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Determination of The Release Mechanism of Polymer  
Supported Pesticides.

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DEDICATED TO MY FAMILY  
AND  
TO THE MEMORY OF MY BELOVED FATHER

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ABSTRACT

DETERMINATION OF THE RELEASE MECHANISM  
OF POLYMER SUPPORTED PESTICIDES

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The release mechanisms, of the two organophosphorus insecticides, malathion and chlorpyrifos, were studied from the polymer films prepared in the Laboratory. Furthermore, the behaviour of the release of chlorpyrifos from the granular commercial sample was also studied.

Thus, the diffusion of the insecticides from the insecticidal polymer films: cellulose acetate impregnated with chlorpyrifos, and cellulose acetate impregnated with malathion, have shown the characteristic features of a Fickian diffusion, at higher temperature ( $100^{\circ}\text{C}$ ), and the apparent diffusion coefficients have been calculated. While, at temperatures lower than  $100^{\circ}\text{C}$ , the release has shown a non-Fickian diffusion. On the other hand, the release of chlorpyrifos from the polyethylene vinyl acetate copolymer and the Suscon polymer films have shown a non-Fickian diffusion at all the temperatures of study ( $70^{\circ}\text{C}$ ,  $60^{\circ}\text{C}$ , and  $50^{\circ}\text{C}$ ).

Moreover, the release behaviour of the Suscon commercial sample was studied at different conditions: in soil, water, and open air. And the release was found to be dependent on the concentration of the insecticide, rainfall and temperature.

## 1. INTRODUCTION

PESTICIDES play an important role in crop protection in a country like Ethiopia where agriculture is the back bone of the country. Roughly one-third of the world's food crop is destroyed by pests during growth, harvest, and storage. Hence, to maintain crop productivity at the highest possible level, intensive use of crop protection chemical is essential ( 1, 2). Starting from the small scale farms up to the large ones (state-farms), various kinds of pesticides are used every year depending on the various pests. Some of the common pesticides - insecticides in particular, used in the Southern Regions of Ethiopia are:

Aldrin	Dimecron	Lindane	Rogor
BHC	DDT	Malathion	Sumithion
Crotenon	Dieldrin	Mitac	Parathion
Cymbush	Endosulfan	Mitigan	

Although the indiscriminate dissemination of pesticides into terrestrial and aquatic ecosystems is reprehensible, the magnitude of the pest control will necessitate the use of these materials in the foreseeable future. However, persistent pesticides are undesirable because of their frequent incorporation into the food chain. On the other hand, pesticides with short lives tend to be ineffective. In both cases, the amounts applied are often grossly excessive to that actually required to control the pest because of the need to compensate for pesticide loss by leaching and evaporation (3). This problem has forced man to investigate a new type of pesticidal formulation.

Recently, the interest of pesticide formulation technology lies on the new carriers - which are micro-porous polymers enabling the sustained release of the

active ingredients. This newly developed formulation extends the period of activity and improves the effectiveness of inherently non-persistent biologically active compounds (4).

#### 1.1. Aim of the Research Work

After the slow release pesticide formulation was known to the formulator, some polymers have been used as carriers for the pesticides. However, the work was mainly concerned with their preparation and their control effect rather than with their release mechanism (5-20).

The aim of this investigation is to study how the pesticides are desorped from the polymers and finally to suggest a possible mechanism of their release. For the above study, some polymer supported insecticidal films like cellulose acetate impregnated with chlorpyrifos, malathion and polyethylenevinyl acetate impregnated with chlorpyrifos were prepared in the laboratory and their release behaviours were studied. The selection of the polymer carriers is based on their availability and physico-chemical properties (glass transition temperature, melting temperature, chain flexibility, and stability). In addition the release behaviour of a commercially prepared polymer supported insecticide - Suscon product sample has been studied under different conditions.

## 2. THEORY

### 2.1. Pesticides

Pesticides are chemical substances used for controlling, destroying, repelling or mitigating any pest (5). It covers a large number of more specific names such as insecticides, fungicides, rodenticides, miticides, herbicides, algicides, nematocides, growth regulators and sterilants(22).

The three most important classes of synthetic pesticides are chlorinated hydrocarbons, organophosphorus compounds and carbamates (21). Nowadays carbamates and organophosphorus pesticides are more often used than the organochlorine pesticides, because organochlorine pesticides have a long residual activity and thus result in undesirable consequences.

#### 2.1.1. Organophosphorus Insecticides

The development of the organophosphorus (OPs) insecticides is largely due to the pioneer work of Gerhard Schrader of Farbenfabriken Bayer, Germany, which began about 1934. Since the publication of his studies in 1947, thousands of phosphorus compounds of many types have been evaluated for insecticidal properties (23). The compounds now available are used for nearly every type of insect control, as contact and stomach poisons, as fumigants, and as systemic insecticides. The OPs exert their toxic action by typing up or inhibiting certain important enzymes of the nervous system, namely cholinesterases (2).



Owing to their ester nature, the OPs offer a fundamental advantage in this respect. Normally, they can be easily degraded hydrolytically, enzymatically or biologically. Also, a further advantage lies in the very low application quantities necessary for the desired insecticidal activity in the field (1,2).

#### 2.1.2. Insecticides used in the Research Work

The two insecticides namely, malathion and chlorpyrifos which belong to the class of organophosphorus insecticides have been used in the research work. The chemical and physical properties, LD<sub>50</sub>, pesticidal action, ... of the above insecticides are summarized in Table 1. (21, 24, 25).

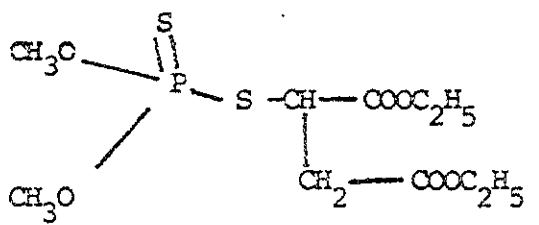
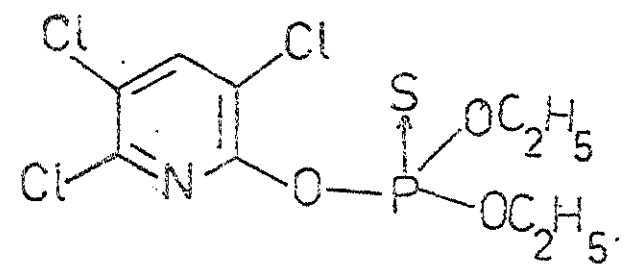
#### 2.2. Pesticide Formulation

Pesticides are biologically active in extremely small quantities; so the chemical has to be prepared in a form that is convenient to use and to spread evenly over large areas (27). Formulation is the processing of a pesticidal compound by any method that will improve its properties of storage, handling, application, effectiveness or safety (2).

The biological property of a pesticide is greatly influenced by the nature of the pesticide and its formulation. A compound will only display optimal biological activity when it is present at the site of action, at the right time, and at the right concentration with optimal formulation. Hence, consideration of the nature of formulation is very essential besides the nature and amount of active ingredient (28).

TABLE 1

PROPERTIES OF THE INSECTICIDES: MALATHION, AND CHLORPYRIFOS

	Malathion (Carbophos, Cythion)	Chlorpyrifos (Dursban, Lorsban)
Class	Organophosphorus Insecticide	Organophosphorus Insecticide
Chemical formula	$C_{10}H_{19}O_6 P S_2$	$C_9H_{11} Cl_3 NO_3 PS$
Structure and Chemical name	 <p>O,O - dimethyl - S - 1, 2 - di (carboethoxy) ethyl phosphoro-dithioate.</p>	 <p>O,O - Diethyl O-(3,5,6 -trichloro 2-pyridyl) phosphorothioate</p>
Molecular Weight	300	351
Physical State	Clear amber liquid	A white granular crystal
Melting point	2.85°C	41.5 - 43.5°C
Boiling point	156 - 157°C/ 0.7 mm Hg	-
Vapour pressure	5.3 m pa at 30°C	2.5 m pa at 25°C
Density	1.23 at 25°C	-
Refractive index	1.4985 at 25°C	-

Contd.

	Malathion	Chlorpyrifos
Solubility	Miscible with most organic solvents of limited solubility in petroleum oil.	2mg/kg of water, 6.5 kg/kg acetone, 7.9 kg/kg Benzene, 6.3 kg/kg chloroform, 4.5g/kg methanol at 25°C.
Chemical Property	It is rapidly hydrolysed at PH about 7.0 or below 5.0; but, is stable in aqueous solution buffered at PH 5.26. It is incompatible with alkaline pesticides.	It is stable under normal storage conditions. It is readily hydrolysed in alkaline media.
ID 50 (lethal Dosage) acute oral for rat	1200mg/kg	135 - 163 mg/kg.
Pesticidal action	It is non systemic insecticide and acaricide of low mammalian toxicity and brief to moderate persistence. It is used for the control of mosquitoes, flies, household insects, animal ectoparasites, and human and head lice. It is mainly used on a wide range of agricultural and horticultural pests. It is generally non-phyto-toxic.	It has a broad range of insecticidal activity and is effective by contact, ingestion and vapor action, but it is not systemic. It persists in soil upto 4 months. As a soil insecticide, it is used in control of peach tree borer, cotton; rice, vegetable and field crop pests.

The choice of the form of the pesticidal product depends (19,20,21,) upon many factors. Some of the factors which should be considered are enumerated below:

1. The purpose for which the pesticide is used will it be an insecticide, herbicide, fungicide, nematocide ...? Will the product be applied to the pest by fogging, spraying, dusting ...? Will it be applied by air plane, applied on or incorporated into the soil, or applied to ponds or water ways?
2. The pest involved - Generally, many different forms of pesticides can be used to treat a single type of infestation, for example both liquid concentrates after dilution, and granules can be incorporated into the soil for soil insects. But one form may be found to be superior to the other type because of better control of a particular pest.
3. Local weather conditions - can also dictate the type of material to be used. For instance, where high wind and drift conditions may endanger nearby crops, the heavier granular product would be superior to dusts, wettable powder concentrates, or emulsifiable concentrates.
4. Phytotoxicity - some plants or indeed individual varieties are susceptible to certain solvents and other ingredients; for instance impurities due to the use of cheap solvents. Phytotoxic effects may be caused by chemical burning, physically by droplets on the plant surface acting as lenses which focus the sun's rays on the plant tissues,

or by subsequent effects on plant growth (11). Moreover, the choice of the pesticide form is decided by what is readily available, and the price.

#### 2.2.1. Types of Pesticide Formulation

The common formulations of pesticides used in agriculture, home and garden as well as those employed in commercial pest control are: Sprays (this includes emulsifiable concentrates, wettable powders, ultralow volume concentrates, fogging concentrates and so on), dusts, aerosols, granulars, fumigants, impregnates, fertilizer combinations with pesticides, smokes and the recently developed slow-release pesticides.

#### 2.2.2. Slow Release Formulations

Slow release formulations are relatively new and only a few are available. One of the recently developed of this type of formulation is Knox Out 2FM<sup>O</sup> (diazinon) used against agricultural and household pests. The principle of this form of slow release involves the incorporation of the insecticide in a permeable covering, microcapsules or tiny spheres, with diameters ranging from 15-50 $\mu$ m, that permits its release at reduced but effective rate. The insecticide diffuses through the sphere wall over an extended period; thus preserving its effectiveness much longer usually two to four times longer, than if formulated as an emulsifiable concentrate (2).

This recently developed formulation has several advantages over the other formulations (3,27 )

- (i) It can be used for most hazardous pesticides (example aldicarb) which should not be applied in spray form.
- (ii) It avoids loss of activity by sorption on soil particles.
- (iii) Chemicals with short persistence may be used and, to off-set problems of poor distribution, activity may continue until roots have grown nearer to it.
- (iv) There may be phytotoxicity under very wet conditions, precise and active ingredients may, therefore, be required.
- (v) Furthermore, controlling the release rate of the active ingredient is very important to weather conditions; especially, if heavy rain occurs, it may not permit a spray application at the most appropriate time. Hence, if there is a prediction of an infestation, this type of formulation can be used before the pest attacks. Moreover, under hot climatic conditions, it prevents the greater loss of the active ingredient due to its high volatility.

As, it is mentioned in the above, the slow release formulation has several advantages over the others, and it has also a draw back particularly in relation to the production of sub lethal doses and induction of resistance by the pests.

### 2.3. Diffusion

Diffusion is a spontaneous transport of matter from one part to another in an inhomogeneous binary-or, to

be more general, multicomponent mixtures of gases, liquids or solids. The force that drives components in this process is of a thermodynamic nature. In a system composed of two components, it is the gradient of chemical potential of the component under consideration, and for a system composed of more than two components, the gradient of chemical potentials of coexisting components also contribute to the driving of a particular component ( 32 ). Except in circumstances where there is a steady field of force (gravitational, centrifugal, etc.) through a mixture, diffusion continues until the mixture finally becomes uniform with respect to chemical concentration.

### 2.3.1. Diffusion Equations

Based on the analogy of the transfer of heat by conduction and mass transfer due to diffusion Ficks (1885) put diffusion on a quantitative basis adopting the mathematical equation of heat conduction derived some years earlier by Fourier ( 1822).

