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Support Material and Column Temperature Effects on
Detector Responses for Organophosphorus
Pesticides Using Gas Liquid
Chromatography

© Mohamméd Haniff

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ABSTRACT

Support Material and Column Temperature Effects on Detector Responses for Organophosphorus Pesticides Using Gas Liquid Chromatography.

Mohammed Haniff

The work presented in this thesis investigated the role of column support and temperature on the gas liquid chromatographic analysis of organophosphorus (Phorate, Disyston and Malathion) and organochlorine (Lindane) pesticides. The organophosphorus pesticides were studied on seventeen columns, containing fourteen different support materials, at column temperatures ranging from 130 to 230 deg C. Only one column was used to study the pesticide Lindane. The pesticides were detected either with an Electron Capture or a Flame Ionization Detector depending on concentrations tested. A comparison of the pesticide responses on different column supports at different column temperatures was made and the optimum supports determined. The effect of liquid phase bleed on responses for the pesticides was also studied, as well as the limitations of the Electron Capture Detector when used with columns exhibiting bleeding of the liquid phase. A comparison of efficiency, resolution, and tailing was made for most of the columns studied in an attempt to determine adsorption effects. A correlation between heats of adsorption, responses, and tailing was attempted. The useful lifetime of a typical column (3.5% (W/W) OV-1 on Chromosorb W-AW support) was determined.

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To Mom and Dad

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CHAPTER

I

INTRODUCTION

1.1 SCOPE AND AIMS OF THE THESIS

It has been previously reported [1] that the type of solid support used in GLC columns would govern the capability of the column to resolve efficiently organophosphorus pesticides. It has also been observed that solid supports do not possess the same performance characteristics from one purchased lot to the next.

Published data on support effects on organophosphorus and organochlorine pesticides with varying GLC column temperatures are scarce. The purpose of this investigation was to answer the following basic questions:

- (1) How does the column temperature affect the response observed for these pesticides?
- (2) What are the factors that shorten the life time of the chromatographic column used for analysis of these pesticides?
- (3) Which supports are best based on peak symmetry?
- (4) How does the liquid phase bleed affect peak areas?
- (5) Which are the best supports based on efficiency, resolution, and minimum detectability considerations?

1.2 PESTICIDES IN THE MODERN WORLD

Recent advances in detector systems of Gas Chromatographs have enabled analytical chemists to determine

microgram, nanogram, and even picogram quantities of pesticide residues [2,3,4]. The importance of the detection of such small quantities of pesticides cannot be overemphasized because of the potential danger of these compounds to humans and their environment. The increased use of various types of pesticides in the modern world has led to much greater emphasis on the possibility of serious environmental contamination.

The scientific attack on pests dates from about the middle of the twentieth century. In 1963 Rachael Carson's book, 'Silent Spring' [5], made people aware of the potential dangers of pollution from pesticides. Whenever certain chemical pesticides are applied to the foliage or seeds of crops or to the soil there is a possibility that some of the material will be persistent and may lead to serious contamination of the ecosystem.

The dinitrophenols (~~DNOC~~) introduced as herbicides in the 1930's are highly poisonous to man and other mammals. Their use has damaged many forms of wild life and they have caused human fatalities. All insects and mammals caught in the insecticide spray are immediately killed. DNOC is so toxic that the quantity normally applied to an acre (about 4.5 kg) is sufficient to kill approximately 100 human beings. Fortunately, these dinitrophenols are rapidly degraded after contact with plants or the soil and they do not, therefore,

leave toxic residues.

Because of economical and toxic reasons, newer synthetic organic insecticides are appearing on the market. These insecticides fall into two main classes - the organophosphorus, and the organochlorine compounds [7]. Organophosphorus insecticides were developed after World War II from work originally carried out in a search for nerve gases. Not surprisingly, therefore, the early organophosphorus insecticides were very toxic to man and other mammals [7,8,9]. Tetraethyl-pyrophosphate (TEPP) was the most toxic material ever to be used on farms. It is estimated that 100 gm of this compound can kill 1800 human beings. Full protective clothing must be worn during its application. However, organophosphorus have the important advantage over the organochlorine insecticides in that they are, comparatively, rapidly degraded biologically and chemically in plants, animals, and soil, to non-toxic materials. The rate of breakdown depends on the nature of the organophosphorus insecticide, its formulation, method of application, climate, and the growing stage of the treated plant crop [10].

The organochlorine compounds represent the other major group of synthetic insecticides, e.g., Lindane, Dieldrin and Endrin. The first and most widely used member was 1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane (or DDT), introduced in 1943, and used extensively during the second World War. The

organochlorine compounds were not known to have any harmful effects on the environment until the 1950's when they were detected in cow's milk after the animals were fed on food-stuffs which had been treated with organochlorine insecticides. Being lipophilic, the chlorinated insecticides are readily stored in fatty tissue with little excretion and are concentrated along food chains causing death to organisms at the end of the chain [7].

Organochlorine and organophosphorus insecticides act as general nerve poisons. Organochlorine insecticides pose a great problem to our ecosystem because of their greater stability compared to organophosphorus compounds. They are generally resistant to biodegradation [11].

Future research on agricultural pesticides will be directed towards the discovery of chemicals, which combine low mammalian toxicity with specific activity against the candidate pest and will not interfere with natural predators.

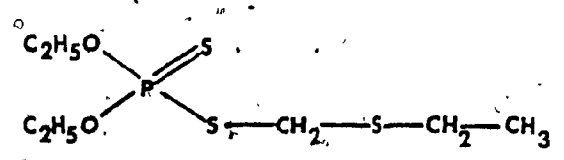
In the meantime, the build-up of organochlorine and organophosphorus insecticides in the environment has to be controlled before they reach toxic levels. One way of monitoring these insecticides is with the use of gas chromatography.

1.3 PESTICIDES STUDIED IN THIS THESIS

The toxicity of pesticides are given by their LD(50) values [12]. The LD(50) value is the dose required to kill 50% of the population of test animals, and is expressed as milligram per kilogram of the body weight of the animal. The smaller the LD(50) value the more toxic the compound.

Phorate (I) is a very toxic compound : LD(50) (oral) to rats is 2 mg/kg.

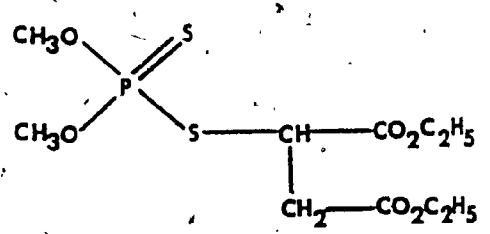
Phorate is employed for the control of aphids, carrot fly, fruit fly, and wireworm in potatoes. A minimum interval of six weeks must be observed between the last application and harvesting of edible crops [12].



I

Phorate (O,O-diethyl-S-2-ethylthiomethylphosphorodithioate).

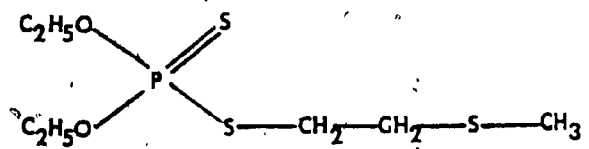
Malathion (II) is a widely used insecticide for the control of aphids, red spider mites, leaf hoppers, and thrips on a wide range of vegetables and other crops. It has a low mammalian toxicity : LD(50) (oral) to rats is 1300 mg/kg.



II

Malathion (0,0-Dimethyl-S-1,2-di(ethoxycarbonyl) ethylphosphorodithioate).

Disyston (III) is an insecticide that is used for the control of insects. It has a duration of about four weeks. The LD(50) to rats is 12 mg/kg. The maximum permissible concentration in air is 0.1 mg/cubic meter.

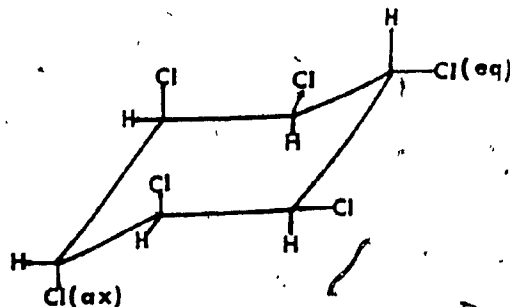


III

Disyston (0,0-Diethyl-S-2-(ethylthio)ethylphosphorodithioate)

Lindane (IV) is an insecticide used against many sucking and biting pests, and for control of pests in grain storage. The maximum permissible concentration of Lindane in air is 0.05 mg/cubic meter.

The physical properties of the above mentioned insecticides are given in Table (1) [13].



IV

Lindane (hexachlorocyclohexane).

1.4 PRINCIPLES OF GAS CHROMATOGRAPHY (GC)

Gas Chromatography, is essentially a separation technique in which the sample mixture in the vapour phase is subjected to a competitive distribution between two phases, one of which is a moving gas stream and the other is a stationary solid or liquid.

There are two separating mechanisms used :

- (a) Adsorption
- (b) Partition

In adsorption chromatography the sample constituents after volatilization are separated by passing them in a stream of carrier gas through a bed (the column) of powdered adsorbent. This technique was first suggested by Ramsey [14] in 1905 and it is called gas solid chromatography (GSC).

James and Martin [15,16] introduced partition chromato-

graphy in 1952. In partition chromatography a competitive partition of the sample between the moving carrier gas and a stationary liquid is used to achieve the separation. This technique is called gas liquid chromatography (GLC).

The apparatus required to produce a gas chromatogram is shown schematically in Figure (1). The heart of every chromatograph consists of a length of tubing filled with a powdered material with or without a liquid phase coating through which an inert carrier gas (nitrogen, helium, etc.) is flowing. This tube, normally coiled for convenience, is responsible for separating the individual components of the mixture and is more properly known as the column. The type of column packing selected depends on the nature of sample to be analysed.

The sample is usually introduced into the carrier gas stream by means of a microlitre syringe via a rubber septum in an injection port at the front of the column. The mixture is then separated according to GSC or GLC mechanisms as the case may be. The speed and efficiency of separation are temperature dependent and the column is therefore mounted in an oven provided with facilities for precise control of temperature to ensure good repeatability of results.

Separation is achieved by virtue of the fact that individual components in the mixture tend to reside in the

column for varying lengths of time, depending on their affinities for the column packing, and therefore reach the column outlet sequentially. A detector, placed at the column outlet, responds to the emergence of these compounds and produces an electrical signal which may be amplified and displayed on a recorder. The response of the detector as displayed on a recorder in the form of a trace or chromatogram is the ultimate objective of the analytical chemist since it is the source of both qualitative and quantitative information on the composition of the sample. Figure (1) gives an example of a chromatogram of a mixture containing four components (A,B,C, and D).

TABLE (1) : Physical Properties of Organophosphorus and Orgānochlorine Pesticides.

<u>INSECTICIDES</u>	<u>COLOUR</u>	<u>BOILING POINT, DEG C (0.4 mm Hg)</u>	<u>VAPOUR PRESSURE</u>
Phorate	Colourless liquid	100	8.4×10^{-4}
Disyston	Colourless liquid	113	1.8×10^{-4}
Malathion	Colourless liquid	120	1.25×10^{-1}
Lindane	White solid	112.8(m.p.)	9.4×10^{-6}

1.5 GAS LIQUID CHROMATOGRAPHY

In gas liquid chromatography (GLC) the separation is achieved by passing the sample, in the gas phase, through a

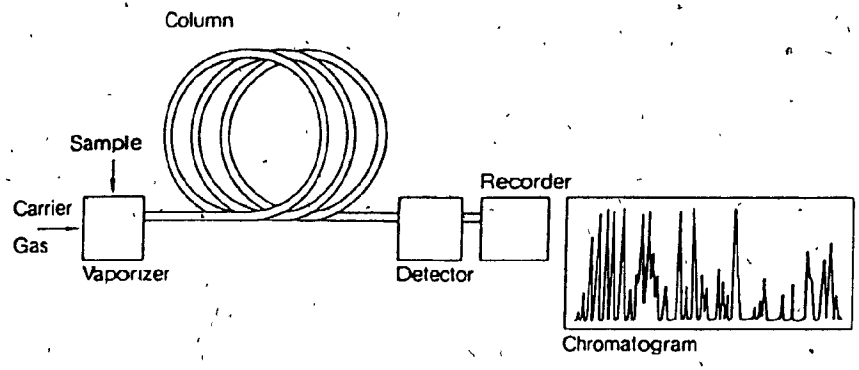


Figure (1) : Schematic Diagram of a Gas Chromatograph.

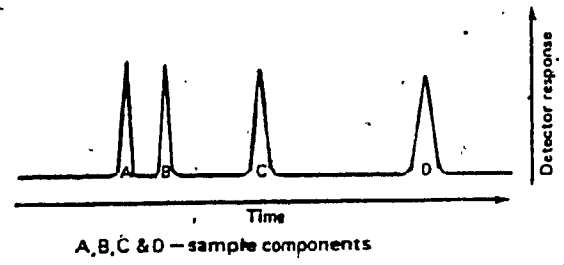


Figure (2) : Typical Chromatograph of a Four Component (A,B,C and D) Mixture.

tube packed with an inert powder (called the support) on the surface of which is coated a film of an involatile liquid (the stationary phase). The separation is achieved by a partition process involving the sample, the moving carrier gas and the stationary liquid phase.

