Determination of Methylisothiocyanate in its Commercial Formulation and Different Soils by a Simple Spectrophotometric Method

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ABSTRACT: Methylisothiocyanate is used as soil fumigant for nematodes, fungi etc. It is volatile, contaminate the nontarget 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 in soil is described. It is treated in acetonitrile medium with an 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-butyldithiocarbamate through reaction with carbon disulphide and copper(I) perchlorate. The yellow colour formed is stable for at least 120 min and is measured at 360nm. 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^o) and (GUS) have also been calculated. The very low values of K_{oc} suggest that methylisothiocyanate is very weekly 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, copper(I)perchlorate, Spectrophotometric method, soil adsorption.

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INTRODUCTION

Methylisothiocyanate (MITC), CH_3CNS, marketed as Di-trapex and is 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 methyl bromide 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 and its exposure can cause various adverse effects to other organisms including human beings. At low levels of acute exposure to its vapours, 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[3,4]. The reported oral LD_{50} is 72 mg/kg[5]. Di-trapex is a commercial pesticide formulation based on methylisothiocyanate which contains 235g methylisothiocyanate and 931g dichloropropane/dichloropropene per litre of the formulated product. It is used as a soil fumigant for control of nematodes, soil fungi, insects and weeds. It is used prior to planting because it is phytotoxic.

In the present work a simple spectrophotometric method for the determination of methylisothiocyanate in soil is described. The isothiocyanate is treated in acetonitrile medium with an 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-butyldithiocarbamate 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 360nm. It may be mentioned here that the pesticide is not directly involved in its determination but is stiochiometrically 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 methylisothiocynate - 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^o) and (GUS) have also been calculated.

MATERIAL AND METHODS

Reagents and equipments: Acetonitrile (Merck, AR) was kept over phosphorus pentoxide (5 g L^{-1}) and distilled twice. The analytical standard of n-butyl amine (Fluka, Switzerland) was used and its stock solution (2×10^{-3}M in acetonitrile) was prepared. The purity of n-butyl amine was checked by a known method[6]. A standard solution of copper(I) perchlorate, (5×10^{-3}M 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 20D$^+$ spectrophotometer with 1cm matched glass cells.

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 2mm sieve. Dried and sieved soil samples were placed in sealed glass jars and stored at room temperature.

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

Determination of pure methylisothiocyanate: Aliquots (0.05–1.0 mL) of standard solution of methylisothiocyanate (2×10^{-3}M in acetonitrile) were taken in 5mL measuring flasks, diluted to 1.5mL with acetonitrile, mixed with 1.5mL of n-butyl amine (2×10^{-3}M in acetonitrile) and kept for 5min. Each solution was mixed with 0.5mL of carbon disulphide solution (2% in acetonitrile) and kept for another 5min to ensure the completion of reaction. To each solution was added 1mL of copper(I) perchlorate (5×10^{-3}M in acetonitrile) and finally volume made to 5mL with distilled water. The absorbance of yellow brownish solution so obtained was measured at 360nm, 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.
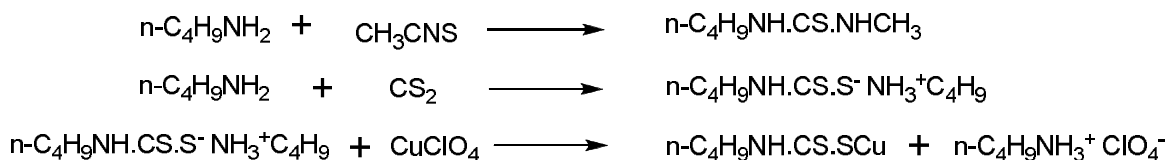
Formulation analysis: One insecticide formulation 'Di-trapex' containing 23.5% active ingredient, emulsifiable concentrate (EC) was used. A single large sample of the formulation was dissolved in fixed volume of acetonitrile. Aliquots of the acetonitrile solution of methylisothiocyanate formulation (Di-trapex) were taken and processed for analysis in the same manner as given above for pure compound.