The mathematical theory of diffusion in isotropic substances is, therefore, based on the hypothesis that the rate of transfer of diffusing substances through unit area of a section is proportional to the concentration gradient measured normal to the section (33). If  $x$  be the coordinate chosen perpendicular to the reference surface, and  $c$  the concentration of the diffusing substance, given as amount of substance per cubic centimeter, Fick's first law of diffusion may be stated in the form ( 34 ).

$$J = -D \frac{\partial c}{\partial x} \quad \text{--- 1}$$

Where J is the rate of transfer per unit area section, and D is the diffusion coefficient. In c.g.s. units, the dimension of J is the quantity of substances per cm<sup>2</sup> per second, and D has the dimension cm<sup>2</sup> sec<sup>-1</sup>.

Generally, however, it is not possible to investigate diffusion under conditions of constant concentration gradient, which implies the establishment of a steady state. One, therefore, has to determine the change of concentration with time caused by diffusion within a gas mixture, a liquid solution or a solid. When there is diffusion in the x - direction only, when it is observed the increase of the amount of substance within a volume element bounded by two parallel planes of unit area situated at x and x+dx. this increase is

$$\begin{aligned} (J)_x - (J)_{x+dx} &= D \left[ \left( \frac{\partial c}{\partial x} \right)_{x+dx} - \left( \frac{\partial c}{\partial x} \right)_x \right] \\ &= D \left( \frac{\partial^2 c}{\partial x^2} \right) dx \quad \text{--- 2} \end{aligned}$$

After dividing equation 2 by the volume dx·1cm<sup>2</sup> of the element, we obtain for the increase of the concentration with time, in the limit dx→0.

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \text{--- 3}$$

Which is Fick's second law of diffusion, derived on the assumption that D is constant. If diffusion occurs in an arbitrary direction,

$$\frac{\partial c}{\partial t} = D \left[ \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right] \quad \text{--- 4}$$

and if D is not constant, equation 4 is written as

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) + \frac{\partial}{\partial y} \left( D \frac{\partial c}{\partial y} \right) + \frac{\partial}{\partial z} \left( D \frac{\partial c}{\partial z} \right) \quad \text{--- 5}$$

### 2.3.2. Diffusion in Polymer Solids

The two methods used for the measurement of the permeability of substances are, the transmission method and the sorption - desorption method (35). The latter method will be discussed here.

### 2.3.3. Sorption - Desorption Method

This method is largely used for condensable vapor - polymer systems in which appreciable amount of vapor is sorbed and the solubility coefficient and  $D$  are often dependent on concentration. This method can be applied either in vapor phase or in liquid phase. In this method a thin film of a given polymer or a polymer - diluent (solvent, swelling agent or plasticizer) mixture is exposed to vapor of a given diluent at a given pressure; the gain or loss in weight of the film is measured as a function of time (35). The common way in presenting the data from the sorption - desorption method is to plot  $M(t)$ , the amount of a given diluent absorbed in ( or desorbed from) unit volume of a given polymer for a time  $t$  from a start of the experiment against the square root of time  $t$ . When the pressure  $p$  of the ambient vapor is maintained constant,  $M(t)$  eventually approaches a limiting value, usually denoted by  $M$ . Once this limiting value is reached the film does not absorb or desorb any more diluent and is a thermodynamic equilibrium with the surrounding vapor. Often the ratio of  $M(t)/M(\infty)$  is plotted against  $t^{1/2}/l$ , where  $l$  is the thickness of the sample film, to give the reduced sorption curve. This form of representation of data is convenient for theoretical analysis, including the calculation of  $D$  (32).

#### 2.3.4. Characteristic Features of Fickian and Non-Fickian Diffusion

A number of experiments have demonstrated that sorption - desorption curves of polymer-diluent systems can be classified into two types - Fickian and non-Fickian (32).

The diffusion behaviour of many polymers cannot be described adequately by a concentration dependent form of Fick's law with constant boundary conditions especially when the penetrant causes extensive swelling of the polymer. Generally, this is the case with the so called glassy polymers which are said to exhibit "anomalous" or "non-Fickian" behaviour. In rubbery polymers, on the other hand, diffusion is generally Fickian (33).

Alfrey, Grunee; and Lloyd (1966) proposed a useful classification according to the relative rates of diffusion and polymer relaxation. The three classes are:-

- (i) - Case I or Fickian diffusion in which the rate of diffusion is much less than relaxation.
- (ii) - Case II diffusion, the other extreme in which diffusion is very rapid when compared to the relaxation process.
- (iii) - Non Fickian or anomalous diffusion which occurs when the diffusion and relaxation rates are comparable.

Under Case I, systems are controlled by the diffusion coefficient. Under case II the parameter is the constant velocity of an advancing front which

which marks the inner most limit of penetration of the diffusant, and is the boundary between swollen gel and glassy core. Case II is also a second extreme or limiting case with respect to the shape of the Sorption - time curve. If we denote the amount sorbed at time  $t$  by  $kt^n$ ; with  $k$  and  $n$  constants, then case II systems are characterized by  $n = 1$  and case I systems by  $n = \frac{1}{2}$ . While non Fickian System lies between Case I and Case II in that  $n$  takes an intermediate value between  $\frac{1}{2}$  and 1, or changed sigmoidally from one to the other. The qualitative description of the main characteristic features of diffusion in polymers can be given as follows:

(i) Fickian Diffusion

Various features of this type of diffusion have been clarified through extensive studies especially by Crank and co-workers. Some of them, which are of a particular importance are: (32, 33).

In the early stages, when diffusion takes place essentially in a semi infinite medium, the amount sorbed or desorbed is directly proportional to the square root of time.

When  $D$  increases with concentration increasing, the linear behaviour may extend well beyond 50% of the final equilibrium uptake in the case of sorption. The same is true for desorption when  $D$  decreases with concentration increasing (Figure 1 (a) ).

- Above the linear regions both absorption and desorption curves are concave against the time axis and steadily approach the final equilibrium value.
- When the initial and final concentrations are fixed, the reduced absorption curves for films of different thickness all coincide, yielding a single curve. The same is, also, true for the desorption curves.
- Both the curves coincide over the entire region of  $t$  only when  $D$  is independent of surface concentration.

(ii) Non-Fickian Diffusion

Sorption curves which do not conform to the above features for Fickian sorption - desorption are all referred to as non-Fickian or anomalous.

Sigmoid Curves - curves of the general shape of Figure 1(b) have been observed experimentally in many systems. The sorption curves are sigmoid in shape with a single point of inflexion often at about 50% equilibrium sorption. The initial rate of desorption exceeds that of sorption, but desorption soon becomes slower and the curves cross (35). Two stage curves: Figure 1(c) shows that the film absorbs vapor rather quickly upto a concentration corresponding to B; then the absorption becomes very slow and follows a sigmoid curve until the final equilibrium is reached. This anomalous behaviour was discovered by Long and co-workers (36), when they studied absorption of acetone and methanol by cellulose acetate; and has been observed subsequently by many authors for other polymer diluent systems including amorphous and crystalline

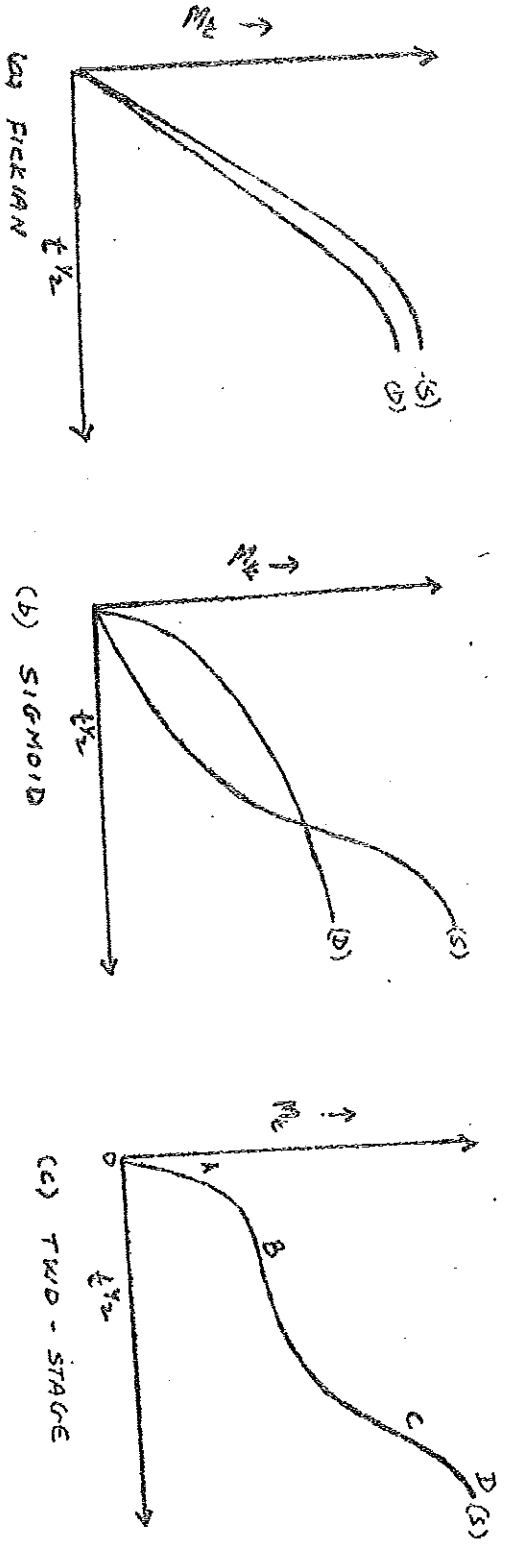


Figure 1. Non-Fickian sorption (S) and desorption (D) curves compared with Fickian type curves.

polymers. At present, it may be regarded as one of the most general features of glassy polymer systems. Detailed studies have demonstrated that vapor absorption from O to B via A not merely looks Fickian but really obeys various criteria for the Fickian sorption; where as the process from B to the final equilibrium via C is decidedly non Fickian.

(iii) Advancing Boundaries: Case II

When a liquid penetrant diffuses into a polymer sheet or filament a sharp boundary can often be seen under a microscope. Three boundaries are observed. The inner boundary marks the limit of penetration of the liquid, while the outer boundary shows the limit of the swollen gel. The third, intermediate, boundary is usually thought to lie between polymer in the elastic rubbery state and glassy polymer. Often the positions of the boundaries are proportional to  $t^{1/2}$ . From the interferometric fringes of photographs of chloroform penetrating cellulose acetate, the concentration was seen to change very rapidly in the region of the inner boundary, implying the existence of large internal stresses due to the interaction of the swelling polymer and the central unattacked core of the sheet. This stress can result a change in the orientation of the polymer molecules (33).

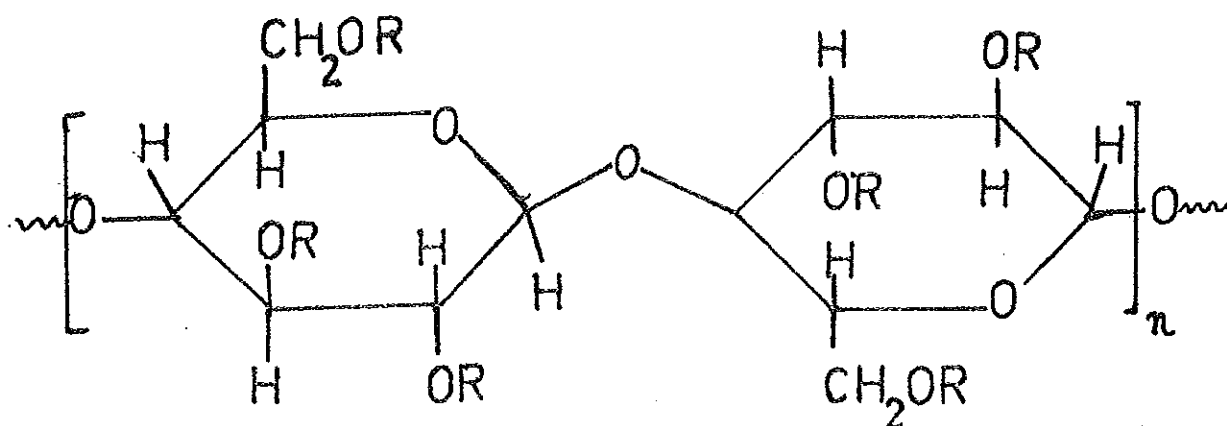
The main characteristic features of diffusion in polymers are described in the above. Generally, it is observed that, Fickian and non-Fickian diffusions are obeyed by the rubbery and glassy polymers respectively (33). Furthermore, experimental results have shown that whether the polymer is polar (like cellulose nitrate or poly vinylacetate) or non polar ( like

polystyrene) and independent of the character of the diffusing molecule, diffusion is Fickian if the polymer - is above its second order transition (glass transition) and anomalous if the polymer - solvent mixture is below glass transition temperature ( $T_g$ ). Moreover for systems below  $T_g$  the diffusion process causes increased orientation in the direction of diffusion. This change in the character of the diffusion at  $T_g$  is undoubtedly a result of the marked change in the mobility of polymer segments which occurs at the second order transition. Presumably above  $T_g$  the polymer - penetrant system can adjust to changes in penetrant concentration with sufficient rapidity that the normal process of hole formation is the rate determining step and hence the diffusion is Fickian. The anomalous diffusion which occurs below  $T_g$  can formally be explained by postulating that the diffusion coefficient is a function of variables other than concentration. A more specific suggestion is that, because of the low mobility below  $T_g$ , the diffusion coefficient ( $D$ ) does not immediately reach its equilibrium value as the penetrant concentration changes, leading to a  $D$  which depends on time as well as concentration. As Crank and Park have pointed out such an added dependence of  $D$  on time can easily lead to the of anomalous diffusion that is observed (33,37-39).