In GLC analysis of any mixture the accuracy and precision depends on a vast amount of variables. Some of the most important variables are the temperature of the column and detector, the support and liquid phase in the column, the surface area and composition of the column tubing, the flow rate of hydrogen and air in the case of the FID detector, the carrier gas flow rate (especially if peak height instead of peak area is used for quantitative analysis), impurities present in the carrier gas (e.g., oxygen), and electrode corrosion in the case of the FID.

1.5.1 THE SUPPORT

The support material is used to provide a surface on which is coated the stationary phase film (Figure (5), page 43). The support should have a large surface area relative to its volume, it should be inert towards both the stationary phase and the sample, and the particles should be of uniform size.

Many materials have been investigated as potential supports but the only ones that are used to any extent are

diatomites and teflon. The diatomite supports can be divided into three main types whose designation depends on the supplier. For this thesis chromatographic supports manufactured by Johns Manville were used. They label their products as follows:

(a) Chromosorb P

(b) Chromosorb W

and,

(c) Chromosorb G

Ottenstein [17,18] and Supina [19] have published good reviews on solid supports. According to these reviews, the Chromosorbs are prepared by heating to high temperatures, sometimes after mixing the diatomite with a small amount of flux.

When the diatomite, alone, is calcined at temperatures of up to 1600 deg F, a pink support is produced. The pink colour of the support is caused by the mineral impurities (iron, aluminum, etc.) present. The mineral impurities form complex oxides which impart the pink colour to the support. This support is called Chromosorb P, where P stands for pink.

When the diatomite is mixed with a small amount of flux, sodium carbonate, and calcined at temperatures of 1600 deg F, a fused material is produced. The original grey diatomite becomes white in colour because of the conversion of iron

oxide to a colourless complex, sodium iron silicate. This support is called Chromosorb W. The W stands for the white colour of the support.

While neither Chromosorb P nor W may be regarded as an ideal support, both are suitable for a wide range of application. Chromosorb P has a greater density than W, it is less fragile than W, and is capable of holding a larger volume of liquid phase on its surface. However, when Chromosorb P is used with polar solutes severe tailing is often encountered. This arises from adsorptive centres in the support and gives rise to non-linear isotherms, an effect which is much less pronounced with the white supports. In a comparison of the pink and white supports Blandenet et al [20] found that the properties varied with respect to surface area and pore-size distribution. The difference in pore-size was considered by Ottenstein [21] who reported that the white support had pore sizes of about 9 μm while the pink support had a smaller pore size, about 2 μm . It was shown that this difference explained the variation in behaviour of the two supports, Chromosorb W holding the liquid phase in large pools, and Chromosorb P in small ones. The column efficiency is controlled by the mass transfer between the liquid and the gas phase, the larger pools of liquid phase require longer transit times for the solute, and peak broadening is the result.

Johns Manville introduced Chromosorb G, which is also a diatomite, especially processed for use in GLC, for which high efficiencies and greatly reduced surface activity are claimed. In a survey of comparative column efficiencies of some common solid supports Blandenet [20] showed decreasing potential efficiency through Chromosorb P, Chromosorb W, to a minimum for Chromosorb G. Chromosorb G has a density of about two and a half times that of Chromosorb W, which means that a 5 percent (W/W) loading of liquid phase on G would be equivalent to a conventional 12 percent loading on Chromosorb W for the same column volume. Chromosorb G is particularly useful when low loaded columns are required to achieve high sensitivities.

Table (2) gives a comparison of the physical properties of Chromosorbs P, W, and G. Table (3) gives the typical chemical analysis of Chromosorb P and W [18,22,23].

From Table (3) it is seen that diatomite supports are siliceous materials with about 10% mineral impurities. It is well established in the literature that the surface of siliceous materials is covered with the silanol (-Si-OH) and siloxane (-Si-O-Si-) groups. The surface of the diatomite can be represented as

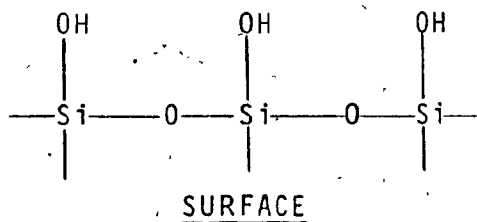


TABLE (2) : Comparison of Physical Properties of Chromosorbs.

<u>PROPERTIES</u>	<u>P</u>	<u>M</u>	<u>G</u>	<u>104**</u>	<u>C-750</u>
Free Fall density (g/ml)	0.39	0.18	0.47	.032	-
Packed density (g/ml)	0.47	0.24	0.58	-	-
Surface area (sq.m/g)	4.0	1.0	0.50	1000	0.5 to 1.0
Surface area (sq.m/ml)	1.88	0.29	0.29	-	0.35
pH	6.5	8.5	8.5	-	-
Friability (% breakdown)*	27.6	53.4	8.6	-	-
Pore volume (ml/g)	1.1	2.78	-	-	-
Colour	Pink	White	Oyster	Oyster	White
Pore diameter (um)	0.5	9.0	-	0.08	-
Silanol groups per sq.m	4.0×10^{19}	2.5×10^{19}	-	-	-

QUANTITY OF LIQUID PHASE

IN 100 CC OF SUPPORT :

a) Wt of support (gm)	47.0	24.0	58.0
b) Liquid phase 5% (gm)	2.47	1.26	3.05

** porous polymer solid support. It is made from a copolymer of acrylonitrile and divinyl benzene.

* breakdown after 10 minutes shaking

TABLE (3) : Typical Chemical Analysis
of Chromosorbs, %(W/W).

<u>CONSTITUENTS</u>	<u>CHROMOSORB P</u>	<u>CHROMOSORB W</u>
Loss on Ignition	0.3	0.3
SiO ₂	90.6	88.9
Al ₂ O ₃	4.4	4.0
Fe ₂ O ₃	1.6	1.6
TiO ₂	0.3	0.2
P ₂ O ₃	0.2	0.2
CaO	0.8	0.6
MgO	0.7	0.6
Na ₂ O+K ₂ O	0.5	3.6

Perrett and Purnell [24] have studied the surface of Chromosorb P and W supports. They found that the two supports differ in the extent of the surface rather than the nature of the surface. Their results were obtained by study of the reaction of hexamethyldisilazane (HMDS) with the supports. The extent of the reaction indicated the amount of silanol groups present. They reported the following concentrations of silanol groups :

Chromosorb P : 4.0×10^{19} groups / sq meter

Chromosorb W : 2.5×10^{19} groups / sq meter

This gives a Chromosorb P / Chromosorb W silanol group ratio

of 1.6 : 1.

Scholz and Brandt [25] measured the number of active sites on Chromosorb P and W supports by measuring the amount of n-butylamine adsorbed on the support surfaces. They reported the following results :

Chromosorb P : 7×10^{-3} millimoles amine / gram

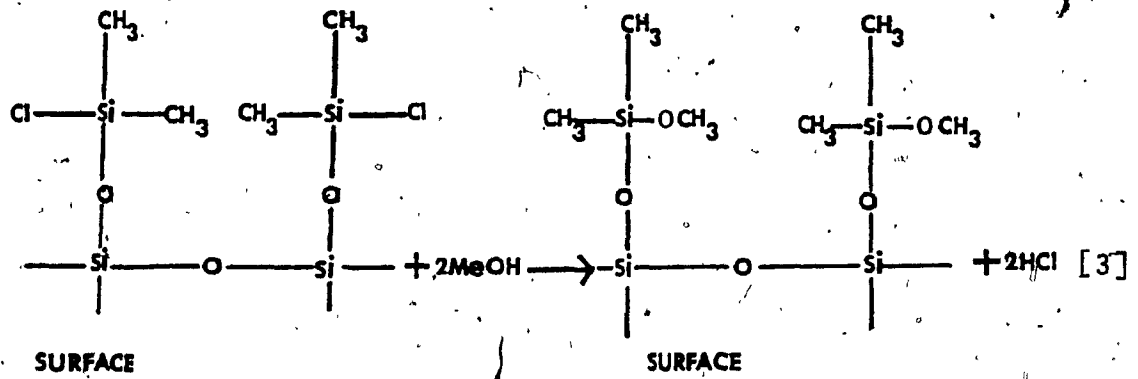
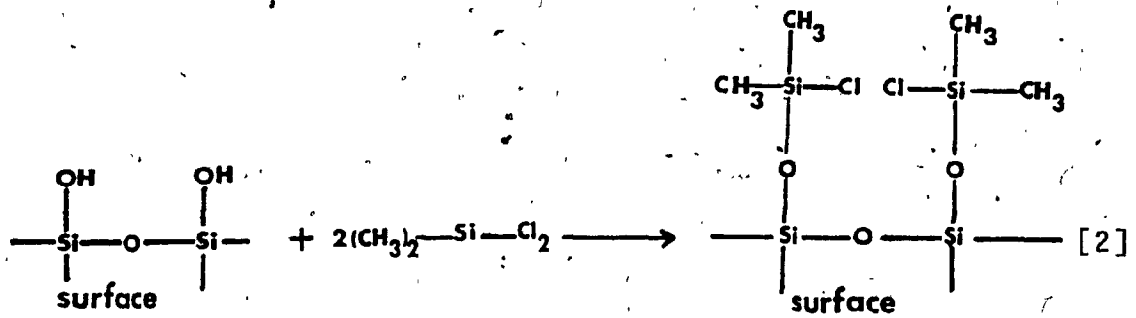
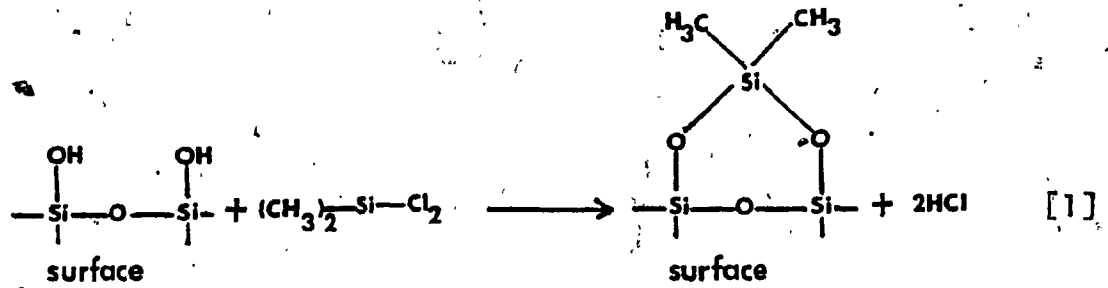
Chromosorb W : 6×10^{-4} millimoles amine / gram

This gives a Chromosorb P / Chromosorb W ratio of 12 : 1.

It is accepted that the Chromosorb P support is considerably more adsorptive than the Chromosorb W support. The difference appears to be due primarily to the greater surface area per unit volume of Chromosorb P over Chromosorb W.

1.5.2 TREATMENT OF DIATOMACEOUS EARTH SUPPORTS

Limitations in the usefulness of the support imposed by the effects of solute adsorption have encouraged a number of studies to be made directed at the elimination of the 'active centres'. It is generally agreed that these sites consist of -OH groups associated with silicon, aluminium and iron [26]. Many workers have pre-treated the supports by prolonged extraction with hydrochloric acid of various strengths which is claimed to leach out surface alumina and iron. Although treatment with acid can be effective in removing active -OH



groups associated with surface impurities such as iron and aluminium, it does nothing to eliminate the effects of the silanol ($-\text{Si}-\text{OH}$) groups. A method, which has been used with great success, is the modification of the surface hydroxyl groups by silanisation. (A procedure for this, involving the use of dimethyldichlorosilane, was reported by Horning et al [27]. The dimethyldichlorosilane (DMCS) is assumed to react with the hydroxyl groups on the silica surface as shown in reaction (1) and (2). As two adjacent $-\text{OH}$ groups are required for complete reaction (Reaction (1)), it is unlikely that all the reactive sites are removed. A single $-\text{OH}$ group might leave an undesirable $-\text{Si}-\text{Cl}$ linkage as in reaction (2). Silanisation by means of DMCS must be followed by removal of the $-\text{Si}-\text{Cl}$ by washing with methanol. It appears that the $-\text{Si}-\text{Cl}$ reacts with the methanol to form a methoxy compound (Reaction (3)).

An alternative reagent, hexamethyldisilazane (HMDS) was used by Boheman et al [28] to eliminate silanol groups from the surfaces of Chromosorb P, W, and G. As some reactive sites are still observed on these modified surfaces, Littlewood [26] suggested that not all adsorption is associated with $-\text{OH}$ groups.

The main forces contributing to adsorption are considered to be weak Van der Waal's forces and stronger hydrogen bonding forces. Di Corcia et al [29] suggested that all polar liquid

phases neutralize the weak Van der Waal's forces, but that liquid phases capable of undergoing hydrogen bonding are required to de-activate the polar adsorption sites. The hydrogen-bonding sites are of two types. The first arises from silanol (-Si-OH) groups, where the support is the proton donor in the hydrogen bond, and the second from siloxane (-Si-O-Si-) groups, where the support acts as the proton acceptor. Ottenstein [30] has pointed out that the siloxane group is much more effective in forming a hydrogen bond than the silanol oxygen, and that it is the strength of the hydrogen bond that determines the extent of solute adsorption. Therefore, compounds that form strong hydrogen bonds, e.g., water, alcohols, and amines, cause severe tailing, whereas ketones, esters, etc., which show less tendency to form hydrogen bonds, cause little tailing.