Soil adsorption study: Methylisothiocyanate 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 (2g) were equilibrated with aqueous-acetonitrile methylisothiocyanate solutions in the concentration range from 14.62-43.87 μg mL^{-1} for methylisothiocyanate by shaking in Incubator Shaker PT-422 at room temperature (25±1°C) for 12 hr. equilibrium time. After equilibration, the suspensions were centrifuged and the equilibrium concentrations (Ce) were determined in supernatants by the spectrophotometric procedure described above for the pure compound. Adsorption isotherms were evaluated by using Freundlich's adsorption equation.

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[7]. The reagent forms a colourless solution in acetonitrile which is extremely stable. That copper(I) is stabilized as tetraacetonitrilocopper(I) perchlorate (CuClO$_4$.4CH$_3$CN) in acetonitrile is well established[7]. That n-butylamine can be smoothly quantitatively transformed into bright yellow copper(I)n-butyldithiocarbamate through reaction with

carbon disulphide and copper(I) perchlorate has been made the basis of a spectrophotometric method for the determination of methylisothiocyanate. The most plausible mechanism for the proposed spectrophotometric method is shown below:

$$n\text{-}C_4H_9NH_2 \; + \; CH_3CNS \longrightarrow n\text{-}C_4H_9NH.CS.NHCH_3$$

$$n\text{-}C_4H_9NH_2 \; + \; CS_2 \longrightarrow n\text{-}C_4H_9NH.CS.S^- NH_3^+C_4H_9$$

$$n\text{-}C_4H_9NH.CS.S^- NH_3^+C_4H_9 \; + \; CuClO_4 \longrightarrow n\text{-}C_4H_9NH.CS.SCu \; + \; n\text{-}C_4H_9NH_3^+ ClO_4^-$$

It may be mentioned here that the methylisothiocyanate is not directly involved in its determination but is stiochiometrically 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 method has successfully been applied to the analysis of a commercial formulation of methylisothiocyanate (Ditrapex) 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%.

The adsorption isotherms of methylisothiocyanate on four soils (Figure 1) of different soil characteristics (Table 2) were evaluated by Freundlich's adsorption equation which is written as:

$$X = K_f C_e^{n_f} \qquad \text{------------(1)}$$

Where X is the amount of pesticide adsorbed $mgkg^{-1}$ of the adsorbent; C_e is the equilibrium concentration in solution (mgL^{-1}); K_f and n_f are adsorption coefficients that characterize the adsorption capacity of the adsorbent and these are calculated from the least square methods applied to the linear form of the Freundlich's adsorption equation (2) by the plot of log X verses log C_e (Figure 2).

$$\log X = \log K_f + n_f \log C_e \qquad \text{------------(2)}$$

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[8-10] and are presented in Table 3.

$$K_d = \frac{X}{C_e} \qquad \text{--------------------(3)}$$

$$\Delta G^{\circ} = -RT \ln K_d \qquad \text{-----------(4)}$$

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

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

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,[11,12] the isotherms obtained for methylisothiocyanate are almost S-type (Figure 1) depending on the initial slope of the curve which is further supported by n_f values. Observed value of n_f is more than 1 (1.77-2.12) which infer that there is competition between methylisothiocyanate and solvent molecules for adsorption sites on the surface of soil[13]. The adsorption coefficient K_f represents the amount of pesticide adsorbed at an equilibrium concentration of $1mgL^{-1}$. The values of K_f indicate (Table 3) that methylisothiocyanate is weakly adsorbed and it has tendency to move in soil. The cation exchange capacity (CEC) soil is directly proportional to hydrophobic nature of adsorbent and higher the value of CEC, more will be the adsorption of hydrophobic pesticides. The low K_f values and higher n_f values obtained for methylisothiocyanate may be due to its less hydrophobic nature and greater solubility in water. The K_d and K_{oc} are important adsorption parameters which represent the extent of adsorption. The K_{oc} is less soil specific (less variable) and is calculated by normalizing K_d with the organic carbon (OC) content of the soil[14]. The low values of K_d and K_{oc} suggest that methylisothiocyanate

is poorly adsorbed to soils and it is highly mobile in the soils. The organic matter content and the clay content of soils play a very important role in the sorption of pesticides as these provide soils with an increased number of adsorptive sites onto which pesticides molecules can bind.[15] The leaching potential of methylisothiocyanate 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 methylisothiocyanate. 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).[16] The GUS values for methylisothiocyanate ranged from 1.84-2.02 which classifies it as a transient pesticide.