## 2.4. Polymers Used in the Research Work

### 2.4.1. Cellulose Acetate

Acetylation of cellulose with acetic anhydride in the presence of catalysts such as zinc chloride or sulfuric acid gives Cellulose acetate with different degree of substitution.



Monomer Unit in Cellulose Acetate.



The degree of substitution (DS) is expressed as the average number of hydroxyl groups per anhydroglucose unit having been substituted, and thus range from 0-3. Pure cellulose acetate has an acetyl content of 44.8% by weight (DS value close to 3) (40).

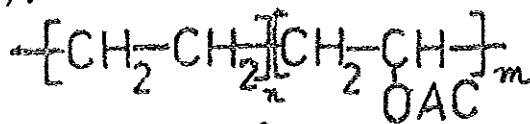
Physical and chemical properties cellulose esters depend on the amount and type of acyl groups present and the molecular weight. The product of

complete acetylation (triacetate flake) and partial deacetylation (acetate flake) are white, amorphous solids and can be produced in granular or powder form. The commercial products do not have a sharp melting point; acetate flake starts to soften at 220°C, and as the degree of acetylation increases, the softening point also increases. Cellulose triacetate has a glass transition temperature 157°C and melting temperature around 306°C (40-42). The solubilities of the various acetate are dependent on the degree of acetylation; the principal commercial solvents are acetone for the secondary acetate and methyl acetate, dimethyl formamide, and chloroform for triacetate (41).

#### 2.4.2. Polyethylene vinyl acetate (EVA) copolymer

Although ethylene copolymers have been known since the 1930s, it has been only recently that these materials, due to their unique physical and chemical properties, have become substantial articles of commerce.

EVA Copolymers are prepared, from the two monomer units polyethylene and vinyl acetate both at very high pressure (1020 atm) and also at relatively low pressure (upto 102 atm) in an emulsion polymerization. Due to equal reactivities of the two monomers, uniform copolymers are relatively formed ( 43).



Monomer Unit in Eva Copolymer.

The mechanical properties of polyethylene are largely dependent upon the crystallinity of the polymer. Since copolymerization acts to break up chain uniformity and crystallization, the property of ethylene copolymer will depend, to a first approximation on the molar amount of the comonomer present rather than the chemical nature of the comonomer. It is observed that the percentage of crystallinity of the polymer decreases with increasing the comonomer unit. With the percentage composition of 50-80% of vinyl acetate the polymers are non crystalline and in the rubbery state. The solubility of the EVA copolymers also depend on the amount of the comonomer. For instance, pure polyvinylacetate is soluble in methanol, while EVA copolymer with 25% ethylene is not soluble in methanol, but is soluble in methanol - butanol mixture. EVA copolymer has a glass transition temperature in the range of  $-25^{\circ}\text{C}$  ( for pure polyethylene) to  $30^{\circ}\text{C}$  (for pure viny acetate), depending on the percentage composition of the comonomer units ( 43,44).

#### 2.5. Analytical Methods for Pesticides Determination

The approach, and essentially the attitude, of the formulation chemist to the analysis of the formulated product is that of determining the percentage present using a procedure reasonably well adapted for this purpose. Occasionally, the same procedure that would be used in the residue analysis is also employed for the formulation analysis (45).

Residue methods almost invariably require, among other special processing procedures, that a rigorous clean-up technique be applied. This is necessitated because large samples are required for analysis and

extraneous materials may be coextracted with the pesticide (45, 46).

#### 2.5.1. Formulation Analysis

Many of the samples can be analyzed directly without involving a preliminary extraction procedure. If a sample is a multicomponent dust mixture; it will involve analysis by chromatographic separation, hence it requires a standard extraction procedure. Various other analytical procedures also require an extraction step of the formulated prior to the actual analysis.

The more commonly used measurement techniques in pesticides procedure involve titration ( aqueous or non-aqueous), polarography, spectrophotometry (Infrared, Visible, Ultraviolet, and Fluorimetric), total chlorine values, and more recently Gas chromatography ( 47).

In total chlorine methods, the organic chlorine is converted to chlorides with a suitable method, and the total chlorine is determined by methods such as the volhard, electrometric, or gravimetric.

Spectrophotometric methods are widely used for aromatic or hetrocyclic pesticides. The methods include direct UV measurements of the pesticide after extraction or dilution with a suitable solvent, UV measurement of a cleavage product after hydrolysis with a strong base or acid, or the hydrolysis cleavage product is reacted with a specific reagent to yield chromophore which is measured in the visible region of the spectrum. Some pesticides upon hydrolysis yield hydrolyzates that fluoresce and can be measured spectrofluorometrically. IR technique

is also employed for pesticides analysis, but the technique lacks sensitivity and large sample size is necessary. Polarographic procedures have not been used extensively for the analysis of pesticide formulations. The main application of this technique to pesticide formulations has been the analysis of compounds with reducible groups.

#### 2.5.2. Residue Analysis

Any complete coverage of the principles of residue analysis should cover the necessary preliminaries of field experimentation and pre-analysis manipulators. This includes, sufficient field control studies on a number of economically important crops, selection of representative field and sub-sample, and quantitative removal of the pesticide or its metabolites from the surrounding biological environment. Extraction techniques must be adequate to yield extracts which accurately reflect the toxicant residue level of the sample taken for analysis.

The most commonly used analytical measurements for the pesticides residue are: photometric (UV, Visible, IR, Nephelometry), electrometric (potentiometric, amperometric, polarographic, coulometric, electron-affinity, conductometry), and Radiometric (radioactive tracers, and Neutron activation). Moreover biological methods like bio assays, and enzymatic are also employed for the analysis (45,46).

#### 2.5.3. Gas Chromatographic Analysis of Pesticides

The gas chromatograph for the separation, identification, and measurement of pesticidal compounds is undoubtedly the most widely used instrument in the

field of pesticide residue chemistry (47). GC is adaptable to samples in the micro- or picogram ( $10^{-12}$ g) range. The selectivity and sensitivity of the technique is constantly being increased by improved resolution of the components with improved column packings and with the design of more sensitive detectors (45).

The column is the heart of the gas chromatograph. It affects the actual separation of the sample, and the key of good separation is the selection of the proper column. If the column packing is incapable of resolving the components in a sample mixture, the most sensitive detectors are little value (45,47,48). The movement of a component through the column depends on its distribution between the stationary and moving phases. Separations are achieved when there is a different distribution between the components being assayed. The difference is dependent on temperature and flow rate. The temperature selected should give a separation that can be performed in a reasonable time without sacrificing column resolution. Carrier gas flow rates are optimized at the selected operating temperature so that peak broadening will be minimum and the separation efficiency will be greatest. GLC quantitation of pesticide formulations or mixtures are usually performed with the column maintained at constant temperature, that is isothermal operation. This mode of operation is preferable to programmed temperature because of (1) base line stability, and (2) the ability to control and reproduce more accurately the column temperature conditions (47) .

### 3. MATERIALS AND METHODS

#### 3.1. Apparatus

The Gas chromatograph (GC) used for the study was a varian model 3700, having a coiled glass tube with 3% OV 17 on chromsobr Q. The GC is equipped with an Electron Capture detector, Nitrogen generator, a varian model 9176 automatic integrator, and model CDS 111 recorder. The Infrared spectrophotometer was a Pye Unicam PU 9512..

#### 3.2. Reagents

The following insecticides and polymers were used:  
Insecticides: Malathion (99.5%) and Chlorpyrifos (98%). Samples were obtained from Shola Plant Protection Laboratory (Ministry of Agriculture).

Polymers\_ Cellulose acetate Polymer and polyethylene vinyl acetate copolymer. Samples were obtained from Leuna ( GDR).

Polymer supported insecticide: A Suscon product granular sample impregnated with 14% by weight chlorpyrifos. Sample was obtained from Australia through Shola Plant Protection Laboratory.

#### 3.3. Solubility test of the Suscon product granular sample

Equal amounts of the Suscon sample were taken into different test tube. The solubility test of the sample was performed in solvents like water, methanol, ethanol, acetone, benzene, carbon tetrachloride and n-hexane.

#### 3.4. GC - analysis of Chlorpyrifos in the Suscon product sample

For this analysis, a newly developed procedure was described and applied for the determination of the insecticide in the granular sample.

A field having an area of one square meter located in the Geophysical observatory was selected for this study. Complete meteorological data were obtained.

From the field about 10 cm of the top soil was removed. And sample holders (plastic rings) were placed in a row. On each of the sample holders, samples having a weight of 3g each were placed and then the samples were covered with the soil.

#### 3.4.1. Pre-Analysis

In the weekly intervals, three batch of samples were removed from the soil, washed with water and dried in the laboratory at room temperature. From the dried sample, two test samples having a weight of 1.0000 g each were taken for the analysis. The weighed test sample was transferred into a 250 ml round bottomed flask, 8 ml of n-hexane was added to it and refluxed for 30 minutes at a temperature of 60-65°C. Most of the solvent was allowed to evaporate at room temperature and the semi-dried sample was quantitatively transferred into a separatory funnel for the extraction of the insecticide. The sample was extracted successively with 20ml of n-hexane(distilled) four times. The extract was transferred into a sintered glass funnel and filtration was performed under reduced pressure. Finally, all the extracts were collected and diluted to 100 ml with a n-hexane.

#### 3.4.2. Preparation of Standard Solutions for GC

50.0 mg of chlorpyrifos standard was weighed and transferred into a 50 ml volumetric flask. The sample was dissolved and diluted to the mark with n-hexane. From this solution, 0.1 ml was taken and diluted to 10 ml to give solution B. A series of solutions were prepared from solution B by taking 1, 2, 3 and 4 ml and diluting each of them to 10 ml. The solutions

were designated as solution c,D,E and F respectively. The solvent used for the dilution was a distilled n-hexane.

### 3.4.3. GC - Operating Conditions

Based on the sensitivity, high efficiency (narrow and symmetrical peaks), and reasonable retention time; the following gas chromatographic conditions were used:

Column oven temperature	190 <sup>o</sup> C
Injection port temperature	220 <sup>o</sup> C
Detector temperature	300 <sup>o</sup> C
Nitrogen flow rate	30ml/minute
Attenuation	512x10-11A
Recorder Chart Speed	0.25 inches/minute
Sample Size	5 micro litres
Retention time	11.6 minutes

### 3.4.4. Preparation of Sample Solutions

0.1 ml of the extract solution was transferred by a pipette into a 10 ml volumetric flask and diluted to the mark with n-hexane. From this solution 1 ml was taken and diluted to 10 ml. All the extracts were prepared in the same way for the injection.

### 3.4.5. Analysis of sample solutions by GC

After the appropriate GC conditions were maintained, identical volumes ( 5 micro litres) of the standard solutions were injected using a 10 = micro litre syringe. Maximum reproducibility was obtained using the solvent flush injection technique ( 47). The linearity response was checked by plotting peak areas against quantity of standard. Since calibration curves having the identical slope cannot be re-produced exactly from time to time, the external

standardization method was applied (47). In this method, one of standard, two of sample 1, one of standard, two of sample 2 and so on were injected sequentially. By comparing the areas of the standard and the sample solution, the amount of the insecticide in the extract was determined.

3.5. Determination of the Release Behaviour of the Suscon sample in Water

At the beginning, three samples each with the weight of 1.0000 g were taken into a beaker. To each of these samples a 50 ml of distilled water was added, and samples were kept at room temperature in the laboratory. After keeping the samples for a definite time ( hours), their weight changes were recorded with an analytical balance at different times. Every sample was weighed, after the adhered water was removed from the surface of the sample.

3.6. Determination of the Release Behaviour of the Suscon sample in Open Air

Three samples each with the weight of 3 g were placed in a plastic buchner funnels and kept in the open air. The weight changes of each of the samples were recorded as a function of time (weeks).

3.7. Preparation of a Slow Release Insecticidal Polymer Films

A slow release insecticidal polymer films were prepared by impregnating the polymers with the insecticides.

3.7.1. Cellulose acetate impregnated with malathion

1 g of cellulose acetate and 100 ml chloroform were transferred into a 250 ml round bottomed flask fitted with a condenser, and the sample was refluxed for 1 hr

at a temperature of 60-65°C. The solution was transferred, while hot, into a 100 ml volumetric flask; and to this was added 0.5 ml of malathion. The solution was diluted to the mark with chloroform and mixed well. 10 ml of the solution was taken and films were cast from this solution by pouring it into a glass petridishes ( 8 cm in diameter). After casting, the solution was allowed to stand at room temperature in order to permit the complete evaporation of the solvent. Finally films with thickness of 40µm were obtained. Film thickness was determined with a deep throat micrometer.

3.7.2. Cellulose acetate impregnated with chlorpyrifos

A similar polymer film was prepared from cellulose acetate and chlorpyrifos, using the same procedure as stated in section 3.7.1. But here, instead of malathion, 0.5 g of chlorpyrifos was added. Films with a thickness of 30µm were obtained.