1.5.3 CLASSIFICATION OF MODIFIED DIATOMACEOUS SUPPORTS

(a) THE WHITE SUPPORTS [31]:

These are derived from flux-calcined diatomite. They are friable but relatively inert, and are useful for the analysis of polar samples. They are commercially available in several forms :

(1) The unmodified diatomaceous supports. e.g., Chromosorb W-NAW (non acid washed).

(2) Acid-Washed (AW) diatomaceous supports. These have been modified by various acid-washing procedures to remove some of the adsorptive sites, e.g., Chromosorb W-AW (washed with hydrochloric acid):

(3) Silanized diatomaceous supports. For further reduction of active centres many supports are available in a silanized form. These are recommended for analysis of very polar materials and for use in making low loaded columns. Silanized supports are incompatible with certain highly polar liquid phases. e.g., Chromosorb W-AW-DMCS.

(b) THE PINK SUPPORTS [31]

These are derived from diatomite calcined without flux. They have better handling characteristics than the white supports. They give greater efficiencies but are less inert and so less suitable for analysis of polar solutes. The same chemical treatments are given to this support as are given to the white support.

(1) Unmodified pink supports, e.g., Chromosorb P-NAW.

(2) Acid-washed pink supports. These are less active than the untreated support, due to removal of surface iron. They are, however, still unsuitable for analysis of polar materials. e.g., Chromosorb P-AW.

(3) Silanized pink supports. These are the least active of the pink supports but still are not as inert as the best white supports. They are efficient supports for semi-polar materials but are not satisfactory for low liquid-phase loaded columns. e.g., Chromosorb P-AW-DMCS.

(c) CHROMOSORB G [31]

This is specially prepared by Johns Manville as a support for gas chromatography. As it is very inert, non-fragile and dense, it is particularly useful for columns carrying less than 5% (W/W) loadings of liquid phase. It is available as Chromosorb G-AW, Chromosorb G-AW-DMCS, and Chromosorb G-AW-DMCS.

(d) CHROMOSORBS HIGH PERFORMANCE (H.P.) [31]

These have been developed for use with steroids, alkaloids, and other pharmaceutical, medical and toxicological compounds. Chromosorbs H.P. are high quality, carefully acid washed, silanized, and flux-calcined diatomites. Their features include superior inertness and column efficiency, no catalytic surface activity and short column conditioning times [31]. Chromosorb W and Chromosorb G are available in the 'H.P.' grade.

(e) CHROMOSORB 750

This is claimed by the manufacturer to be the most inert,

non-friable, free flowing, and highly efficient support on the market. It has been designed specifically for biomedical and pesticide analysis. It is prepared by exhaustive acid-washing and effective silane treatment of high purity diatomite.

1.5.4 POROUS POLYMER SUPPORTS

Johns Manville [32] produces porous polymer supports under the name Chromosorb Century series. These supports [36] are resins of the polyaromatic type. These resins have a uniform rigid structure with a distinct pore size, and are 'infusible' and 'insoluble' in most solvents. Porous polymers are especially effective in providing excellent separations of a variety of gases and compounds with boiling points up to about 250 deg C.

Chromosorb Century series polymers are produced by copolymerizing monofunctional monomers with difunctional monomers. For example, Chromosorb 104 (Table (2)) is produced by the copolymerization of acrylonitrile monomer (ACN) and divinyl benzene monomer (DVB). It is a very polar support and has a large surface area. Similar products are produced by other companies. Generally, porous polymer supports are used primarily in gas solid chromatography (GSC) because of their poor wettability by liquid phases [33].

1.5.5 ULTRA BOND SUPPORT

Ultra-bond supports [35] are prepared by extensive deactivation of a diatomaceous earth followed by coating with a liquid phase and treating at high temperatures. The heat treated phases are then exhaustively stripped with solvents to produce a support having a 0.2% loading of non-extractable liquid phase. In 1976, Ultra-bond 20m (Table (-2)) was introduced as a bonded GC packing. The liquid phase bonded to Ultra-bond 20m is Carbowax 20m which is very polar. Bonded phase supports are attacked by oxygen at high temperatures. Therefore, care must be taken to protect them from oxygen. These supports are especially good for GC/mass spectroscopy systems since they have zero bleed, high efficiencies and high temperature stability.

1.6 THE STATIONARY PHASE

The separation of the sample into its constituents is achieved by a partition process involving the stationary liquid phase [34] and the moving carrier gas. The stationary phase must be involatile and thermally stable at the temperature employed for the analysis, and should be coated as a thin, even film onto the support. The stationary phases in general use are high boiling point organic compounds and can be classified as being either selective or non-selective (non-polar). Phases in the latter category separate on the

basis of differences between the boiling points of the sample components (the highest boiling component eluted last and the lowest boiling component eluted first) whereas the selective phases separate on the basis of chemical differences. Generally, it is found that a polar substance is most satisfactorily analyzed using a polar stationary phase, whereas non-polar compounds will be best resolved by a non-polar phase (like separates like).

Urone et al [35] found that when polar solutes (e.g., organophosphorus and organochlorine) are resolved on a support coated with a non-polar liquid phase (OV-101, SE-30, Squalane, etc.) the solutes easily penetrate the non-polar phase to interact with the support surface as if the liquid phase were not there. When squalane was used as the liquid phase on a support, it was shown that the support surface was only slightly modified, and the amount of polar solute (methanol, acetone) sorbed was essentially the same as that sorbed by the uncoated support. When a polar compound was added to the non-polar liquid phase which was then coated onto the support most of the active sites were removed. Reduced adsorption was observed on the support.

Unlike OV-101, OV-17 and Squalane which are fluids, OV-1 is a solid (rubber) at room temperature. At elevated temperatures, about 310 deg C, OV-1 changes from a compact rubber to a gel like solid (swollen). Lindgren et al [36]

claimed that OV-1 allows organophosphorus pesticides to penetrate its surface more readily when compared to OV-101. As will be explained later, OV-1 and OV-101 are both polydimethylsilicone compounds with different molecular weights. OV-1 has a higher molecular weight than OV-101, and it has some cross-linking. Hence, the solid nature of OV-1 and the fluid nature of OV-101. Lindgren et al attributed the greater tailing and adsorption on OV-1 to the higher diffusibility through this phase.

1.6.1 WETTED AND UNWETTED SUPPORTS

The way in which the liquid phase is distributed on the support depends on the structure of the solid support, on the relative surface tensions of liquid and solid surfaces, and on the solid-liquid interfaces [37].

the process of silanization, the character of the surface is changed from hydrophilic (water-loving) to hydrophobic (water-hating), making it particularly effective for the retention of non-polar phases. However, the resulting production of a support of low surface energy makes it difficult to coat with polar phases because of the poor wetting of the surface [38]. If the solid has a lower surface energy than the liquid the contact angle must be greater than zero and the support is not completely wetted. The liquid then tends to be distributed discontinuously in

isolated pools or droplets. The surface of diatomaceous earth supports, when treated with silanizing agents, is predominantly covered with methyl groups giving it a low surface energy. Serpinet [39,40,41] has shown that even liquids of relatively low surface energy do not wet the major part of the surface area of silanized supports.

According to Giddings [42] a porous wettable solid holds the liquid partly by adsorption forces and partly by capillary forces. Capillary liquid in the narrow recesses of the solid is in equilibrium with a reasonably uniform adsorbed layer over the remainder of the surface, as illustrated for an ideal surface in Figure (3A). The adsorption forces are strong for the first monolayer of liquid but fall off rapidly with distance from the surface. Figure (3B) represents Serpinet's model for liquid which does not wet the support. An unwetted support would normally cause tailing of a polar solute whereas a completely wetted support would eliminate tailing. The exposed support material, contributes to the retention term, $K_S A_S$, in equation (26) page 48.

If particles are broken during packing of the column, tailing and adsorption will occur [19]. The Chromosorb W supports are especially likely to be broken during packing because of their low friability [31].

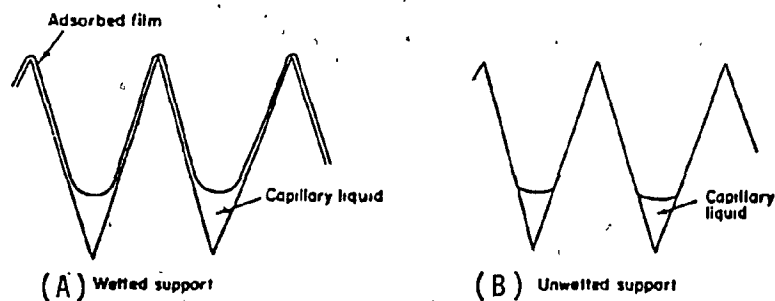


FIGURE (3) : Liquid Distribution Models:

- (A) Giddings Model for Liquid Wetting an Idealized Porous Surface.
- (B) Serpinet's Model for Liquid Which does not Wet the Support.

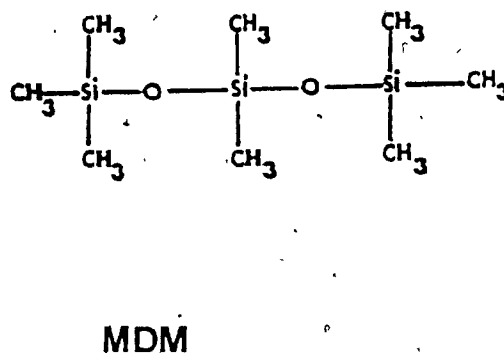
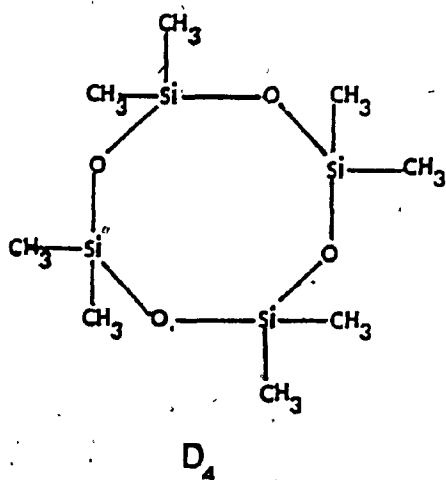
In retrospect what is being said here is that the surface energy of OV-1 is relatively high, for example, by comparison with OV-101, and hence it will spread less readily on diatomaceous supports, leading to a greater likelihood of adsorption effects.

1.6.2 POLYDIMETHYLSILICONES

Polydimethylsilicones (PDMS) are the most widely used liquid phases in GC today because of their good temperature stability and their essentially non-polar separating characteristics. Recently, refined versions of the PDMS,

such as OV-1, OV-101 and SE-30 have been produced and marketed exclusively for use as GC liquid phases [43].

For the purpose of simplification and understanding of the language of the chemistry of silicones, Table (4) is presented to show the symbols and formulae used in discussing silicones [43]. In Table (4) R represent a methyl group. Examples of the use of the symbols, D₄, and MDM are given by the structures below.



PDMS, in general, are represented by the symbolic formula MD_xM . When $x = 0$, MD_xM reduces to MM which has a molecular weight of 162 and a boiling point of 100°C. When x is greater than 10,000 the product may be a viscous oil or even a stable rubber as is the case with OV-1 (high molecular weight). SE-30 (medium molecular weight) which is a gum

TABLE (4) : Symbols and Formulae of PDMS.

<u>SYMBOL</u>	<u>STRUCTURAL*</u> <u>FORMULA</u>	<u>COMPOSITION</u>	<u>FUNCTIONALITY</u>
M	$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{Si}-\text{O}- \\ \\ \text{R} \end{array}$	$\text{R}_3\text{SiO}_{1/2}$	Monofunctional or end blocker
D	$\begin{array}{c} \text{R} \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{R} \end{array}$	$\text{RSiO}_{2/2}$	Difunctional or backbone
T	$\begin{array}{c} \text{R} \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{O} \end{array}$	$\text{R}_2\text{SiO}_{3/2}$	Trifunctional or crosslinker
Q	$\begin{array}{c} \text{O} \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{O} \end{array}$	$\text{SiO}_{4/2}$	Tetrafunctional or crosslinker

*R - methyl group

has an x value less than that of OV-1. OV-101 (low molecular weight) which is an oil has an x value even less than does SE-30.

The separating characteristics of all PDMS should be essentially the same. The main reason for concern to a chromatographer using a PDMS as a liquid phase is its instability. Residual traces of catalyst (strong acids and bases) used to initiate polymerization, can have a definite effect on stability, and PDMS will appear to depolymerize or bleed when being used as a liquid phase at high temperatures.

The catalyst in the liquid phase makes it virtually impossible for the chromatographer to improve upon the temperature stability of the specific PDMS. Not only is the chromatographer at the mercy of the commercial manufacturer, but he must also make certain that potential catalysts are not induced in the process of coating the support [43].

The chromatographer must also be careful in the sample types which are analyzed using a PDMS as liquid phase. Strong acids or strong bases may cause depolymerization of the liquid phase at elevated temperatures and hence bleeding. The column has to be re-equilibrated every time there is depolymerization. These effects may all tend to shorten the life of a PDMS column which is used at elevated temperatures.

If no depolymerization occurs due to catalyst or strong acid and base solutes, then, the PDMS are extremely inert liquid phases and may be used to analyze most compounds at elevated temperatures with excellent results.

