	0.036	1.87	0.63	42	-1.147	2.00
IV	0.041	1.85	0.65	40	-1.065	2.02

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