3.7.3. Polyethylene vinyl acetate copolymer impregnated with chlorpyrifos

Solubility tests indicated that the copolymer was miscible with chlorpyrifos in the given concentration range. 0.85g of the copolymer and 50 ml of chloroform were taken into a 250 ml round bottomed flask fitted with a condenser, and the sample was refluxed for 1 hr at a temperature of 60-65°C. The solution was transferred, while hot, into a 100 ml volumetric flask, and to this 0.15 g of chlorpyrifos was added. The solution was diluted to the mark with chloroform and mixed well. 10 ml of the solution was taken and films were cast from this solution by pouring it into a glass petridishes. After casting, the solvent was allowed to evaporate at the beginning at

a temperature of 30-40°C on an electric stove for about 30 minutes and then left at room temperature. Films with thickness of 60µm were obtained.

It was attempted to prepare EVA impregnated with malathion, but the insecticide was found to be immiscible with the polymer and the film obtained was unstable.

#### 3.7.4. Preparation of Suscon Film

The same procedure was used as described in section 3.7.3, but here 1 g of the suscon granule was refluxed and its solution was cast. Films with thickness of 60µm were obtained.

#### 3.8. The Study of the Release Behaviours of the Insecticidal Polymer films.

The release behaviours of the insecticidal polymer films were studied at different temperatures.

The weights of polymer films were taken, before they were exposed to higher temperatures. Then the films were suspended in an oven adjusted to the desired temperature.

Films composed of cellulose acetate - malathion and cellulose acetate - chlorpyrifos were exposed to temperatures of 100°C, 90°C, 80°C, and 70°C. While films composed of EVA - chlorpyrifos, suscon were exposed to temperatures of 70°C, 60°C, and 50°C. The changes in the weight of the films were recorded as a function of time (hrs). The observed variation in temperature was  $\pm 1^\circ\text{C}$ .

#### 3.9. IR - Analysis of the pure polymer films

Comparison of the IR spectra of the polymer films was done by preparing the pure polymer films.

Thus, the pure polymer films were obtained by solution film casting as described in section 3.7. No insecticide was added during this film preparation. For the preparation of the suscon film, first the insecticide was extracted from the carrier on soxhlet apparatus with acetone for about 18 hrs until no more of the insecticide was observed in the extract. This was checked using a gas chromatograph. During this test, a small amount of the extract was taken after each extraction, and it was injected into the GC. This had continued until there was no GC response for the chlorpyrifos.

After the extraction was complete, the sample carrier was dissolved in chloroform and its film was cast as described in section 3, 7, 4.

Finally, the IR spectra of the films were taken on the demountable sample holder.

#### 4. RESULTS AND DISCUSSION

##### 4.1. Gas Chromatographic Analysis of Suscon Sample

Since there was no available procedure for the extraction of the insecticide from the polymer carrier, several experiments have been conducted, and the described method was found to be successful for the extraction.

Several organic solvents such as ethanol, methanol, acetone, chloroform, carbon tetrachloride and n-hexane were examined for the choice of the proper solvent for dissolving the granular sample. Results of the observations are given in table 2. It was found that the sample dissolves in nonpopular solvents, and from these solvents, n-hexane was selected because of the following major reasons:

- At room temperature, the polymer carrier is insoluble in n-hexane but the insecticide ( chlorpyrifos) incorporated in it is soluble.
- At a temperature of 60-65°C, both the polymer carrier and the insecticide are soluble in n-hexane.

Hence, in order to extract the insecticide efficiently, first the granular sample was refluxed with n-hexane and then the solvent was partially evaporated. This had helped to increase the surface contact of the sample with the solvent. Then the insecticide was extracted with the same solvent at room temperature.

After setting the appropriate GC conditions (as described in section 3.4.3, the extract and the standard solutions were injected into the GC alternately ( External) standard technique was applied) and maximum reproducibility of the results was obtained. The precision expressed in the relative standard deviation

Solvent	Room Temp.	Elevated temp. (60+65°C)
Water	Insoluble	Insoluble
Methanol	Insoluble	Insoluble
Ethanol	Insoluble	Insoluble
Acetone	Insoluble	Insoluble
Chloroform	Soluble	Soluble
Benzene	Soluble	Soluble
Carbon Tetrachloride	Soluble	Soluble
n-hexane	Insoluble	Soluble

Table 2: Solubility Test of Suscon Sample.

of the different injections of the same standards and the extracts was found to be 1.6%. And the relative standard deviations of the different extracts are given in table 3.

Calculation:

In determining the amount of the pesticide in the granule, the following relationship was used (46).

$$\text{Amount of pesticide} = \frac{\bar{A}_s}{\bar{A}_{std}} \times C_{std} \times D \times V_T$$

Where  $\bar{A}_{std}$  = Average area of the standard sample

$\bar{A}_s$  = Average area of the sample solution

$C_{std}$  = Concentration of the standard sample  
(in g/ml)

$D$  = Dilution factor (for this specific work =  $10^3$ )

$V_T$  = Total volume of the sample solution (in ml)

The amount of the insecticide released was calculated by comparing the original amount of the insecticide in the granule (which was found to be 15%) with that amount remained in the granule (calculated from the above given relation). Results obtained are given in table 3 and the curve is shown in figure 3.

When we closely examine the curve we can get the following points:

- The total amount of the insecticide released in 22 weeks is 36.75%.

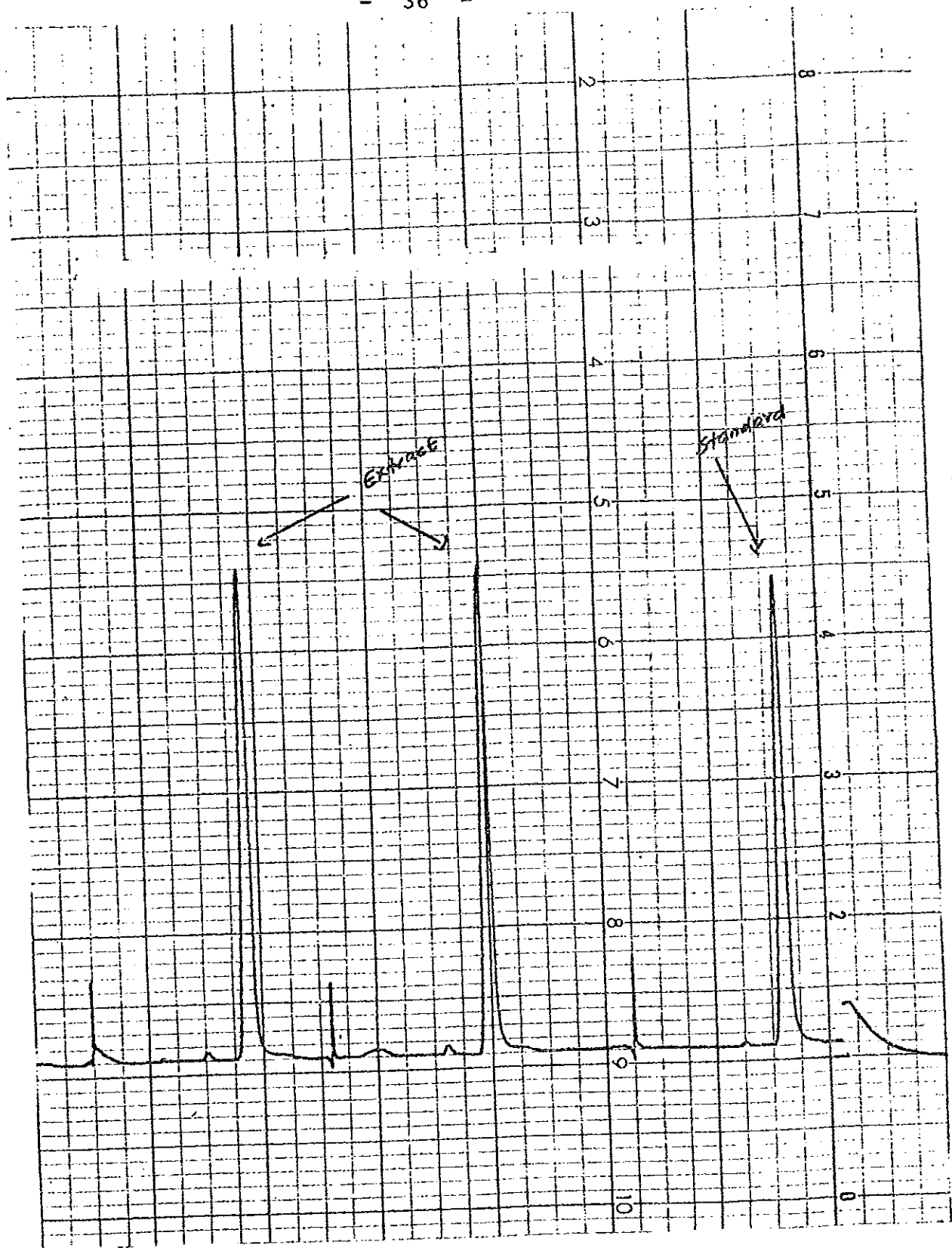


Fig. 2. GC- Chromatogram of Chlorpyrifos.

t (Weeks)	$M_R$	$M_t$	$(\%)M_{t/M}$	% RSD
0	0.150	0	0	0.57
1	0.148	0.0015	0.99	0.43
4	0.141	0.0092	6.12	0.0
8	0.140	0.0102	6.79	0.51
10	0.132	0.0182	12.10	2.10
12	0.127	0.0232	15.45	2.20
16	0.124	0.0262	17.44	1.10
18	0.113	0.0372	24.76	2.50
21	0.099	0.0510	33.95	2.80
22	0.095	0.0552	36.75	2.98

Table 3; Cumulative release of chlorpyrifos by Suscon Sample. Sample Applied in Soil.

Where  $M_R$  = amount of insecticide remained in carrier(ing)  
 $M_t$  = amount of " released at time t( " )  
 $M_i$  = Initial amount of the insecticide before the release = 0.15 gram.  
RSD = Relative standard deviations of the extracts

Time (Weeks)	% Released	Average Temperature (°C)		Rainfall
		Maximum	Mininum	
0-4	6.12	23.37	7.46	No
4-8	0.67	23.19	8.13	Low
8-12	8.66	24.12	9.62	Low
12-16	1.99	24.63	9.77	Moderate
16-20	13.56	25.70	10.45	High
20-22	5.75	23.10	10.94	High

Table 4: Extent of release of Chlorpyrifos by the Suscon Sample (soil) in relation to the climatic conditions.

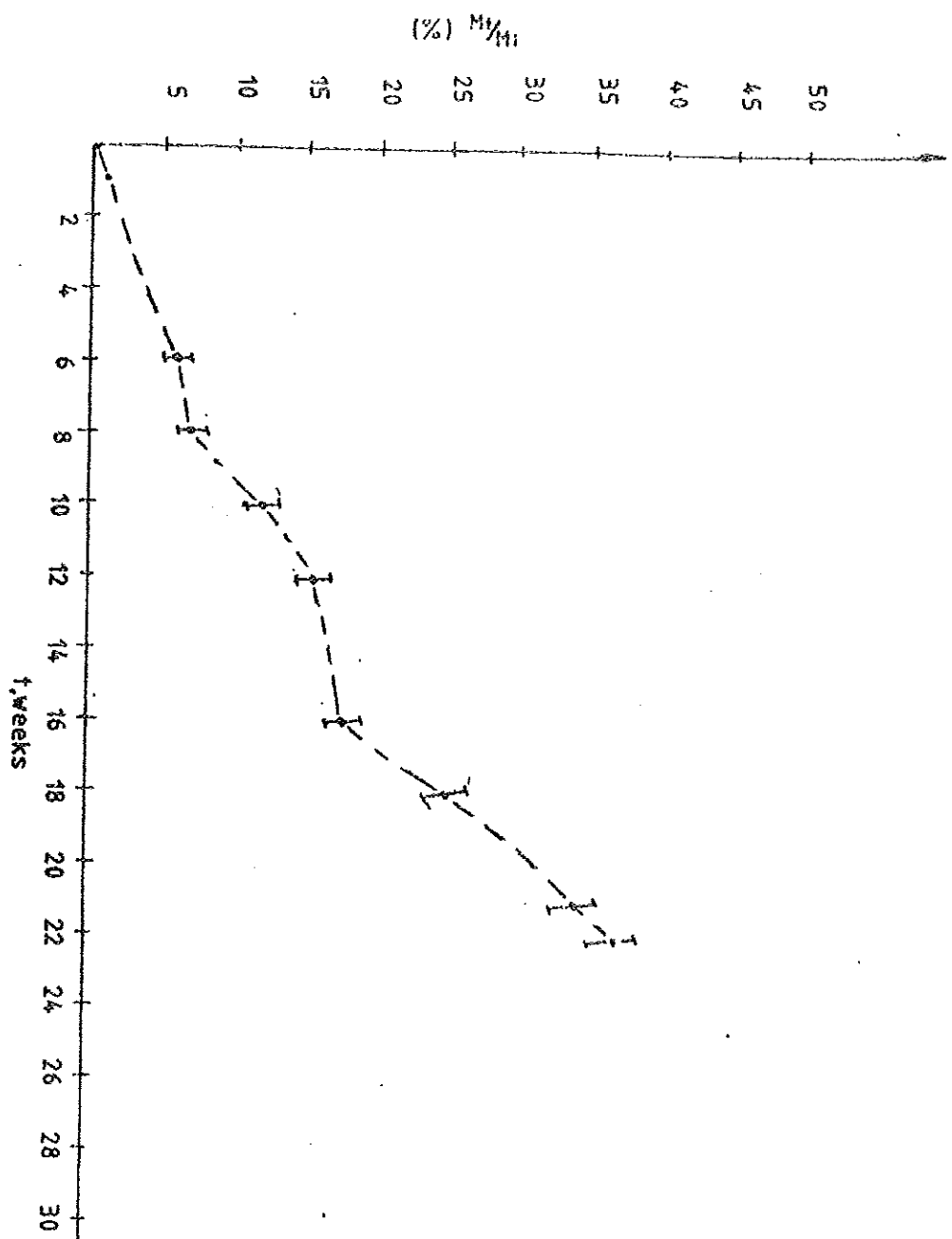


Figure 3. (%) Cumulative release of chlorpyrifos by suscon sample.  
Sample applied in soil.