The higher molecular weight PDMS are stable at 150 deg C in air for extended periods of time. Above this temperature, viscosity will increase with time and eventually the material will gel [44,45].

The PDMS are considerably more stable in the absence of oxygen, as in GC columns. In this application, OV-1, OV-101, and SE-30 may be used for extended periods of time at up to 350 deg C, and programmed temperature operation up to 400 deg C is routinely performed. Any bleeding which does occur under these conditions usually indicates the decomposition of the polymer chain to the smaller cyclic species (i.e., D₄ on page 30). Figure (4) shows the type of infrared that might be obtained for components collected from a bleeding column. The broad band between 9 and 10 microns is characteristic of linear polysiloxanes, and the band at 7.9 microns is for methyl silicon [44].

Generally, the PDMS are quite chemically inert. However, solutes which are strongly acidic or basic are to be avoided. Electrophiles, such as chlorine, may cause cleavage of silicon-carbon bonds [43,44].

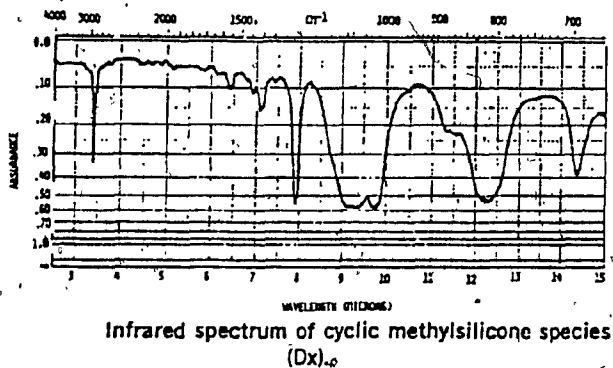
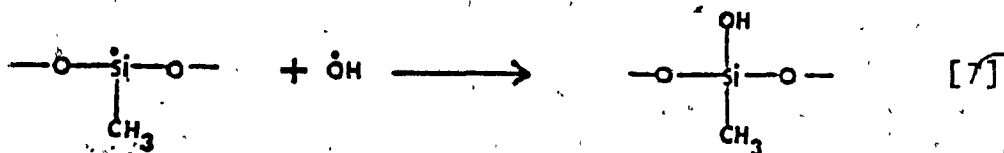
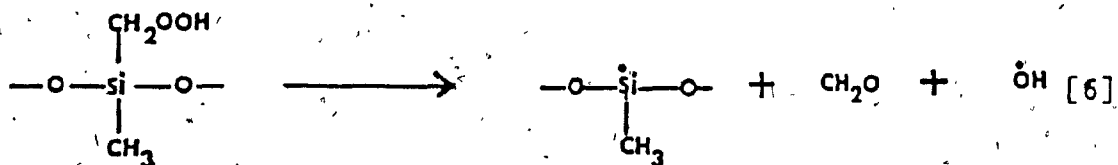
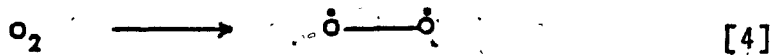
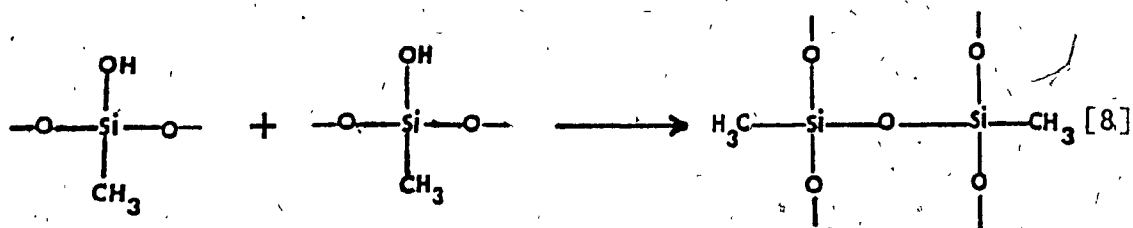


FIGURE (4) : Infrared Spectrum of Cyclic Methylsilicone Species (Dx).
(Reference [44]).

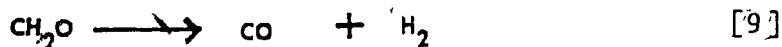
The thermal oxidation of polyorganosiloxanes begins at 150 deg C [45]. The organic groups attached to the silicone in PDMS lower the thermal stability of the siloxane bond, and this stability decreases as the number of such groups increases from zero to two. The lower stability is due not merely to higher concentration of organic matter, but also to the fact that the polymer is linear rather than three-dimensional, Q in Table (4). Volatile products of the thermal oxidation of PDMS consist mainly of carbon dioxide (2%), carbon monoxide (25%), water (17%), formaldehyde (3.7%), methanol and traces of formic acid. The mechanism involves oxygen attack on the carbon. The initial products are hydroperoxides which rapidly decompose [45,46,47]. Product (I) decomposes to formaldehyde and the OH radical.

The latter adds to a silicone of the polymer (Reactions (4) to (8)).

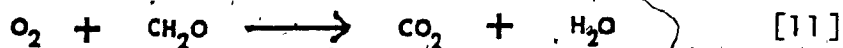




Thermal decomposition of formaldehyde yields mainly carbon monoxide and hydrogen (Reaction (9)).



Carbon monoxide is therefore the principal gaseous degradation product. A portion of the formaldehyde is, however, oxidized to formic acid and carbon dioxide (Reactions (10) and (11)).



PDMS are degraded by oxygen not only by the rupture of the Si-C bonds, but also by rupture of the Si-O-Si bonds. The latter starts at 300 deg C and is very intense at 400 deg C.

1.7 REACTIONS OF THE PESTICIDES

Both trivalent and pentavalent phosphorus compounds

react with silicone compounds to give -P-O-Si- compounds [9,12]. The $\overset{\text{H}}{\underset{\text{H}}{\text{P}}}$ -O-Si- compounds are much more common than the $\overset{\text{H}}{\text{P}}$ -O-Si- compounds.

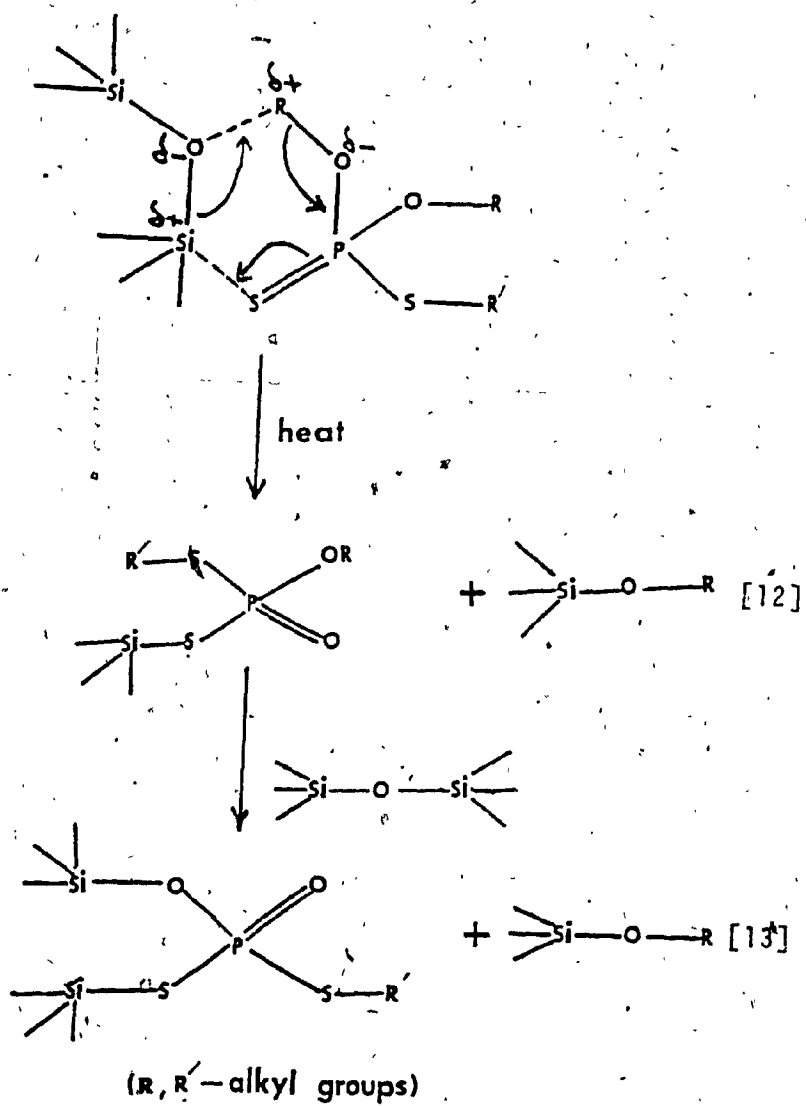
The organophosphorus and organochlorine pesticides studied in this project can be considered as Lewis bases because of the lone pair of electrons on sulphur, oxygen and chlorine. Some of the reactions that are possible with these pesticides on the OV-1 liquid phase are demonstrated in Scheme I. These reactions are similar to those of the phosphate compounds (Scheme II). Reactions (14) and (15) occur upon heating the trialkylacetoxysilanes with hydroxymethylphosphinic acid (molar ratio 3:1) at 150-210 deg C [48].

The organophosphorus pesticides can also be oxidized. The sulfur atom of the thiophosphoryl and thioether groups are replaced with oxygen [49].

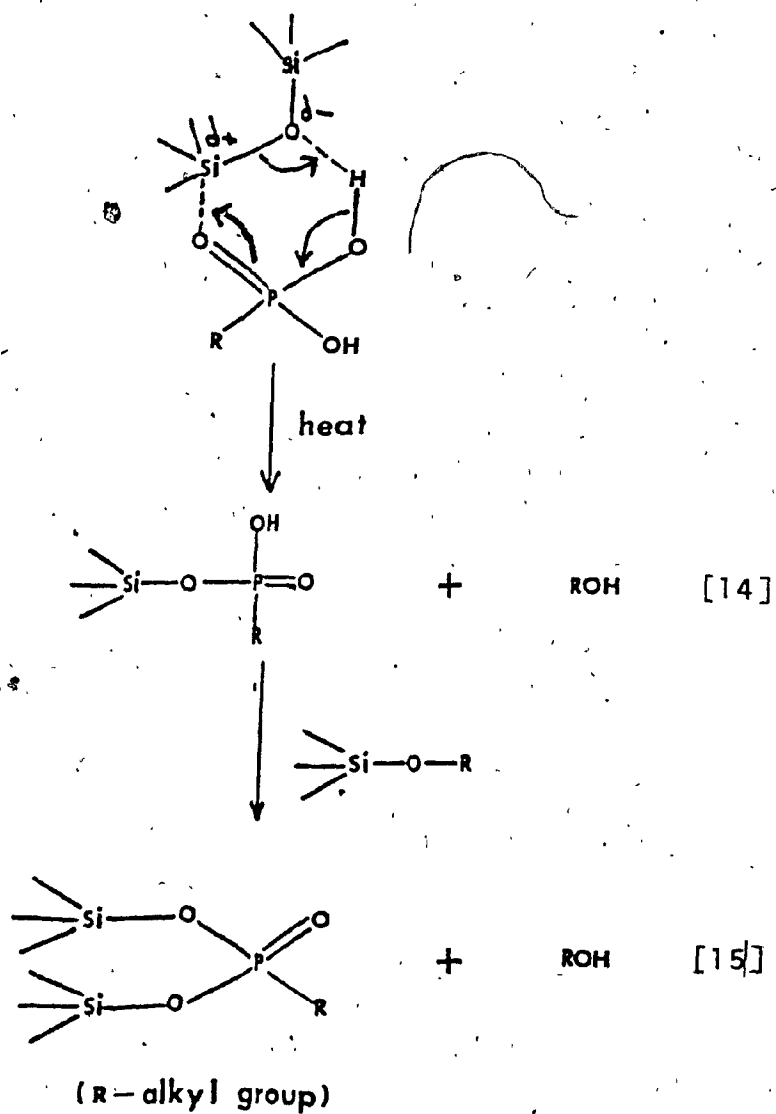
The thioether group in a side chain is oxidized to sulfoxide and then sulfone.

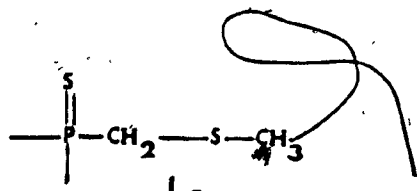
The thioether group is more susceptible to oxidation than a thiophosphoryl group. Reactions (16) and (17) demonstrate the oxidation of the thioether group.