Table 1: Assay results of Di-trapex containing 23.5% methylisothiocyanate using copper(I) perchlorate.

| Active ingredient taken, µg	Active ingredient found* %
4.8	98.4±0.70
9.6	99.0±0.80
14.4	97.9±0.82
24.0	98.2±0.90

Values are mean of five determinations with standard deviation (±).

Table 2: Characteristics of the different Indian soils used in the adsorption study of methylisothiocyanate.

Soil Sample	pH	Clay (%)	Organic carbon (%)	Cation Exchange Capacity (meq/100g)
I	7.2	32.6	0.8	13.1
II	7.6	18.2	0.9	12.9
III	6.5	20.0	1.5	11.0
IV	6.8	23.4	1.6	12.8
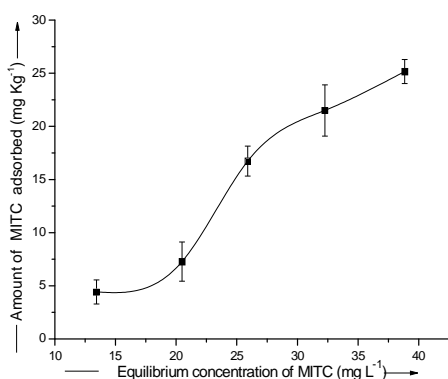
| I-Adsorption isotherm of methylisothiocyanate on soil I | II-Adsorption isotherm of methylisothiocyanate on soil II |

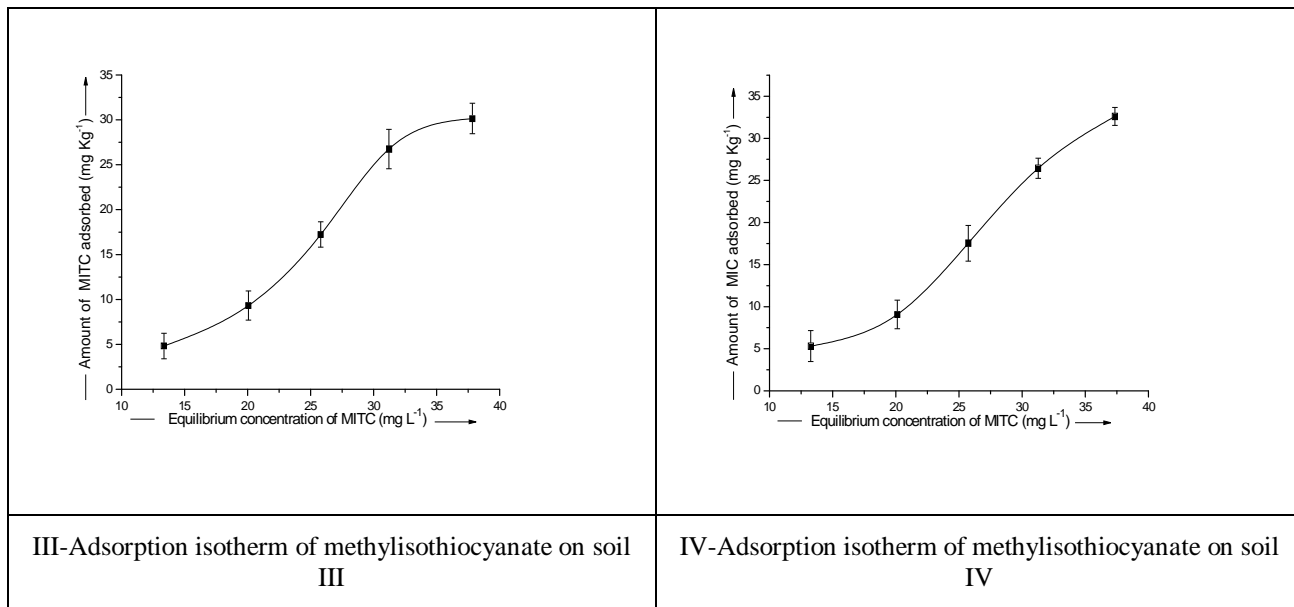| III-Adsorption isotherm of methylisothiocyanate on soil III | IV-Adsorption isotherm of methylisothiocyanate on soil IV |
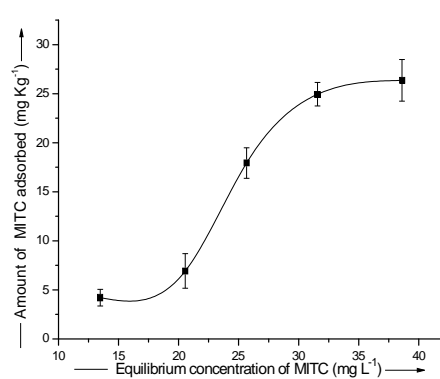
Figure 1: Adsorption isotherms of methylisothiocyanate (error bars represent the standard deviations of three replicates).