- The minimum amount of the insecticide released is 0.67% in the second month and the maximum amount release is 13.56% in the fifth month.

In a system where there are no external forces which affect the diffusion (like moisture, large differences in temperature and so on), the mass transfer of the insecticide is expected only due to the diffusion through the membrane pores. In this case, initially due to the high concentration gradient of the insecticide, there will be a maximum release, then decreases and finally it attains the steady state. But here, the expected phenomenon was not observed due to the existence of some external forces as mentioned in the above. Hence, the possible explanation of the observed release can be given in relation to the climatic conditions (Table 4):

The minimum release rate which was observed in the second month can be accounted mainly due to the following reasons:

- (i) In this period, the concentration of the insecticide close to the inner surface was expected to be low, and hence the insecticide first migrates from the bulk to the surface, and then diffuses out mainly through the membrane pores. Due to these processes, the rate of diffusion could be slow.
- (ii) Since there was a low temperature, condensation of the insecticidal vapor may happen, as a result, the rate of the diffusion could also be slow.

On the other hand a maximum release was observed in the fifth month which is contrary to the predication. That is since the concentration of the insecticide in the granular inner surface is expected to be very low, a slow rate of diffusion could have been predicted. But this was not the case, and the following argument may account for the above observation. In this period there was high temperature and high rainfall, hence, these factors may have influenced the rate of the diffusion in the following way:

Commonly for the granules prepared from a polymer as a carrier the formulator adds porosity inducing agents to regulate the release rate of the pesticide. This was also true with the Suscon sample. These porosity inducing agents are salts, and those salts having high solubility in water are fast porosity inducing agents and those which have low solubility in water are slow porosity inducing agents. In the fifth month, there was high rainfall, moreover the soil used for the study was a tropical soil ( in particular a vertisol) and this soil is characterized by its high retaining capacity for water. Hence, after the rainfall, the retained water will have a long time surface of contact with the sample; as a result, the salt will dissolve and this will lead for the formation of the capillaries in addition to the membrane pores. Thus, due to the high rainfall and high temperature, high rate of diffusion is expected and this is observed in the curve. Similar behaviour was also observed in section 4.3.

4.2. The Study of the Release Behaviour of the Suscon Sample in Open Air.

The Suscon sample was studied for about 14 weeks by directly exposing it to the open air. The weight changes of the samples were recorded as a function of time (weeks). The results are given in table 5 and the curve is shown in figure 4.

By closely examining the curve, the following points can be observed: Here the area under the curve is sub-divided into regions with an interval of two weeks, the corresponding absolute weight changes are given in table 6.

- the maximum weight decrease is observed in the first interval (0-2 weeks), and
- the minimum weight decrease is observed in the sixth interval (10-12 weeks).
- beyond the sixth interval, there is a drastic change in the curve due to the weight gain of the carrier.

The possible explanation for the above observations might be stated as follows:

The maximum and minimum weight loss of the sample are mainly explained on the basis of the amount of the insecticide incorporated in the polymer carrier. During the first interval, high concentration of the insecticide was expected in the carrier, hence direct exposure of the sample to the sun light, will enhance the rate of the diffusion of the insecticide as a result, the insecticide adsorbed in the inner surface of the carrier will diffuse out easily, with a high rate of diffusion. Hence, this will result a maximum weight loss. But in the sixth interval,

t (weeks)	$M_t$	$M_t/M_t^{\%}$
1	0.0272	0.91
2	0.0375	1.25
3	0.0469	1.56
4	0.0536	1.79
5	0.0637	2.12
6	0.0732	2.44
7	0.0897	2.99
8	0.0976	3.25
9	0.1052	3.50
10	0.1134	3.78
11	0.1163	3.88
12	0.1183	3.94
13	0.0501	1.67
14	0.0548	1.83

Table 5. % weight changes of the suscon sample, sample applied in open air.

$M_t$  = weight loss of the granular sample at different weeks, (in grams)

$M_t$  = Original weight of the granular sample (= 3.00 grams)

TIME (WEEKS)	% Loss	Ave. Temperature (°C-	
		Maximum	Minumum
0-2	1.25	23.64	8.04
2-4	0.54	24.23	10.66
4-6	0.65	23.21	11.39
6-8	0.81	25.17	10.48
8-10	0.53	25.78	9.04
10-12	0.16	26.32	9.80

Table 6. The absolute weight changes of the suscon sample in two weeks interval, in relation to the climatic conditions.

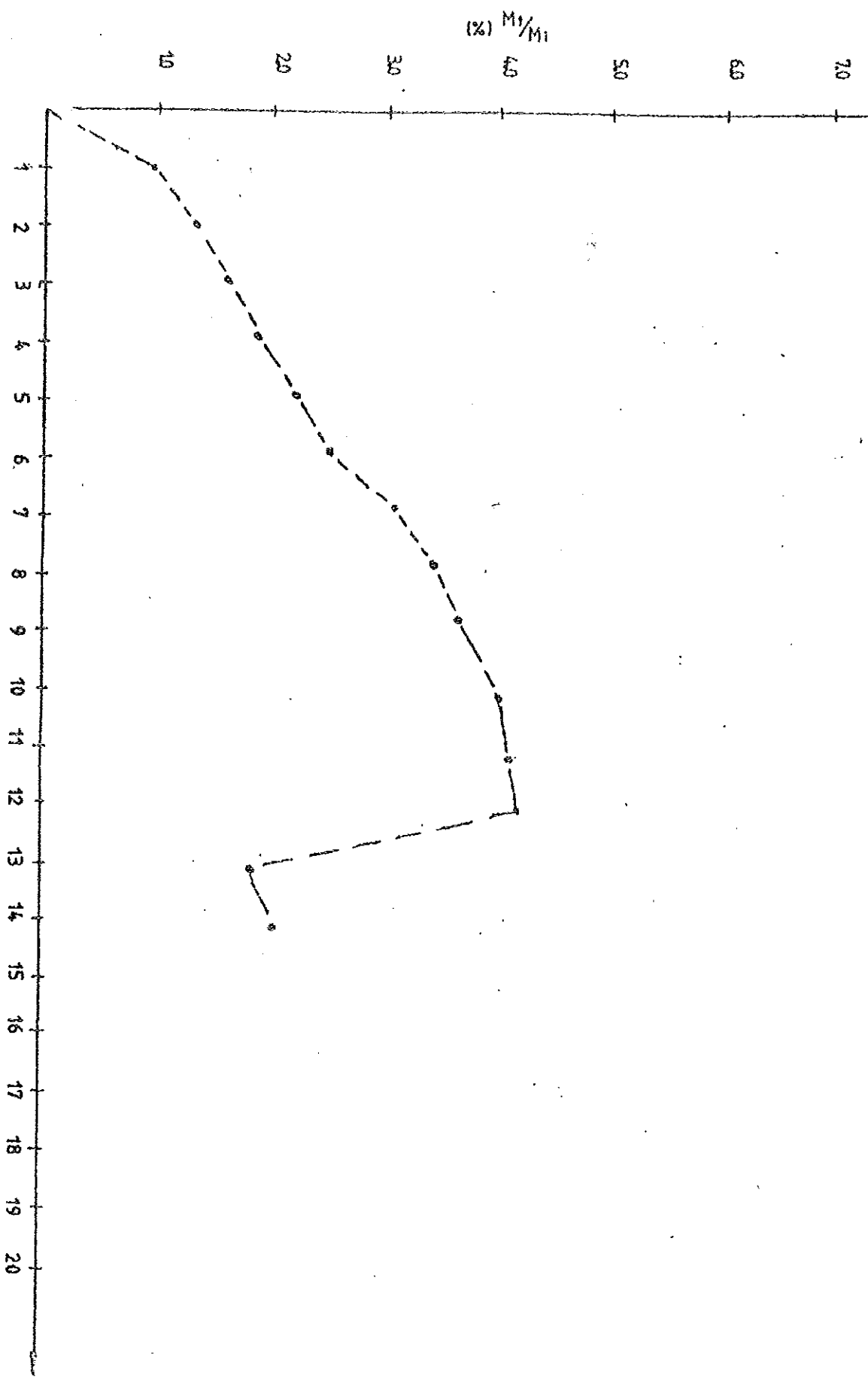


Figure 4.  
% weight changes of the suscon sample.  
Sample applied in open air.

the concentration of the insecticide in the carrier was expected to be very small, hence the rate of diffusion will be governed mainly by the migration of the insecticide from the bulk to the inner surface (which is a very slow process), and then diffusion through the pores of the membrane. Due to the above reason the rate of the release is expected to be very slow. Therefore, there will be a minimum weight loss. In the above two periods there was a moderate rainfall, but its effect was not significant because there was no long contact of the sample with the rain water. But beyond the sixth interval (12th week) there was a high rainfall and due to this the weight of the carrier increased, and this was mainly because of the high absorption of water by the sample carrier.

#### 4.3. The Study of the Release Behaviour of the Suscon Sample in Water

The release behaviour of the sample in water was studied for several hours and the change in the weight of the sample was recorded as a function of time (hours). Results are given in table 7 and the curve is shown in Figure 5.

From the curve the following points have been observed

- In the first and the third portion of the curve, there is a decrease in the weight of the sample and
- In the second and the fourth portion of the curve, there is a gain in the weight of the sample.

Thus, the following explanations may account for the above observations:

TIME (HOURS)	SAMPLE 1		SAMPLE 2		AVERAGE Value (%)
	$M_t$	$\frac{\%M_t}{m_i}$	$M_t$	$\frac{\%M_t}{m_i}$	
1	0.9984	99.82	0.9998	99.93	99.9
3	0.9995	99.93	0.9962	99.57	99.6
5	0.9904	99.02	0.9860	98.55	98.8
7	0.9884	98.82	0.9811	98.06	98.4
9	0.9825	98.23	0.9778	97.73	98.0
22	0.9952	99.50	0.9930	99.25	99.4
31	1.0018	100.16	0.9983	99.78	100
33	0.9977	99.75	0.9961	99.56	99.7
41	1.0091	100.89	1.0017	100.12	100.5
48	1.0403	104.01	1.0381	103.76	103.9
72	1.0587	105.85	1.0514	105.09	105.5
96	1.0694	106.92	1.0665	106.6	106.8

Table 7

Results of the weight changes of Suscon Samples applied in water.

$M_t$  = Weight of the Sample at time t.

$m_i$  = Initial weight of the Sample (weight of Sample 1 = 1.0 weight of Sample 2 = 1.0005 g)

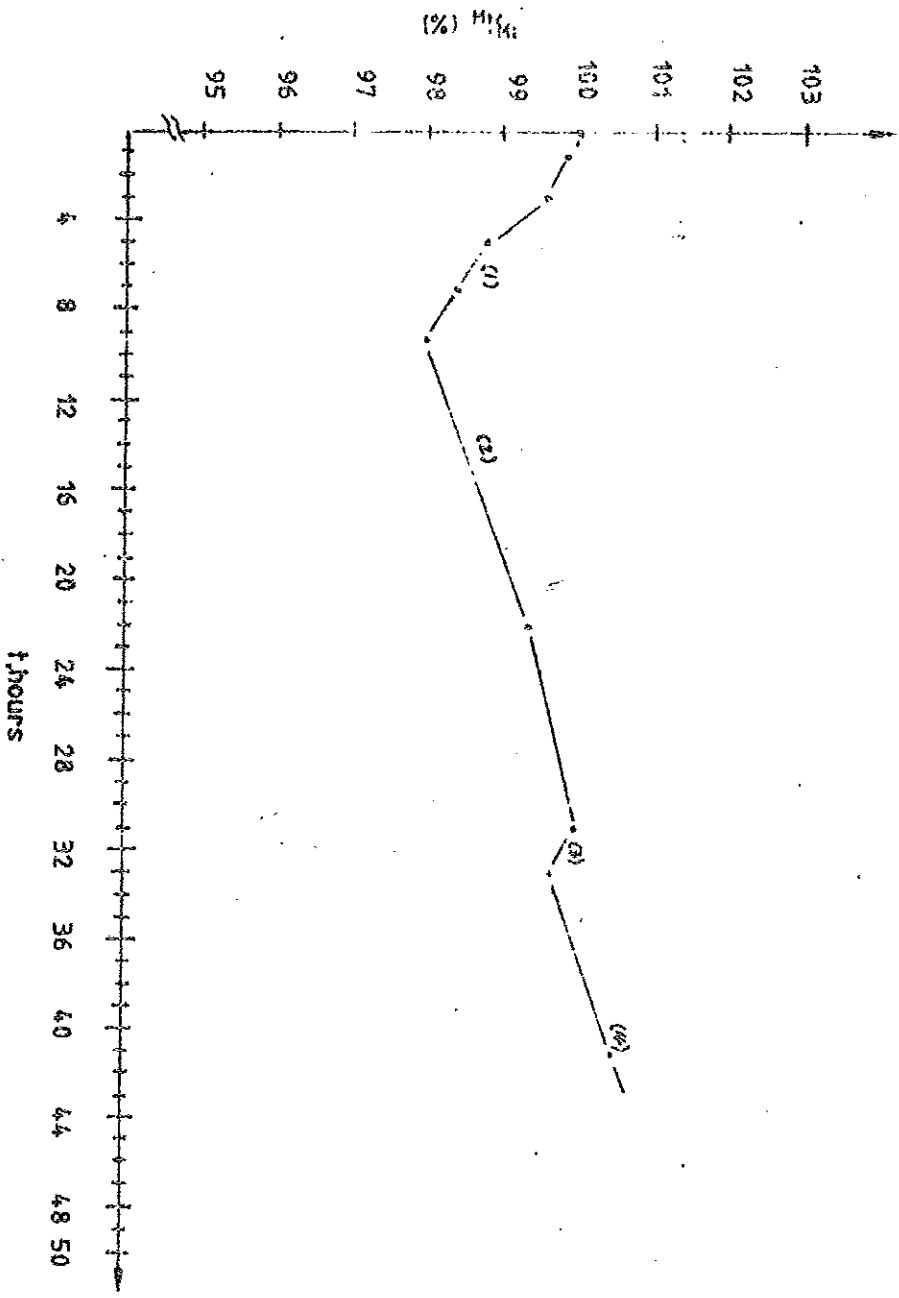


Figure 5.1(x) weight changes of suscon sample.  
Sample applied in water.