SCHEME I

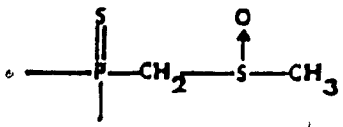


SCHEME II



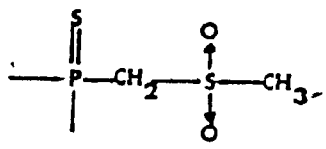


[O]



[16]

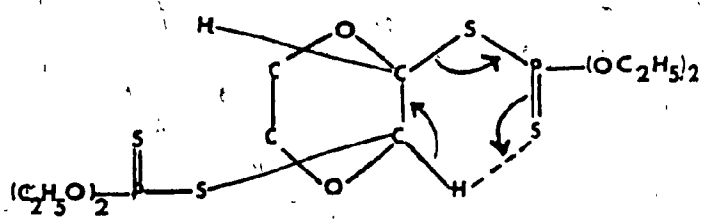
[O]



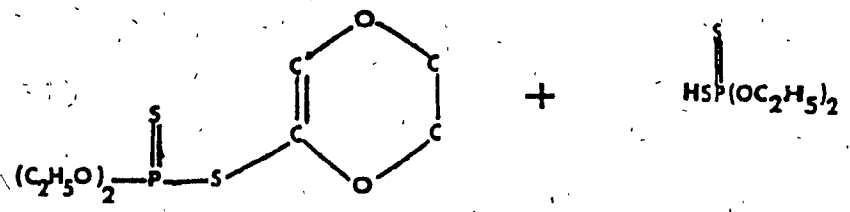
[17]

Organophosphorus pesticides undergo thermal decomposition starting from about 135 deg C. The trans form of Dioxathion undergoes pyrolysis more readily at 135 to 140 deg C than the cis isomer, which decomposes at 160 to 165 deg C [50,51].

TRANS DIOXATHION

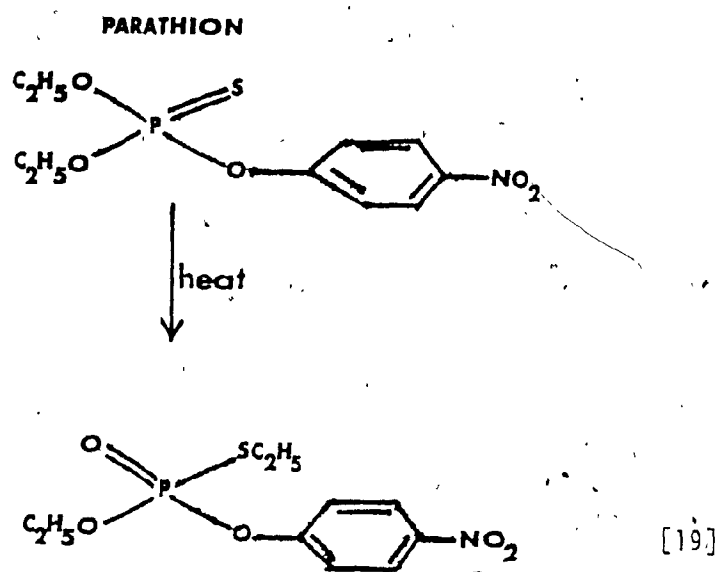


heat



[18]

Isomerization also occurs at elevated temperatures [50]. Metcalf et al [51] showed that methyl Parathion is 91% isomerized into 5-Methylphosphorothiolate by heating at 150 deg C for 6.5 hours. Parathion is isomerized 90% by heating at 150 deg C for 24 hours (Reaction (19)).



The above discussion gives some idea of the chemical changes that can occur during the GLC of organophosphorus and organochlorine pesticides. The critical variables that are relevant to the above reactions are the chemical make up of the GLC column, the oxygen present in the liquid phase, the temperature of the column and the basicity of the pesticides. As will be seen later, one or more of these variables can indirectly explain the shape of the thermograms in Appendices (I) and (II).

1.8 THE COLUMN

As has already been mentioned, in GLC the stationary phase is a liquid coated onto a solid support material. The separating principle depends on the difference in the partition coefficients (between the liquid and gas phase) of the constituents of a mixture. Those constituents with a high affinity for the stationary phase will tend to dwell in it and therefore take longer to travel through the column than those with little or no affinity for the stationary phase [53].

Columns are generally constructed of glass or stainless steel tubing and are filled by forcing the packing into the tubing using a pressurized gas supply, by drawing the packing into the tubing, by using a vacuum line, or by introducing the packing via a funnel without application of pressure. In all cases the filling process may be assisted by vigorous tapping or vibrating of the column [19].

After filling, it is necessary to condition or 'age' the column. This is done by heating the column to a temperature 20 or 30 deg C above the maximum temperature intended for its operation, whilst maintaining a flow of carrier gas through the column. This process removes residual solvent and other volatiles present in the stationary phase, which would otherwise bleed and contaminate the detector during

analysis. It should be noted, however, that there is a temperature above which the liquid phase will begin to bleed off at an excessive rate, leading to impaired column performance. Figure (5) represents a typically packed GLC column.

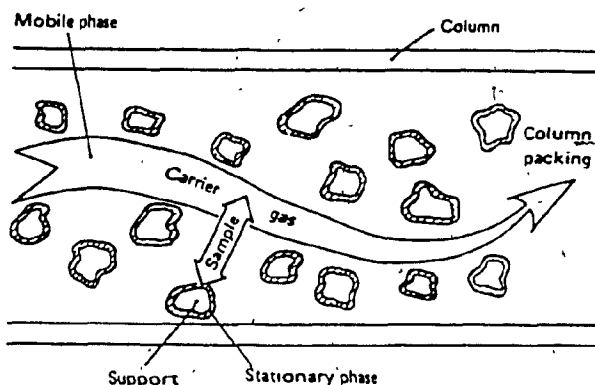
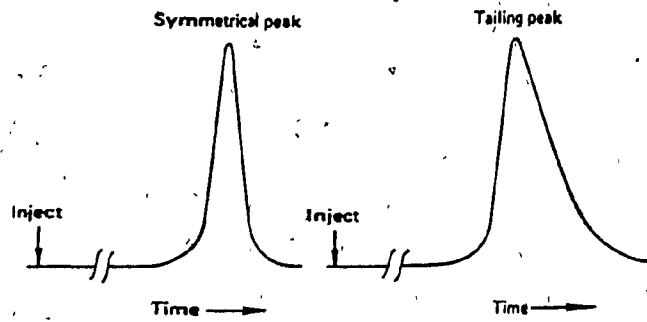


FIGURE (5) : Typically Packed Gas Liquid Chromatographic Column.

The requirement for the support to be inert is important since any degree of interaction between the sample and the support is likely to lead to distortion of the chromatographic peak which is known as 'tailing' (see Figure (6X)). For this reason pre-treatments such as washing with acid and alkali or deactivation by silanization may be necessary, especially when low (i.e., less than 5% (W/W)) loadings of stationary phase are to be used [19]. The degree of tailing of a peak can be calculated as shown in Figure (6Y). Here, the tailing factor is calculated as $10 (a/2b)$ where the factor ten is used to expand the scale so as to obtain

convenient numbers [54].

X



Y

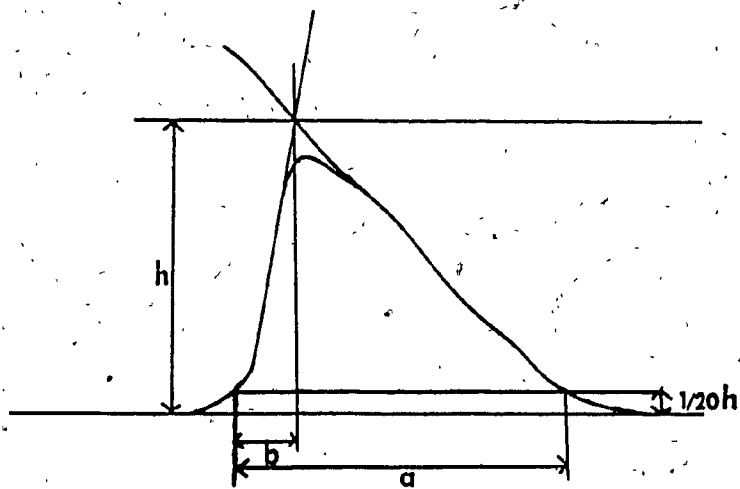


FIGURE (6) : X) Symmetrical and Tailing Peaks.
Y) Calculation of Tailing Factor.

Impregnation of the support with stationary phase is achieved by mixing a known weight of support with a measured quantity of stationary phase dissolved in a suitable solvent. The solvent is then removed by evaporation during which gentle agitation must be used to produce a free-flowing powder without lumps.

The stationary phase loading is a measure of the amount of phase present on a weight/weight basis, i.e., 10 gm stationary phase + 90 gm support would provide a 10% (W/W) loading of stationary phase [53,54].

1.9 COLUMN PERFORMANCE

The success of any GLC analysis depends upon the separating ability of the column. Column performance is influenced by a number of factors. The overall efficiency of the column is usually expressed as the number of theoretical plates, n . The concept of theoretical plates is derived from considerations of fractional distillation processes, and refers to the number of equilibrium stages occurring within the column. This measure of efficiency is obtained by reference to the elution curve or peak produced by the detector and displayed on the recorder during the analysis. At the peak maximum, a finite volume of carrier gas will have travelled through the column. This is known as the retention volume (V) and is related to the retention

time (t) by the expression given in equation (20) where F_c is the (volume) flow rate of the carrier gas and t is the time for the emergence of the peak maximum after the injection of the sample [55]. (See Figure (7) page 51). In practice, the retention time is obtained directly from the recorder chart, since the chart speed is constant. However, in some cases it is necessary to measure the retention time from an air peak or solvent peak. This is called the relative retention time (RRT).

$$V = F_c t \quad (20)$$

For physicochemical interpretation, often, the 'specific retention volume' is required. The specific retention volume (V_g) is obtained by converting the retention volume (V) to a standard value at a given temperature and pressure and per unit weight of stationary phase [56].

$$V_g = \frac{273 \cdot RRT \cdot F_c \cdot f}{T_c \cdot W \cdot U} \quad (\text{ml/gm}) \quad (21)$$

where RRT is the relative retention time (inches); F_c is the flow rate of the column (mls/min); U is the recorder chart speed (inches/min); W is the weight (gm) of liquid phase in the column; T_c is the temperature of the column in degree Kelvin; and f is the correction factor for the pressure gradient in the column. f is given by equation (22).

$$f = \frac{3(p_i/p_o)^2 - 1}{2(p_i/p_o)^3 - 1} \quad (22)$$

where p_i is the carrier gas pressure at the inlet of the column and p_o that at the outlet of the column.

The time taken for a substance to pass through a gas chromatographic column (the retention time, t) depends on the column temperature, the carrier gas, the flow rate, the column length, etc. But if all these parameters are kept constant the retention time will be constant and repeatable. Retention time is a physical characteristic analogous to melting or boiling points and as with these parameters can be used as evidence of sample identification.

1.9.1 GENERALIZED RETENTION MECHANISMS

The partition coefficient K_1 in GLC is defined by the equation (23).

$$K_1 = Q/C \quad (23)$$

where C is the concentration of solute in the gas phase (mole/volume) and Q is the concentration of solute in the liquid phase when the solute is distributed between a gas (carrier gas) and a liquid (liquid phase) at equilibrium [55].

Assuming that the stationary and mobile phases remain

in equilibrium as the solute moves through the column, and that the liquid phase behaves as a bulk liquid whose properties are not affected by distribution on the support, then it can be shown that the measured net relative retention volume, V_R° , is related to K_L and the volume of the stationary phase, V_L , by equation (24).

$$V_R^\circ = K_L \cdot V_L \quad (24)$$

V_R° is related to the specific relative retention volume by the following formula [56].

$$V_g = \frac{273 \cdot V_R^\circ}{T_c \cdot W} \quad (25)$$

Equation (21) holds only if the chromatographic peaks are symmetrical, i.e., there is no tailing due to adsorption. Liao and Martire [57] used a generalized equation to account for partition of the solute in the liquid phase, adsorption of the solute on the liquid phase (this is typical for polar solutes on non-polar liquid phases), and adsorption of the solute on the exposed support. For asymmetrical peaks all three of these mechanisms take place [58,59]. The equation is,

$$V_N = K_L \cdot V_L + K_1 \cdot A_1 + K_S \cdot A_S \quad (26)$$

where K_L and V_L have the same meaning as defined in equation (24). K_S and K_1 are, respectively, the partition coefficients

relevant to the solid support and interfacial adsorption, A_1 and A_s are the corresponding total surface areas. In this thesis all of the columns gave tailing peaks. For these columns equation (26) should represent the mechanism contributing to the retention time.

1.9.2 HEATS OF ADSORPTION

It has been well established that plots of $\log V_g$ as a function of reciprocal absolute column temperature are frequently linear, particularly over narrow temperature spans [55,56]. This behavior arises from the thermodynamic properties of the solute-sorbent system. The following equation may be deduced for such systems [61].

$$\text{LOG } V_g = \frac{\Delta H_a}{2.303 \cdot R \cdot T_c} + k \quad (27)$$

where ΔH_a is the heat of adsorption (or solution as the case may be) [62], T_c is the absolute column temperature, R is a gas constant, and k is an experimentally determined constant for a given solute-sorbent system.

Since tailing is an adsorptive effect, an attempt will be made in this thesis to correlate peak tailing and heats of adsorption for the supports studied.

1.9.3 EFFICIENCY

The width of the peak at its base, W , is taken as the distance between tangents drawn as shown in Figure (7), and is expressed in the same units as t . The number, n , of theoretical plates [54] is given by equation (28).

$$n = 16(t/W)^2 \quad (28)$$

It can be seen from this formula and Figure (7) that the narrower the peak, the more efficient is the column.

Since the length of the column will affect the total number of plates, the 'height equivalent to a theoretical plate (hetp)', H , is usually calculated from the equation (29).

$$H = \frac{\text{length of column}}{n} \quad (29)$$

Alternatively, one may quote the number of plates per unit length. A good packed column will, for example, produce about 500 theoretical plates per foot [53].