Table 3: Adsorption parameters of methylisothiocyanate on four different soils at 25 ± 1°C.

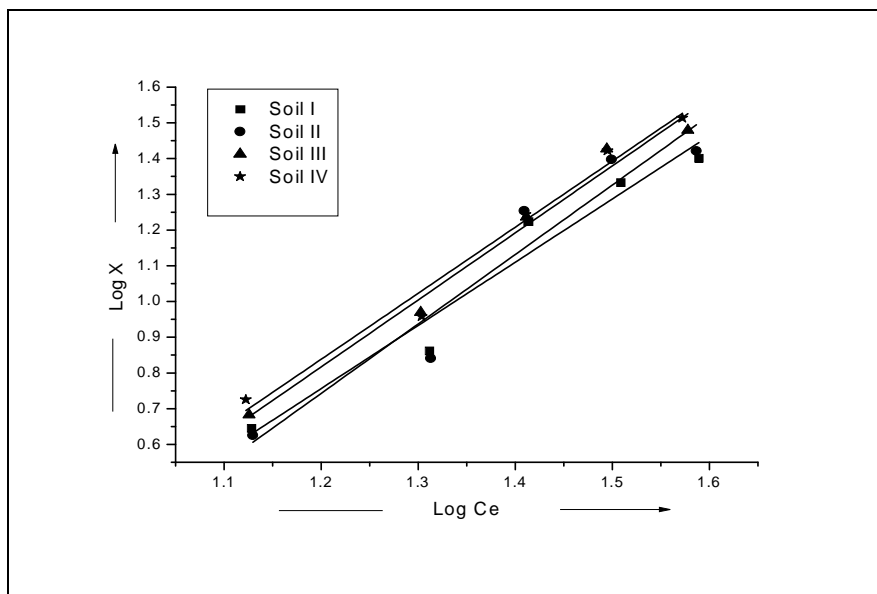| Soil	k_f	n_f	K_d	K_{OC}	ΔG^0	GUS
I	0.043	1.77	0.53	66	-1.578	1.84
II	0.025	1.94	0.56	63	-1.417	1.86
III	0.036	1.87	0.63	42	-1.147	2.00
IV	0.041	1.85	0.65	40	-1.065	2.02

Figure 2: Plot of log X versus log Ce for the evaluation of Freundlich's adsorption coefficients K_f and n_f for methylisothiocyanate.

CONCLUSION

The proposed method for the determination of methylisothiocyanate is simple, rapid and reliable and is of wide applicability. Adsorption studies indicates that adsorption isotherms of methylisothiocyanate are almost of S-type which are further supported by n_f values ($n_f > 1$). The very values of K_d and K_{oc} suggest that methylisothiocyanate is very poorly adsorbed to soils and it is highly mobile in the soils. The low values of K_{oc} and the GUS values further indicate that methylisothiocynide is a transit pesticide and can leach to groundwater sources. The toxicity due to pesticides in general and methylisothiocyanate in particular can be reduced by adjusting the application dose according to soil properties.

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