- (i) the decrease of the weight of the sample in the first portion of the curve:

When the sample is in contact with water added into it, the porosity inducing salts will dissolve, and as a result there will be a decrease in the weight of the sample. This decrease in the weight is mainly expected due to the above reason rather than the solubility of the chlorpyrifos (= 2mg/1 litre of water), which is very small.

- (ii) The increase of the weight of the sample in the second portion of the curve:

Some of the surrounding water will enter through the capillaries and membrane pores. Here diffusion of the insecticide will be hindered due to the filling of the capillaries with water and consequently there will be an increase in the weight of the sample.

- (iii) the decrease of the weight of the sample, in the third portion of the curve:

If the water stays for a long time, besides to the salt some of the insecticide is expected to leach out (confirmed by the GC) and as a result of this there will be a decrease in the weight of the sample.

For determining the amount of the insecticide in water, first it was tried to extract the insecticide from water with n-hexane, but due to the formation of an emulsion, the method was not successful. But, it was determined indirectly, by extracting the

amount of the insecticide remained in the carrier and comparing it with the original amount of the insecticide in the sample carrier ( =0,15g/1g of sample). This gave an average amount of 0.025g which is equal to 16.67%.

(iv) the increase in the weight of the sample in the Fourth portion of the curve:

Due to the long contact of water and the polymer carrier, at certain stage, the polymer will start to swell, by absorbing some water from its surrounding. As a result of this there will be an increase in the weight of the sample.

#### 4.4. Desorption method for the Study of the Release Behaviour of the Insecticidal Polymer Films

The aim of this work is to study the diffusion of the insecticides from the polymer films as a function of temperature. The polymer films impregnated with the insecticides were exposed to different temperatures; and the amount released was recorded as a function of time (hours).

The selection of the temperature ranges was based on:

- the physico-chemical properties of the polymers (i.e., glass transition temperature, melting temperature, stability and so on).
- the amount released. Here a maximum release of the insecticide is desired so that it will be convenient for the study. Hence high temperature presumably above the  $T_g$  of the polymer - diluent mixtures were selected for the maximum release.

4.4.1. Cellulose acetate - chlorpyrifos and cellulose acetate malathion Films

The two insecticidal polymer films (cellulose acetate - chlorpyrifos and cellulose acetate - malathion) were exposed to temperatures of  $100^{\circ}$ ,  $90^{\circ}$ ,  $80^{\circ}$  and  $70^{\circ}$ C. Results are given in table 8 and 9 and curves are shown in Figures 6 and 7 for chlorpyrifos and malathion respectively.

Examining the curves, the following points can be observed:

- (i) At  $T=100^{\circ}$ C: In both of the figures, the first portion of the curves are linear (The linear region is more than 50%) whereas, above this region the curves are concave against the time axis.
- (ii) At  $T=90^{\circ}$ C: In both of the figures, a sigmoid shape with a limited linear portion is observed.
- (iii) At  $T= 100^{\circ}$ C: About 72.2% of the chlorpyrifos and 84.22% of malathion were released.
- (iv) Comparing the release rate of the two insecticidal polymer films:

At temperatures of  $100^{\circ}$ C and  $90^{\circ}$ C high release of malathion and at temperatures  $80^{\circ}$ C and  $70^{\circ}$ C high release of chlorpyrifos were observed.

Comparing the nature of the curves with those of the characteristic features of diffusion in polymers, curves obtained at  $100^{\circ}$ C ( in both cases), are in a good agreement with the characteristic features of the Fickian diffusion, while those curves obtained at  $90^{\circ}$ C,  $80^{\circ}$  C and  $70^{\circ}$ C, they do not show the characteristic features of the Fickian diffusion, and hence

TIME (MINUTES)	100°C			90°C		
	t	t <sub>1/2</sub>	m <sub>t</sub>	m <sub>t</sub> /m <sub>∞</sub>	m <sub>t</sub>	m <sub>t</sub> /m <sub>∞</sub>
30	5.5		245	0.40	75	0.12
60	7.8		346	0.56	111	0.18
90	9.5		436	0.71	187	0.30
120	11.0		463	0.75	282	0.46
150	12.2		485	0.79	336	0.54
180	13.4		495	0.81	354	0.58
210	14.5		503	0.82	377	0.61
240	15.5		506	0.82	398	0.65
270	16.4		514	0.84	416	0.68
300	17.3		516	0.84	430	0.70
330	18.2		517	0.84	445	0.72
360	19.0		518	0.84	449	0.73

Table 8 : Desorption data of chlorpyrifos from cellulose acetate films at different temperatures.  
 (a) at 100°C and 90°C. (b) 80°C and 70°C.  
 (M<sub>∞</sub> = 0.50g)

TIME (MINUTES)	80°C			70°C		
	t	t <sub>1/2</sub>	m <sub>t</sub>	m <sub>t</sub> /m <sub>∞</sub>	m <sub>t</sub>	m <sub>t</sub> /m <sub>∞</sub>
30	5.5		40	0.06	25	0.04
60	7.8		55	0.09	43	0.07
120	11.0		103	0.17	61	0.10
180	13.4		152	0.25	89	0.14
240	15.5		207	0.34	112	0.18
300	17.3		241	0.39	143	0.23
360	19.0		271	0.44	166	0.27
420	20.5		310	0.50	186	0.30
480	21.9		332	0.54	205	0.33
540	23.2		347	0.56	224	0.36

TIME (MINUTES)		100°C		90°C	
t	t <sup>1/2</sup>	m <sub>t</sub>	$\frac{m_t}{m_\infty}$	m <sub>t</sub>	$\frac{m_t}{m_\infty}$
30	5.5	240	0.48	100	0.20
60	7.8	318	0.64	158	0.32
90	9.5	335	0.67	242	0.48
120	11.0	338	0.68	271	0.54
150	12.2	344	0.69	285	0.57
180	13.4	347	0.69	287	0.57
210	14.5	352	0.70	291	0.58
240	15.5	355	0.71	294	0.59
270	16.4	356	0.71	298	0.60
300	17.3	358	0.71	300	0.60
330	18.2	360	0.72	302	0.60
360	19.0	361	0.72	304	0.61

(a)

Table 9: Desorption data of malathion from the cellulose acetate films at different temperatures (a) at 100°C and 90°C. (b) 80°C and 70°C.  
( $M_c = 0.615 \text{ g}$ )

TIME (MINUTES)		80°C		70°C	
t	t <sup>1/2</sup>	m <sub>t</sub>	$\frac{m_t}{m_\infty}$	m <sub>t</sub>	$\frac{m_t}{m_\infty}$
30	5.5	65	0.13	40	0.08
60	7.8	109	0.22	75	0.15
120	11.0	187	0.37	122	0.24
180	13.4	229	0.46	161	0.32
240	15.5	250	0.50	185	0.37
300	17.3	266	0.53	204	0.41
360	19.0	273	0.55	221	0.44
420	20.5	277	0.55	233	0.47
480	21.9	282	0.56	243	0.49
540	23.2	285	0.57	251	0.50

(b)

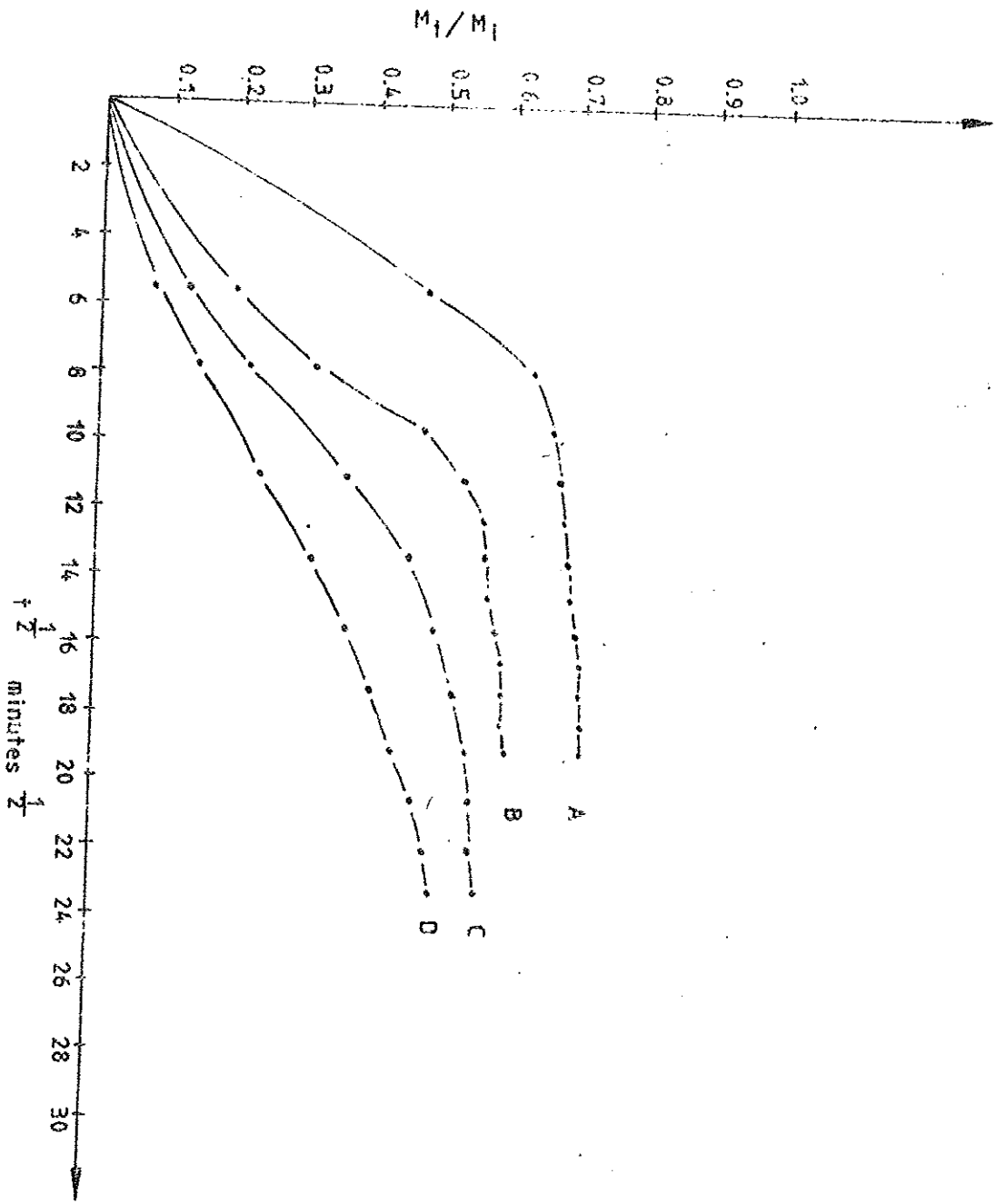


Figure 6. Desorption of chlorpyrifos by cellulose Acetate at different temperatures.  
 A=100° B=90° C=80° D=70° Film thickness 30 μm.