1.9.4 RESOLUTION

Another measurement of column performance is given by the degree of separation between two adjacent peaks [54].

This is known as the resolution, R , or separation factor of the column, and it is given by equation (30) or (31) (Figure (8)).

$$R = \frac{2(t_b - t_a)}{(W_a + W_b)} \quad (30)$$

or

$$R = \frac{2\Delta T}{(W_a + W_b)} \quad (31)$$

In general, if the peak resolution factor is greater than one, the separation may be regarded as adequate.

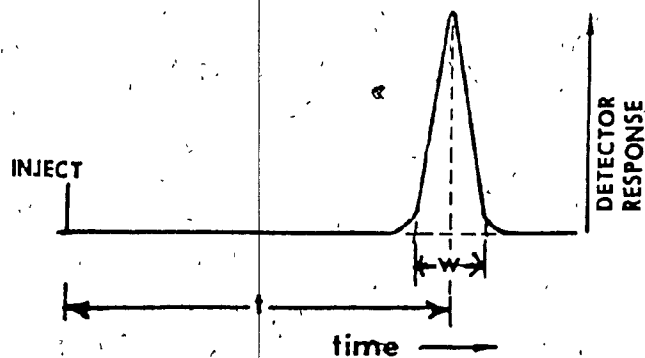


FIGURE (7) : Retention Time (t) and Peak Width (w) of a Sample.

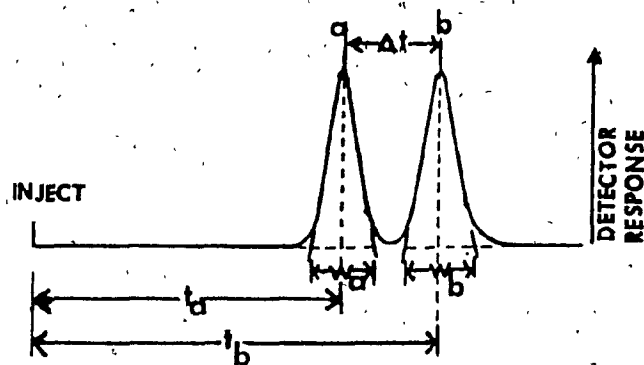


FIGURE (8) : Symbols indicating Variables Used to Calculate the Resolution of a Column,

1.10 QUANTITATIVE ANALYSIS

The size of every peak displayed on the recorder is a measure of the amount of a particular component present in the sample. It is the area under the peak which is proportional to the quantity of the component present.

The height of any peak is a function of its area, and for symmetrical (Gaussian) peaks it may be used directly for quantitative purposes. However, peak shape (and therefore peak height) is liable to be altered by slight variations in operating conditions or injection techniques.

Peak areas can be measured in various ways. Peaks can

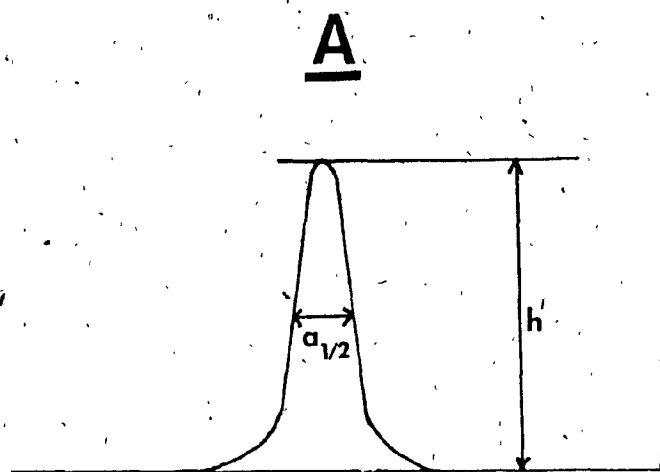
be cut out and weighed to quantitatively estimate a component. It is assumed that the weights are directly proportional to their areas, but variation in paper thickness can introduce errors. This method is time-consuming, tedious, destroys the analytical record, and is difficult to use with small peaks [54].

Triangulation is another method used for approximating areas under a peak. There are two variations of this method. In the first, Figure (9B), tangents to the sides of the peak are drawn, and a baseline is constructed under the peak thus producing a triangle. The area, is given by equation (32).

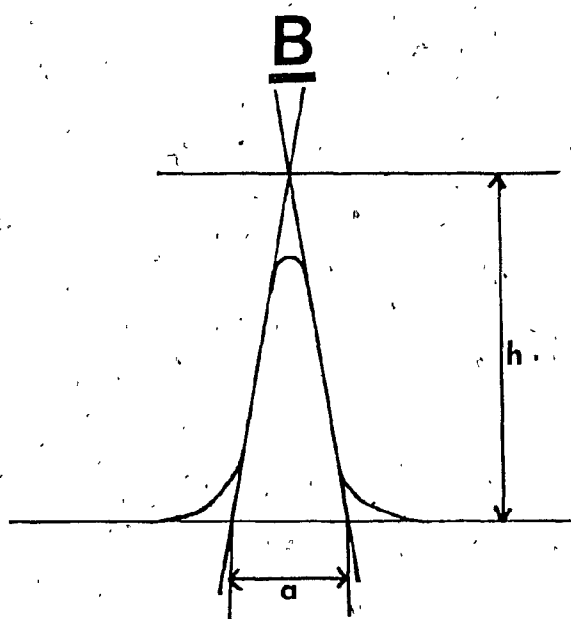
$$\text{Area} = 1/2 \cdot a \cdot h \quad (32)$$

In the second variation (Figure 9A), an imaginary triangle is drawn inside the peak, and the area is obtained by multiplying the actual peak height by the peak width at half height. This method is the most popular and simplest for measuring peak area.

In the first method the area gained between the top of the peak and the intersecting tangents is regarded as an approximate compensation for the area lost at the base. Estimation of the proper positioning of the tangents and of their point of intersection is rather subjective. The second method always underestimates the size of the peak,



$$\text{AREA} = a_{1/2} \cdot h$$



$$\text{AREA} = 1/2(ah)$$

FIGURE (9) : Area Evaluation Under a Chromatographic Peak by Triangulation.

but it has the advantage of removing the subjective element encountered in the first method [53].

Other methods for estimation of peak area are by planimetry, mechanical integration, and electronic integration. The electronic means of evaluating a peak area are faster, but not necessarily more accurate than the triangulation method.

1.11 DETECTORS

The purpose of a detector is to produce a response signal which is proportional to the concentration (or amount) of compound passing through it.

A variety of detection systems may be applied for the analysis of organophosphorus and organochlorine pesticides. Their sensitivity and selectivity parameters are listed in Table (5) [10].

Two types of detectors, electron capture (ECD) and flame ionization (FID), were used to quantitate the amount of pesticide in this thesis.

TABLE (5) : GC Detection Systems Suitable for
Organophosphorus and Organochlorine
Pesticides.

<u>DETECTION</u> <u>SYSTEM</u>	<u>RESPONDING</u> <u>ELEMENT</u>	<u>APPROXIMATE MINIMUM DETECTIBILITY</u>	
		<u>IDEAL</u>	<u>PRACTICAL</u>
Flame Ionization	-C-H	ng	ug
Electron Capture	halogen, $\begin{array}{c} \text{S} \\ \\ \text{P} - \text{S} \\ \\ \text{S} \\ \\ \text{P} - \text{O} \\ \\ \text{O} \\ \\ \text{P} - \text{S} \\ \end{array}$	pg	ng
Flame Photometric	P,S	pg	ng
Microcoulometric	halogen,S,P	ng	ng
Electrolytic	halogen,S,N	ng	ng
Conductivity			

1.11.1 FLAME IONIZATION DETECTOR (FID)

The flame ionization detector is shown schematically in Figure (10).

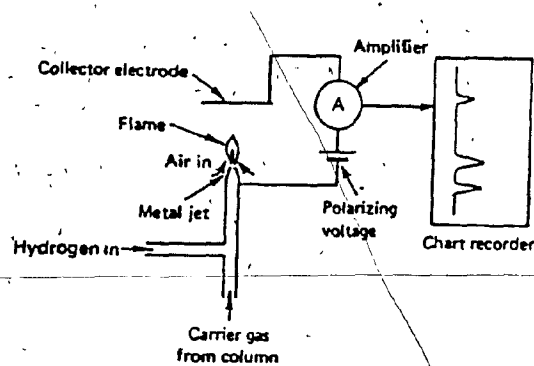


FIGURE (10) : Schematic Diagram of the Flame Ionization Detector (FID).

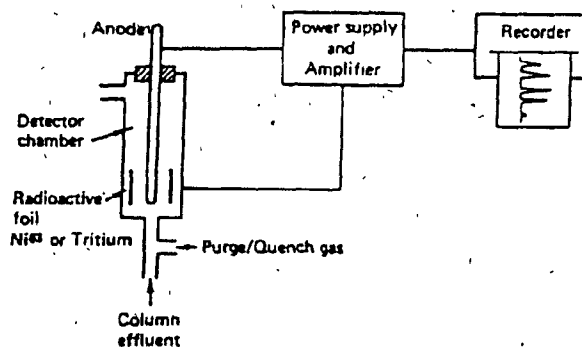
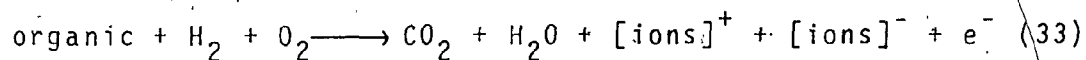


FIGURE (11) : Schematic Diagram of the Electron Capture Detector (ECD).

The operating principle of the flame ionization detector is based on the observation that when organic compounds are burned in a hydrogen and air flame, ions are produced. A number of mechanisms have been suggested to describe the process occurring with the flame, and the net result may be summarized in equation (33).



The sum of these negative ions yields a current flow. The ions are collected by a pair of polarized electrodes inside the detector and the current produced is amplified before being passed to a recorder. In this way the sample components are detected and displayed as 'peaks' on the recorder chart.

The FID is a sensitive detector. It has a linear response range of 10^{-9} gm/sec to 10^{-3} gm/sec, and it is comparatively cheap [63].

The FID responds to all organic substances with the exception of formic acid, formaldehyde and formamide, and it does not respond to species like helium, hydrogen, oxygen, carbon dioxide and water. The FID is, therefore, selective and this feature is often very useful. For example, water or carbon disulphide may be used as a solvent and the resulting chromatogram will not be complicated by a large solvent peak.

However, water may have a quenching effect on the detector response and care must be exercised when using aqueous samples.

The use of varying column temperatures introduce certain complications as far as the FID response is concerned. As the temperature of the column is increased, the vapour pressure of the stationary phase increases and an increasing amount of stationary phase 'bleed' will occur. When the 'bleed' level reaches a significant concentration a drift away from the recorder baseline will occur. This problem is normally minimized by the use of a compensation system using a reference column/detector. The reference column should be identical to the analysis column so that both columns have similar stationary phase bleed characteristics. The electrical signal from the reference detector is subtracted from that generated by the other detector and in this way the effect of column bleed is minimized.

The FID is sensitive to variations in the operating conditions. There are optimum hydrogen and air flow rates for a given detector.

The internal diameter of the metal jet on the FID influences the response of the detector. The smaller the internal diameter of the jet the larger the response from the detector [63]. Also, the smaller the diameter of the collector electrode the greater the response obtained. Figure (10).

1.11.2 ELECTRON CAPTURE DETECTOR (ECD)

This detector is essentially an ionization chamber. It operates on the principle that the conductivity of gases in such a chamber can be markedly altered by the presence of a contaminating gas (soluté) [54].

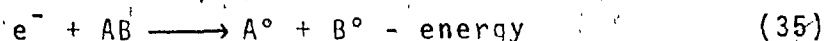
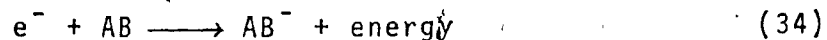
The functional mechanism of the ECD is based on the reduction of an electron current flow due to the removal of free electrons from the system by sample components eluted from a gas chromatographic column [66].

The schematic diagram in Figure (11) illustrates the current flow and ion source. With only purge gas (no sample) in the system, an average background current of 10^{-8} to 10^{-9} amps flows across the cell. This current is produced by electrons present in the cell, which are derived from two sources.

(a) Primary electrons or beta-particles (high energy electrons) are emitted by the nickel 63 at a rate of about 10^9 beta-particles per second, which is equivalent to about 10^{-9} amps [66].

(b) Secondary electrons are formed by the collisions between primary electrons and molecules of the carrier gas. In the latter case, an additional electron and a positive

ion are produced. When an electron capturing component is introduced into the cell it captures the low energy free electron to form negative molecular ions or neutral radicals.



The net result is removal of electrons from the system and production of negative ions having a far greater mass. These ions will combine with positive ions (e.g., positive nitrogen molecule in the case of nitrogen carrier gas) and will be purged from the cell as neutral complexes.

When a potential is applied to the cell, essentially all the free electrons are collected at the anode. However, at least one electron is captured for every molecule of electron-capturing substance that passes through the cell. This loss of electrons results in a corresponding decrease in cell current which, after amplification, is presented on the recorder. The decrease in current is proportional to the quantity of electron capturing sample introduced.