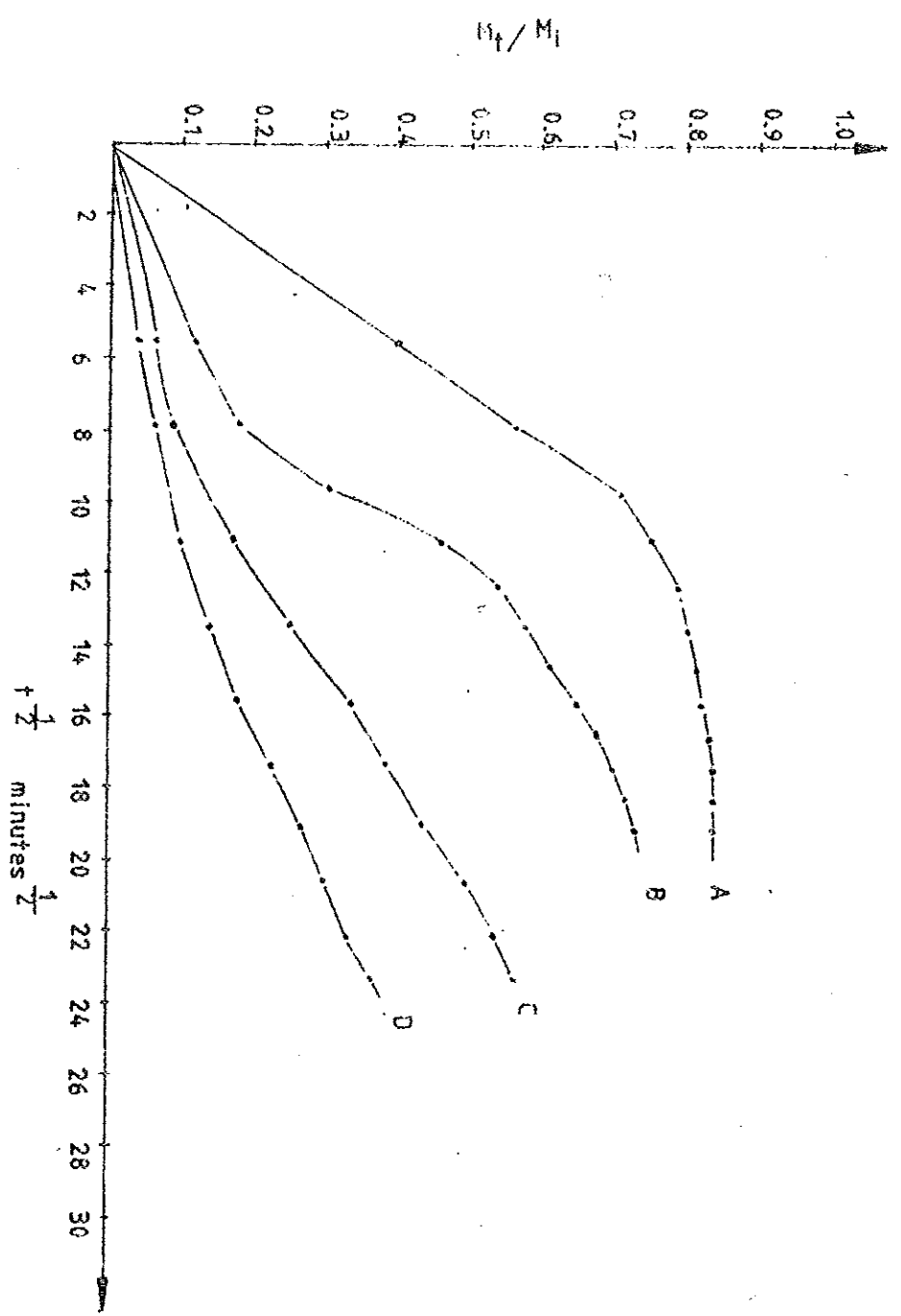


Figure 7. Desorption of malathion by cellulose Acetate at different temperatures.  
A=100° c B=90° c C=80° c D=70° c Film thickness 40 μm

they reflect the anomalous behaviour of the polymer at these temperatures.

Assuming that the Fickian diffusion is obeyed in the linear portion of the two curves at 100°C, the apparent diffusion coefficient can be calculated using the following relationship (36).

$$\frac{M_t}{M_\infty} = k_d \frac{\sqrt{t}}{l}$$

where  $k_d$  = the slope of the desorption curve  
 $l$  = film thickness  
 $M_t$  = amount desorbed at time  $t$   
 $M$  = The maximum amount of the insecticide at equilibrium, = Minitial)

Then  $D$  can be approximated by

$$D = \frac{\pi}{32} [k_d^2 + k_s^2]$$

where  $k_s$  = the slope of the sorption curve.

Assuming  $k_d = k_s$

$$D = \frac{\pi}{16} [k_d^2]$$

For cellulose acetate - chlorpyrifos,  $D = 0.012 \times 10^{-6}$  cm

For cellulose acetate - malathion,  $D = 0.016 \times 10^{-6}$  cm

Comparing the above values with that of the apparent diffusion Coefficients of organic vapors the calculated value is very small.

Correlating the above observed behaviours of the release with those observed in the general diffusion in polymers, those theories which account for the diffusion in polymers may account also here. Hence,

it can be said that the Fickian diffusion resulted at 100°C indicates that the temperature is well above the  $T_g$  of the polymer - diluent mixture and thus the polymer is in the rubbery state. As a result molecular orientations and strain relaxation will not have an affect on the diffusion. But the curves obtained from temperatures of 90,80 and 70°C are far from the Fickian diffusion and these temperatures might be below the  $T_g$ . Therefore, those factors which result in the anomalous behaviour such as slow relaxation of the chain of the segments of the polymer, stress effect and molecular orientations may have affected the observed behaviour. But there is no complete theory available to explain fully for the non-Fickian behaviour.

#### 4.4.2 Polyethylene vinyl acetate - chlorpyrifos and Suscon films

The two insecticidal polymer films were exposed to temperatures of 70°C, 60°C and 50°C. Results are given in table 10 and 11. And the curves are shown in Figure 8 and 9.

The following points can be observed from the curves:

- (i) The maximum amount of chlorpyrifos released at 70°C from the EVA Copolymer is 60% and from the Suscon film is only 38% after 9 hrs.
- (ii) The plateau region was not attained in both of insecticidal polymer films up to 9 hours for the Suscon and 11 hours for the EVA.
- (iii) Both of the figures have shown almost the same type of curves at all temperatures irrespective of the amount of the insecticide released.

TIME (MINUTES)		70°C		60°C		50°C	
t	t <sub>1/2</sub>	m <sub>t</sub>	$\frac{m_t}{m_i}$	m <sub>t</sub>	$\frac{m_t}{m_i}$	m <sub>t</sub>	$\frac{m_t}{m_i}$
30	5.5	14	0.05	-	-	-	-
60	7.8	29	0.01	25	0.08	17	0.06
120	11.0	53	0.18	44	0.15	28	0.09
180	13.4	78	0.26	66	0.22	37	0.12
240	15.5	100	0.33	85	0.28	45	0.15
300	17.3	117	0.39	96	0.32	51	0.17
360	19.0	129	0.43	114	0.38	61	0.20
420	20.5	150	0.50	132	0.44	66	0.22
480	21.9	166	0.55	142	0.47	75	0.25
540	23.2	181	0.60	147	0.49	84	0.28
600	24.5	-	-	-	-	-	-
660	25.7	-	-	155	0.52	100	0.33

Table 10: Desorption data of chlorpyrifos from the EVA Copolymer films at different temperatures.

(m<sub>i</sub> = 0.15 g)

TIME (MINUTES)		70°C		60°C		50°C	
t	t <sup>1/2</sup>	m <sub>t</sub>	m <sub>t</sub> /m <sub>i</sub>	m <sub>t</sub>	m <sub>t</sub> /m <sub>i</sub>	m <sub>t</sub>	m <sub>t</sub> /m <sub>i</sub>
30	5.5	9	0.03	-	-	-	-
60	7.8	17	0.06	16	0.05	10	0.03
120	11.0	31	0.10	29	0.09	15	0.05
180	13.4	42	0.14	39	0.13	21	0.07
240	15.5	59	0.20	54	0.18	24	0.08
300	17.3	68	0.23	63	0.21	30	0.10
360	19.0	76	0.25	74	0.24	35	0.12
420	20.5	94	0.31	86	0.29	42	0.14
480	21.9	104	0.35	95	0.32	45	0.15
540	23.2	113	0.38	97	0.32	50	0.17
600	24.5	-	-	-	-	-	-
660	25.7	-	-	102	0.34	60	0.20

Table 11: Desorption data of chlorpyrifos from the Suscon film at different temperatures.  
(m<sub>i</sub> = 0.15g)

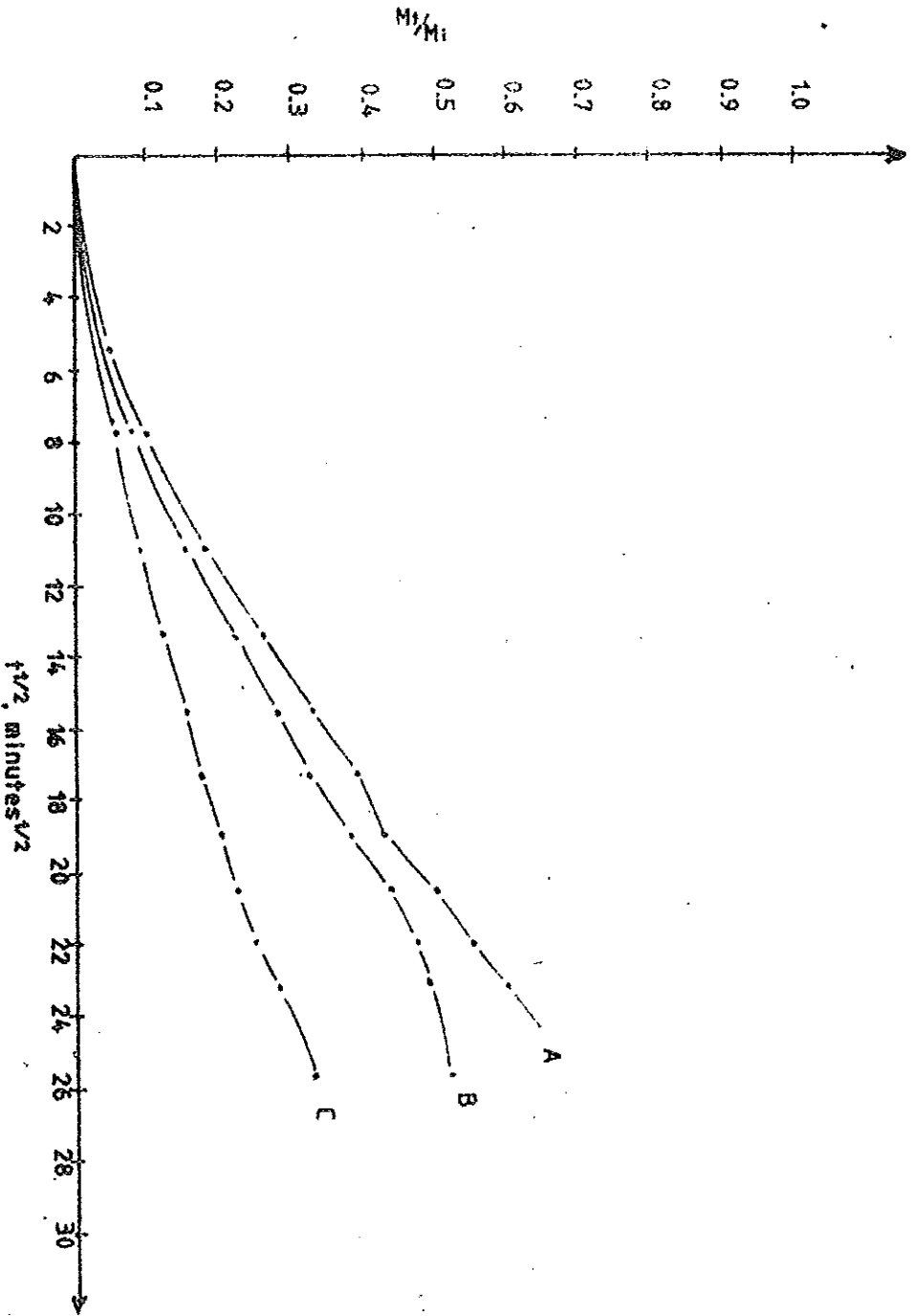


Figure 8. Desorption of chlorpyrifos by polyethylene-vinyl acetate copolymer at different temperatures.  
 A=70°C      B=60°C      C=50°C  
 Film thickness 60µm