The potential across the cell is applied in a pulse mode. The pulse technique is used primarily to establish thermal equilibrium between the free electrons and the gas molecules in the cell chamber. This is achieved by applying a potential

across the cell for a small fraction of the total operating time. As indicated in Figure (12), the actual pulse of +50 volts lasts but a fraction of a microsecond ($w=0.5 \mu\text{sec}$ in this case). The amount of time the potential is applied can be increased by decreasing the interval between pulses. During pulsed operation, the electron concentration varies in a saw-tooth fashion (Figure (12)). When the pulse is applied, the electrons are collected at the anode and their concentration drops rapidly to zero (at 100 and 200 μsec in Figure (12)). During the interval between pulses, the concentration gradually builds up as beta-particles are emitted from the nickel 63 source. The magnitude of electron concentration then depends on the pulse interval, and as the interval decreases, so does the detector sensitivity. The collection of electrons at each pulse constitutes a current flow. Because of their small mass, the electrons accelerate rapidly, reaching the anode before the pulse terminates. The large ions formed hardly begin to move during the 0.5 μsec pulse. Consequently their contribution to cell current is negligible [26].

The sensitivity of the ECD is reduced when there is sample overloading of the cell. The introduction of too much sample can happen very easily when working with the ECD, due to its extreme sensitivity to certain types of compounds. Since response varies widely, depending on the nature of the compound, careful judgement is required of the operator as

to the appropriate amount of sample that should be used for any particular analysis.

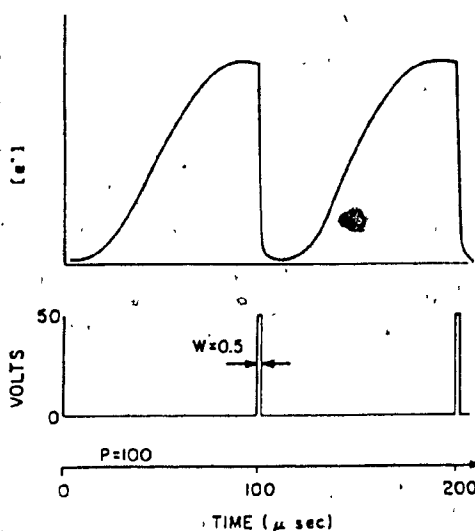


FIGURE (12) : Electron Concentration, $[e^-]$, in ECD During Pulsing ($w = 0.5 \mu\text{sec}$).

In the work reported in this thesis care was taken to ensure that the correct amount of sample was chosen for ECD-analysis. However, the column liquid phase (OV-1) interfered with the ECD operations, and played a significant role in determining the shapes of thermograms shown in Appendix (I). Since the columns are heated and a carrier gas flows through them during GC operations, a certain amount of liquid phase bleed is inevitable.

If the ECD happens to respond well to the bleeding liquid phase, this effect becomes undesirable. A high background signal will result, causing loss of sensitivity due to

cell overloading and random drift will develop because of varying bleed rate. Substrates such as the Carbowaxes and PDMS will cause such problems. Generally, the lower the liquid loading, the lower the bleed rate [67].

Pellizzari [66] in his discussion of parameters affecting ECD warned of the dangers of liquid phase bleed. Of significance to this project is the fact that the problem of bleeding is magnified as the column temperature is increased. Therefore, a depletion of thermal electrons occurs at higher temperatures which lowers the probability of electron attachment reaction between electrons and the solute molecules of interest. At a specific detector temperature the concentration of electrons is constant and a straight recorder baseline is indicative of this.

Devaux et al. [69] and others [79] in a study of various parameters of ECD tried to accommodate the column bleed effect into the Lovelock equation. The base current (or standing current), I_0 , is the current observed when a flow of pure carrier gas is passed through the detector. When there is a concentration, C , of a compound with some electron affinity passing through the detector it gives a current or signal I , smaller than I_0 . The difference $I_0 - I$ is the detector response. Lovelock has shown that the signal is given by equation (36).

$$I = I_0 \cdot e^{-k \cdot c}$$

(36)

where k is the coefficient of electronic adsorption. The response of the detector is given by equation (37).

$$I_0 - I = I_0(1 - e^{-k \cdot c}) \quad (37)$$

It varies linearly with C when C is small. Therefore, the approximation in equation (38) can be made.

$$1 - e^{-k \cdot c} \approx k \cdot c \quad (38)$$

Equation (37) then reduces to equation (39).

$$I_0 - I = k \cdot c \cdot I_0 \quad (39)$$

kI_0 is the response factor of the detector in the linear range.

When bleeding occurs equation (37) can be written as equation (40).

$$I_0 - I = I_0[1 - e^{-(k_1 \cdot c_1 + k_2 \cdot c_2)}] \quad (40)$$

where k_1 and c_1 , k_2 and c_2 are the coefficients of electronic adsorption and the concentrations of the bleeding liquid phase and solute, respectively. If the concentrations are small, equation (39) reduces to equation (41).

$$I_0 - I = I_0(k_1 \cdot c_1 + k_2 \cdot c_2) \quad (41)$$

The response factor, $k_n I_0$, can be derived from peak height or area data. k_n represent the coefficient of electronic adsorptivity for component n.

Devaux et al stated that the rate of phase bleeding increases exponentially with column temperature. The authors emphasized that bleeding decreases the performance of columns. Because it is necessary to work at conditions where the life of the column is reasonable long, the bleeding rate must be kept exceptionally small. The upper permissible temperature may depend largely on the application studied. Even at small bleeding rates there is a large decrease in the baseline current and, consequently, a dramatic loss of sensitivity, if the liquid phase vapour or pyrolysis products of the liquid phase have a large electronic affinity.

Knejci et al [71] stated that every liquid phase has a certain vapour pressure at a given column temperature. The temperature limit for use of the phase in the case of an ECD is far lower than that for other detectors. They recommended, in general, a maximum working temperature of 210 deg C for ECD and 350 deg C for FID.

Devaux et al [69] in a study of liquid phase bleed effects on ECD showed that the order of bleed for eight

phases was Di-n-decylphthalate > Tri.2,4-xyleneylphosphate > Squalane > Carbowax > Apiezon L > Polyethylene glycol succinate > SE-52 silicone gum > SE-30 silicone gum. The nonpolar phases, SE-30, Apiezon L, and Squalane, cause only a small current reduction because of bleeding, most probably, because the bleeding vapours have a low coefficient of electronic adsorption. The sensitivity of the ECD was compared with the sensitivity of the FID under the same conditions (i.e., same column temperature, and flow of carrier gas). A plot of electron capture detector current reduction versus FID signal for the above eight liquid phases showed a strong dependence on the electron affinity of the phases. The plot showed that the silicone had the lowest electron capturing capability of the phases tested and the highest response to FID.

In a study by Simmonds et al [64], it was found that the liquid phase bleeding effect on ECD may be substantially decreased for some phases by increasing the detector temperature. This is particularly true for non-polar phases such as the PDMS and Apiezon L. In the case of 3% JXR silicone phase, a 40% increase in the base current was observed in raising the detector temperature from 200 to 350 deg C.

1.12 GLC OF ORGANOPHOSPHORUS PESTICIDES

Bevenue [1.] found that of all the Chromosorb W supports, the HP grade, gave the best results both in terms of peak symmetry and lower detectable limits for organophosphorus pesticides. The Chromosorb P supports proved to be unsuitable with the pesticides used (Malathion, Paraaxon, Malaoxon and Methyl Parathion). The poor response of Chromosorb P was attributed to the greater adsorption properties of the support. Chromosorb P has a greater surface area per unit volume (ratio of about 3:1) over Chromosorb W. Kawahara et al [72] were unable to chromatograph Methyl and Ethyl Parathion at a column temperature of 195 deg C on Chromosorb P-NAW. Using the silicone liquid phase QF-1 on Aeropak 30 (a diatomaceous earth support), it was found that once a temperature of 200 deg C was reached in the column, the thermal stability of the column changed [72]. Malathion, at 200 deg C, on this column, gave erratic results. It was suggested that Malathion can start to decompose at temperatures as low as 150 deg C depending on the reactivity of the support surface. It was concluded that the variation in the response of the organophosphorus pesticides with the supports gave evidence that some form of interaction of the compounds with the support was taking place. Apparently, the more reactive the support the lower the temperature of decomposition of organophosphorus pesticides.

Gunther and Jaglan [73] found that Teflon is a superior support for gas chromatographic analysis of organophosphorus pesticides with low (2-5%) liquid phase loaded columns. Egan [74] and others [80] reported that stainless steel columns give higher recovery of organophosphorus pesticides than most other metal columns (copper, aluminum, nickel, etc).

Beroza and Bowman [75] found that with lightly loaded columns (less than 4% liquid phase), the adsorption of compounds on the supports became especially critical. Relative retention times of organophosphorus pesticides have been observed to be higher on low-loaded columns than on high-loaded columns (e.g., 3% Apiezon L on Gas-Chrom Q, compared to 12%). This was explained as being probably due to adsorption effects.

Bevenue et al [76] concluded from their work that Chromosorb G-NAW, Gas-Chrom Q, and Chromosorb W-HP were among the best supports for Malathion, Parathion and Malaoxon. Ines and Guiffrida [77] improved non-polar columns for analyses of organophosphorus pesticides by adding a polar phase to the non-polar liquid phase.

Lindgren et al [36] coated Gas-Chrom Q with 1% OV-101 and found that organophosphorus pesticides tailed badly on this column. These authors observed increased relative retention values as the amount of sample used was decreased.

The severe tailing of the peaks indicated strong adsorption to the support material, as could be expected for a polar solute on a low-loaded, non-polar stationary phase [78]. The prolonged retention observed with decreasing amount of sample may be an indication of a convex adsorption isotherm applying to the support. Common means of saturating active sites, such as injection of large amounts of the component itself or of silylating agents, did not improve the results.

Chromosorb G showed similar results to Gas Chrom Q. Chromosorb W-HP was the least adsorptive diatomaceous earth.

Lindgren et al found that columns coated with 1% OV-1 as the stationary phase on diatomaceous supports were inferior to those coated with 1% OV-101. The explanation given for this inferiority was that there is a higher molecular diffusion of the solute molecule into the more viscous OV-1 and hence there is a greater possibility for interaction with the support material. Such differences in molecular diffusion have been observed [79] for the two silicone phases SE-30 and SF-96, which are similar to OV-1 and OV-101, respectively.

CHAPTER

2

EXPERIMENTAL CONDITIONS

The effect of column temperature and nature of support on peak area response for three organophosphorus (Disyston, Phorate and Malathion) and one organochlorine (Lindane) pesticides were studied. Fourteen different supports manufactured by Johns Manville were individually coated with 3.5% (W/W) of OV-1 liquid phase. In the case of the organophosphorus pesticides, the temperature range studied with each column was from 130 to 230 deg C at 10 deg C intervals. Only the Chromosorb W-HP support coated with 3.5% OV-17 was used to study Lindane.

In order to obtain comparative data of all supports, the GLC parameters were held constant, and only the support materials and the temperature of the columns were varied. Lindane was investigated under conditions different from those for the organophosphorus pesticides.

The three organophosphorus pesticides were studied as a solution in benzene solvent. Lindane was studied in hexane solution.

All of the columns were studied on a Shimadzu Gas Chromatograph, Series GC-6AM, using an electron capture detector (ECD), operated in the single column mode. The dual column flame ionization detector system of the Shimadzu was used to study Lindane and the organophosphorus compounds on Chromosorb W-HP support.

Most of the columns made for study of organophosphorus compounds were investigated with the flame ionization detector (FID) system of the F & M Scientific Research Gas Chromatograph, Series 5750.

All of the gases used were manufactured by Union Carbide. The carrier gas available for the Shimadzu instrument (nitrogen) was by chance of a higher purity (less than 10 ppm oxygen) than the carrier gas for the F & M unit (greater than 10 ppm oxygen).

2.1.0 PRELIMINARY TESTS

Before the comparative study of the supports and temperature effects was undertaken, the optimum column parameters were determined as well as the optimum conditions for use with the ECD and FID detector systems.

2.1.1 COLUMN PARAMETERS

For the three organophosphorus pesticides, 8 ft x 1/8" o.d. stainless steel columns packed with supports coated with 3.5% (W/W) OV-1 liquid phase were found to give the best resolution in the column temperature range of 130 to 230 deg C which needed to be studied. This low loading of liquid phase, 3.5% (W/W), was subsequently coated on each of the 14 different supports investigated. The purpose of

maintaining low loading was to reduce retention times of the compounds studied and to magnify any adsorption effects of the support. Low loaded columns are also popularly used in most GLC work today. The use of a dual column system to minimize bleeding effects was found to be desirable. Finally, the optimum carrier gas (nitrogen) flow rate was found to be 60 ml/min.

2.1.2 PARAMETERS ESTABLISHED FOR USE WITH THE FID

The combustion gas flow rates for the FID detector were optimized to maximize the detector response. At an air flow of 400 ml/minute (34 psig), optimum response was obtained at a hydrogen gas flow rate of 28 ml/minute (16 psig).

To ensure rapid vaporization of the pesticides upon injection into the GC, an injection port temperature of 260 deg C was used. A detector temperature of 260 deg C was also used. These temperatures satisfied the requirement that the injection port and detector temperatures be 25 to 30 deg C higher than the maximum column temperature to be used (230 deg C) so as to prevent condensation of the samples [19].