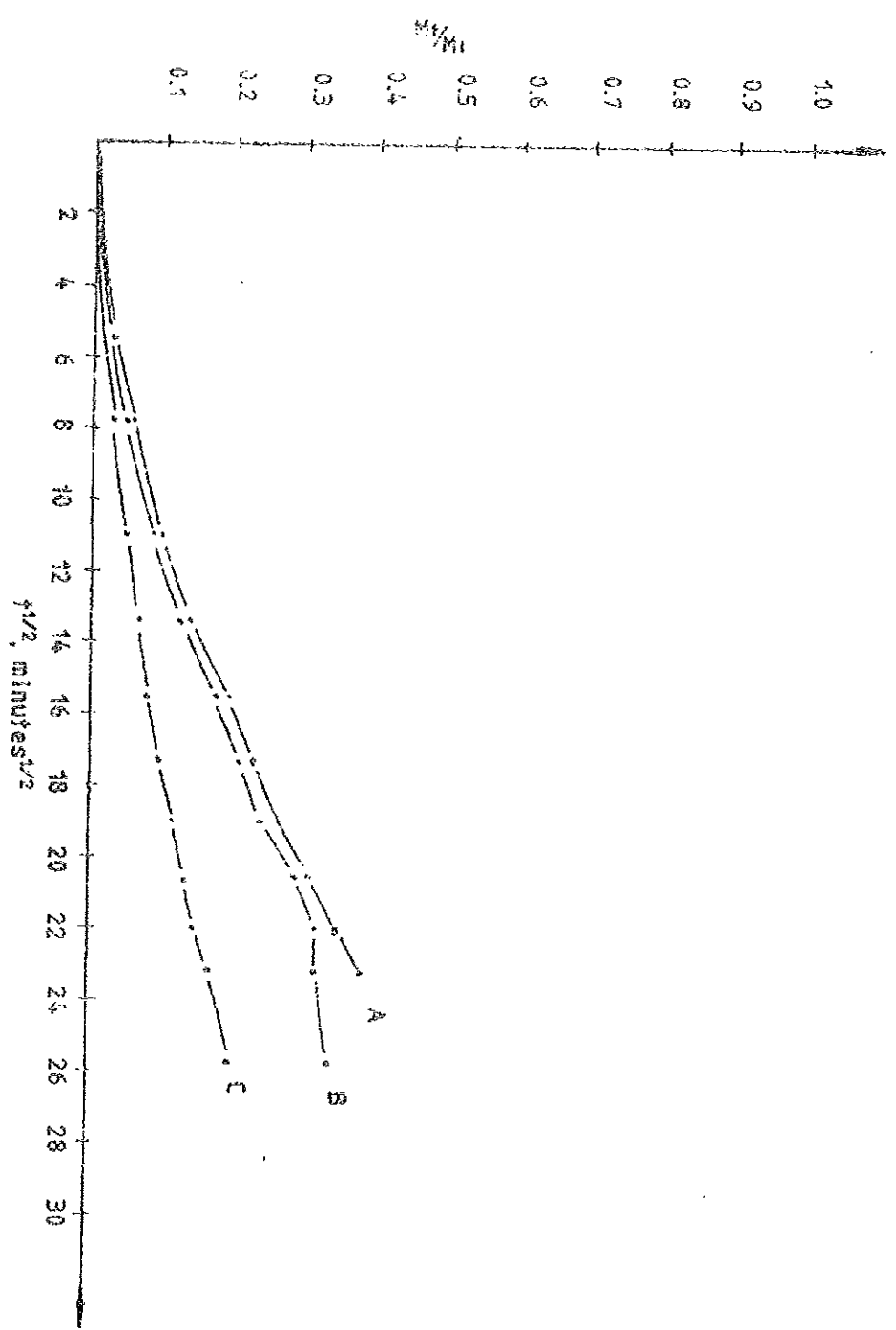


Figure 9. Desorption of chlorpyrifos by suscon polymer carrier at different temperatures.  
A=70°C      B=60°C      C=50°C      Film thickness 60  $\mu$ m

This indicates that there is a very close similarity between the two polymer carriers and this idea was also further supported from the IR spectral data of the two films.

Examining the nature of the curves: it seems that the Fickian diffusion is not obeyed at all the temperatures. From the literature, the glass transition temperature ( $T_g$ ) of the EVA copolymer is found to be in the range of - 25 to 30°C. Due to the addition of the insecticide (chlorpyrifos), the  $T_g$  of the film (EVA - chlorpyrifos) is expected to be lower than the above temperature. Since the temperatures used for the study were well above the  $T_g$  of the film, there was an expectation that a Fickian diffusion to occur but it was not. Therefore, it can be suggested that interaction between the carrier and the insecticide, high viscosity of the polymer at the given temperature and influence from the molecular structure may have strongly hindered the diffusion of the insecticide from the polymer carrier, which led to a non Fickian diffusion.

#### 4.5. Infrared Analysis of the polymer films

The IR spectra of the pure polymer films cellulose acetate, polyethylene Vinyl acetate and Suscon films are given in Figure 10, 11, and 12. The absorption bands are given in table 12. Comparison between the above three polymers indicates that, the two polymer samples, polyethylene vinyl acetate copolymer and the suscon polymer carrier have almost similar absorption bands. This suggests that there is a close similarity between their chemical composition. But further data is required to conclude that the two polymers are identical.

Figure 10 IR - Spectrum of cellulose Acetate film.

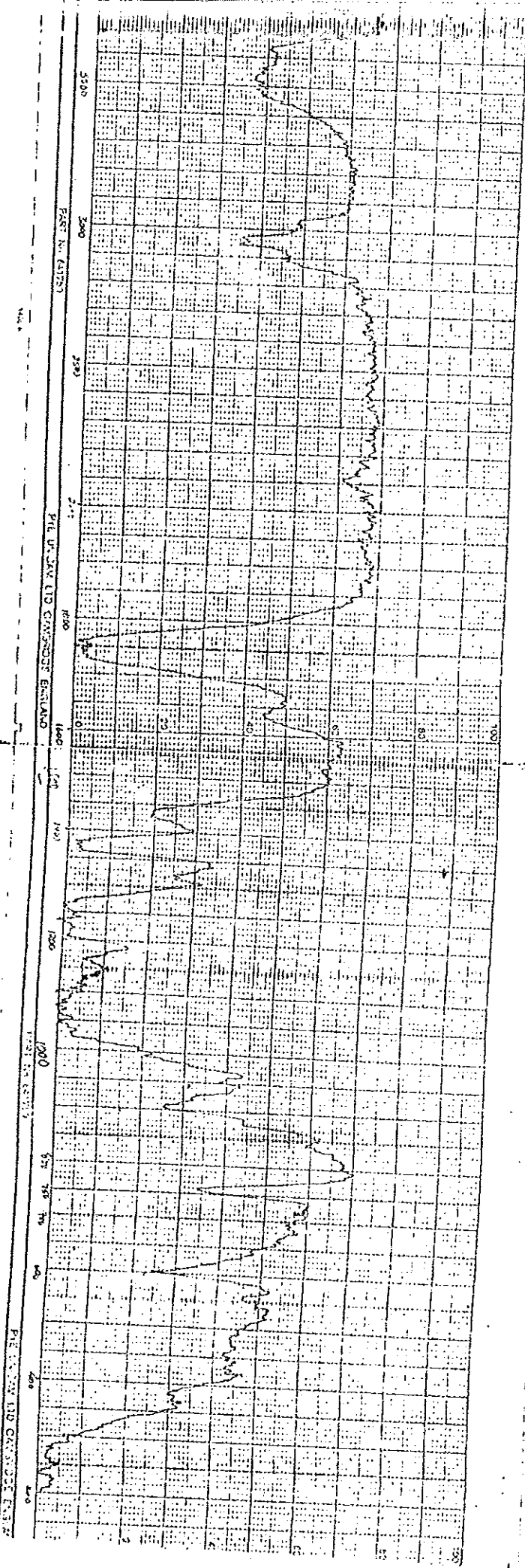
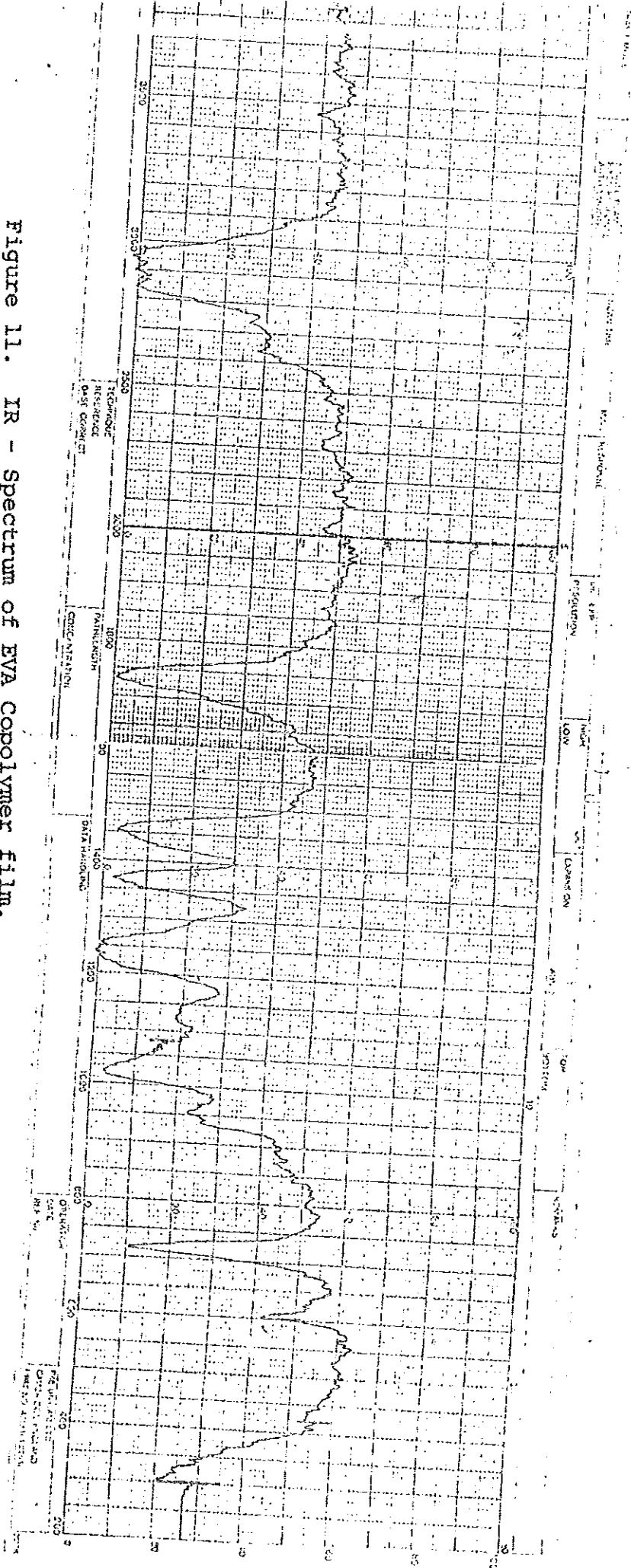


Figure 11. IR - Spectrum of EVA Copolymer film.



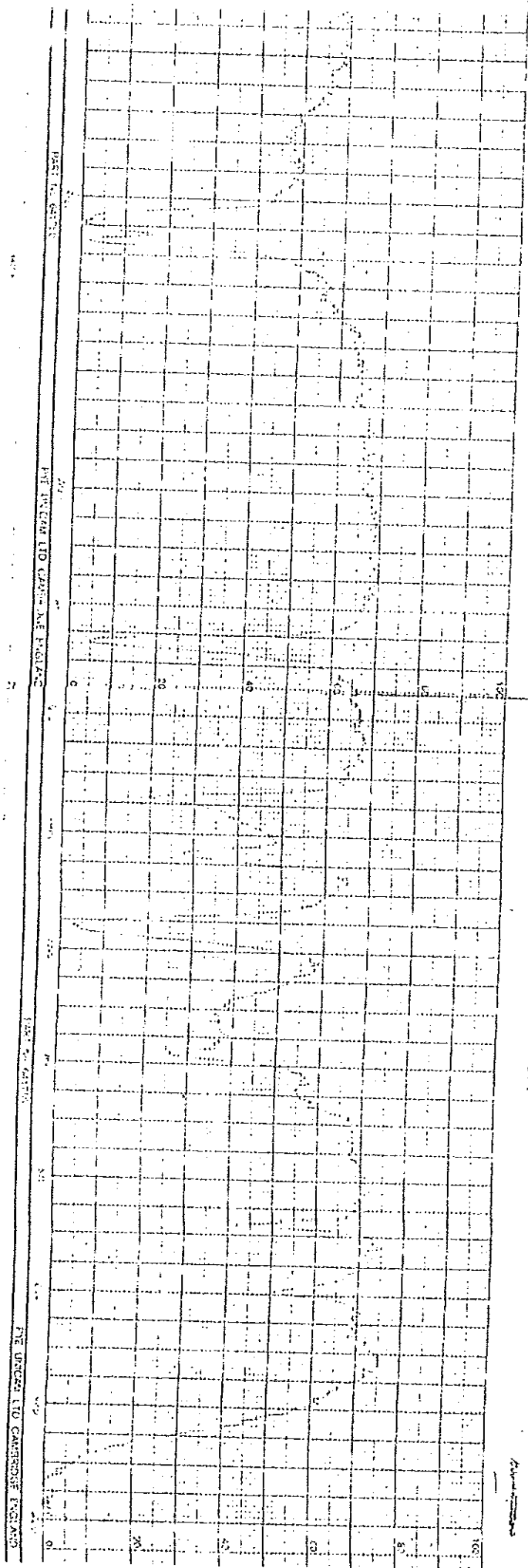


Figure 12 IR - Spectrum of Suscon Film.

Band Absorption (in $\text{cm}^{-1}$ )	Cellulose Acetate Film	Polyethylene Vinyl Acetate film	Suscon film	Absorption Band Assignment
3500 $\text{cm}^{-1}$	Band	No band	No band	OH - Stretching
2880 - 3000	"	Band	Band	C-H Str.
1720 - 50	"	"	"	C=O Str. (acetate)
1470 1370	"	"	"	C-H Def.
1250	"	"	"	$\begin{array}{c} \text{H} \\   \\ \text{C}-\text{O} \\   \\ \text{O} \end{array}$ Str.
1020	"	"	"	C-C-C-
900	"	No band	No band	C-O Str. (Carb hydrate)
720 - 40	"	Band	Band	
606	Band (at 600)	"	"	Characteristic peak of Polyvinyl Acetate.

Table 12: IR spectral data of the polymer films:  
Cellulose acetate, EVA copolymer and Suscon.

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D E C L A R A T I O N

I, the undersigned, declare that this thesis is my work and that all sources of material used for the thesis have been duly acknowledged.

Michael Zaid

Signature

A handwritten signature in cursive script, appearing to read "Michael", written over a horizontal line.

Place and date of Submission: Chemistry Department  
Addis Abeba University  
June 1988.