A volume of 2 microlitres (μ l) of sample solution containing 6.20 microgram Disyston, 3.5 microgram Phorate and 11.86 microgram Malathion was chosen for injection into the columns. All test samples were analytical grade (> 99% purity) and were obtained from Polyscience Corporation. The solvent

used for preparation of these pesticide solutions was pesticide grade benzene. A greater volume was not used in order to avoid too rapid a build-up of carbon deposit on the detector burner electrode. This carbon build-up causes a decrease in response and also causes 'spikes' in the chromatogram. The source of the carbon was the solvent benzene. A sensitivity attenuation of 4×10^3 was chosen because it was the highest sensitivity that still gave a straight recorder baseline. When a higher sensitivity was used, baseline drift occurred. A chart speed of one inch per minute was ideal for peak area calculations, especially at the lower temperatures where a slower chart speed sometimes gave peaks indistinguishable from the baseline. At the same time, a faster chart speed give narrower peaks that were difficult to evaluate by triangulation, especially at higher column temperatures.

2.1.3 PARAMETERS FOR USE WITH THE ECD

Almost the same conditions were used for the ECD as for the FID. One basic difference was that the FID was used with dual columns whereas the ECD was used in the single column mode. This meant that bleeding of the columns was observed in the ECD tests, but was largely cancelled out in the FID tests. Another difference was that ECD was much more sensitive than the FID. Therefore, a two microlitre solution containing 23.26 nanogram (ng) Disyston, 8.76 nanogram (ng)

Phorate and 11.86 nanogram (ng) Malathion in benzene was sufficient sample concentration for ECD tests.

A list of the columns tested in this thesis is given in Table (6). The experimental conditions used with the FID and ECD detectors are summarized in Tables (7) and (8), respectively.

Further on in this thesis reference will be made to specific columns by means of the number appearing in the first column in Table (6). Experimental conditions for each run were as given in Table (7) and (8) unless otherwise specified.

2.2.0 COMPOUNDS ANALYZED

Data for the organophosphorus pesticides was given in Sections 2.1.2 and 2.1.3 of this chapter.

Lindane solution was prepared in a concentration of five micrograms per microlitre of pesticide grade hexane. This solution was used for FID tests. A solution containing one nanogram Lindane per microlitre of hexane was used for the ECD study.

The experimental conditions for Lindane tests are given in Tables (9) and (10).

TABLE (6): GLC COLUMN SPECIFICATIONS.

COLUMN No	SUPPORT NAME	No of COLUMNS	WT. of PACKING; gm	WT. of SUPPORT; gm	WT. of LIQUID PHASE; gm	TUBING MATERIAL	TUBING DIMENSION
1	CW-NAW	D ^d	2.54	2.45 ^f	.089 ^b	SS ^c	8' x 1/8"
2	CW-AW	D	2.63	2.54	.092	SS	8' x 1/8"
3	CW-AW-DMCS	D	2.44	2.36	.085	SS	8' x 1/8"
4	CW-HP	D	2.54	2.41	.088	SS	8' x 1/8"
5	C-750	D ^e	3.25	3.14	.114	SS	8' x 1/8"
6	CG-NAW	S ^e	5.66	5.46	.198	SS	8' x 1/8"
7	CG-AW	S	5.83	5.63	.204	SS	8' x 1/8"
8	CG-AW-DMCS	S	5.92	5.71	.208	SS	8' x 1/8"
9	CG-HP	S	5.18	5.00	.181	SS	8' x 1/8"
10	CP-NAW	D	5.33	5.14	.187	SS	8' x 1/8"
11	CP-AW	S	3.95	3.81	.138	SS	8' x 1/8"
12	CP-AW-DMCS	S	3.95	3.81	.138	SS	8' x 1/8"
13	ULTRA-BOND-20m	D	2.92	2.82	.102	SS	8' x 1/8"
14	C-104	D	2.58	2.49	.090	SS	8' x 1/8"
15	CW-AW	S	5.74	5.54	.201	GLASS	8' x 1/4"
16	CW-HP	S	9.47	9.14	.331	GLASS	8' x 1/4"
17	CW-HP	D	1.55	1.50	.050 ^a	NICKEL	4' x 1/8"

a—3.5% OV-17; column 17
 b—3.5% OV-1; column 1 to column 16
 c—SS means stainless steel
 d—D means dual columns
 e—S means a single column
 f—80/100 mesh particles (177 to 149 μm)

TABLE (7) : GLC Experimental Conditions for
Organophosphorus Pesticides Analyzed
With a Flame Ionization Detector (FID).

<u>PARAMETERS</u>	<u>CONDITIONS</u>
Column	Dual 8 ft x 1/8" Stainless Steel with 3.5% OV-1 on 80/100 mesh support material.
Column Temperature	130 to 230 deg C isothermally at 10 deg intervals
Carrier gas	Nitrogen for all the columns
Flow rate	60 ml/minute
Hydrogen Gas Flow	16 psig (28 ml/minute)
Air Flow	34 psig (400 ml/minute)
Detector Temperature	260 deg C
Injection Port Temp.	260 deg C
Attenuation*	4×10^3
Injection Type	10 μ l (microlitre) syringe onto insert liner (metal)
Sample	2 μ l containing 6.20 μ g Disyston, 3.50 μ g Phorate and 11.86 μ g Malathion in benzene
Recorder Chart Speed	1 inch/minute
Chromatograph	F and M Scientific Research Instrument (by Hewlett Packard), Series 5750

* --> Sensitivity

TABLE (8) : GLC Experimental Conditions for
Organophosphorus Pesticides Analyzed
With Electron Capture Detector (ECD).

<u>PARAMETERS</u>	<u>CONDITIONS</u>
Column	Single 8 ft x 1/8" Stainless Steel with 3.5% OV-1 on 80/100 mesh support (same columns used as in FID tests)
Column Temperature	130 to 230 deg C isothermally at 10 deg C intervals
Carrier Gas	Nitrogen for all the columns except Chromosorb T04 and Ultra Bond, 20m which were done with helium
Flow Rate	60 mls/minute
Detector Temperature	260 deg C
Injection Port Temp.	260 deg C
Attenuation*	16×10^2
Pulse	20 microsecond
Injection Type	10 μ l syringe onto insert liner (glass)
Chart Speed	1 inch/minute
Sample	2 μ l containing 23.26 ng Disyston, 8.76 ng Phorate and 11.86 ng Malathion in benzene
Chromatograph	Shimadzu Series 6-AM

*--> Sensitivity

TABLE (9) : GLC Experimental Conditions for Analysis of Lindane with an FID Detector.

<u>PARAMETERS</u>	<u>CONDITIONS</u>
Column	Chromosorb W-HP
Column Temperature	150 to 240 deg C
Carrier Gas and Flow Rate	Nitrogen at 35.2 ml/min.
Detector Temperature	270 deg C
Injection Port Temp.	270 deg C
Air Flow	680 ml/min.
Hydrogen Flow	70 ml/min.
Attenuation (Sensitivity)	4×10^2
Sample	5 ul hexane containing 25 ug Lindane
Chart Speed	1 cm/min.
Chromatograph	Shimadzu, Series 6-AM

TABLE (10) : GLC Experimental Conditions for Analysis of Lindane With an ECD Detector.

<u>PARAMETERS</u>	<u>CONDITIONS</u>
Column	Chromosorb W-HP
Column Temperature	150 to 250 deg C
Carrier Gas and Flow	Nitrogen at 40.7 ml/min.
Detector Temperature	310 deg C
Injection Port Temp.	310 deg C
Pulse	20 microsecond
Attenuation (Sensitivity)	4×10^2
Sample	5 ul hexane containing 5 ng Lindane
Chromatograph	Shimadzu, Series 6-AM

2.3.0 SUPPORT MATERIALS

Columns were prepared from fourteen different support materials manufactured by Johns Manville, (second column of Table (6)). All the supports were of the same particle size, 80/100 mesh (0.177 mm to 0.149 mm), so as not to introduce another variable into the support study.

2.4.0 LIQUID PHASES

The silicone liquid phases OV-1 and OV-17 were used in the project. All the columns prepared were coated with 3.5% (W/W) OV-1 with the exception of column number seventeen (Table (6)) which was coated with 3.5% (W/W) OV-17 and used for the study of Lindane.

2.5.0 PREPARATION OF COLUMN PACKINGS

The general requirements which need to be satisfied, regardless of the procedure used for making the packing, are the following [19]:

(a) Uniform distribution of the liquid phase on the surface of the particles must be assured.

(b) Breakage of the support particles must be avoided. This is especially critical with Chromosorb W's which are the

least friable (resistant to breakdown) of the supports used in this project (Table (2), Chapter 1). If the liquid phase is not distributed uniformly over the surface of the particles then active sites on the support will be exposed and will cause severe adsorption of the solute. This adsorption is indicated by tailing peaks. If the coated particles are broken during packing, active sites become exposed to the solutes tested and adsorption and tailing occur.

(c) Oxidation and loss of the packing must be minimized.

Taking the above precautions into account, the evaporative method was used to prepare all the columns listed in Table (6).

For preparation of 10 grams of support, 0.35 gram of OV-1 (or OV-17 as the case may be) was dissolved in 120 mls of toluene with stirring, at room temperature, overnight. To the OV-1 solution was added the 10 grams of support, slowly, with delicate stirring. The mixture was allowed to stand at room temperature for ten minutes with intermittent stirring. The beaker containing the mixture was placed on a warm hot plate (about 60 deg C) under a stream of nitrogen gas so as to remove the toluene by evaporation. During removal of the toluene the beaker was swirled so as to maintain uniform coverage of the particles. After the solvent had been removed and the particles became free

flowing, the content of the beaker was gently poured into a large watch glass, spread out, and left overnight to remove any traces of solvent. The weight of the coated packing was then recorded.

An 8 ft x 1/8" o.d. stainless steel tubing was then cut, plugged at one end with silanized glass wool and packed with the prepared packing. During the packing of the column, tapping the sides of the column was necessary in order to make the particles settle compactly without leaving any spaces. The weight of the packing placed in the column was recorded (Column (4) Table (6)). The open end of the column was plugged with silanized glass wool. The column was then fitted with ferrules and placed in the F & M Gas Chromatograph oven and conditioned overnight at 270 deg C with carrier gas (nitrogen) flowing through at a rate of 60 ml per minute. After conditioning for more than 24 hours, the column was ready for testing under the conditions listed in Tables (7) or (8).

2.6.0 TYPICAL CHROMATOGRAPHIC RUN

In this thesis, a run represents a temperature study of a column, starting at a column temperature of 130 deg C, which was increased at 10 deg C intervals to 230 deg C. A total of eleven temperatures were studied in each run. A run had to be completed on the same day and it took about

10 hours. The chromatographic conditions at the beginning and end of each run had to be the same so as to obtain reproducible results. Only the temperature of the column was changed.

At each temperature in a run (130 to 230 deg C) two microlitres of sample were injected for tests with both ECD and FID detectors. Table (7) and (8) list the concentrations of the three organophosphorus pesticides used with FID and ECD detectors, respectively. The same amount of sample was injected at each temperature. Repeated injections were made at each temperature until the chromatographic peak heights for three successive injections were the same. This indicated that priming and/or adsorptive effects had become constant and the peak heights or areas could be used for quantitative interpretations. Before the first injection was made at 130 deg C, the instrument was stabilized for at least three hours to obtain a straight baseline. Instrument destabilization was indicated by random drift of the recorder baseline.

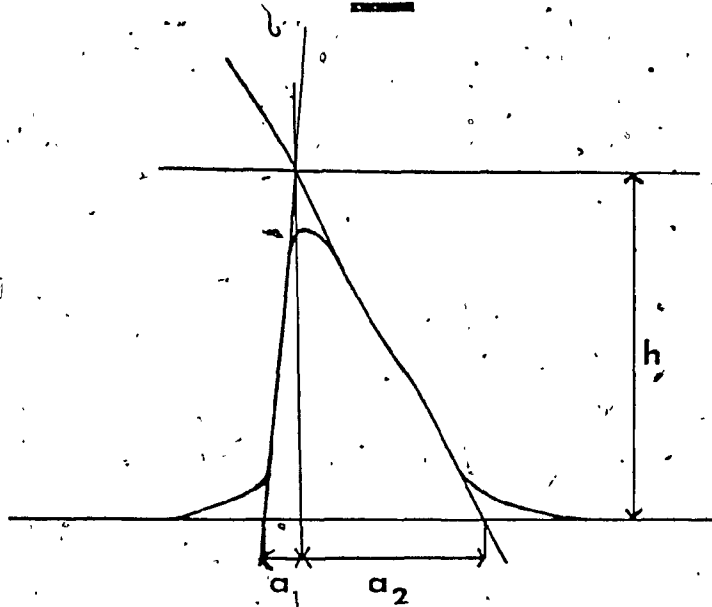
When the column temperature was raised to the next higher temperature (an increment of 10 deg C) to be studied, about ten minutes were required for the instrument to be re-stabilized when a dual column system (FID) was used. With the single-column ECD system, bleeding of the column liquid phase caused the recorder baseline to drift up scale for a

prolonged period of time (more than an hour). In these cases the baseline was brought back to the original zero position with the zeroing control of the recorder. In cases where Malathion was not completely adsorbed, three chromatographic peaks were eluted per injection. Since, on the average, four injections were made at each temperature, this gave an average of twelve response peaks at each temperature, leading to 132 peaks which had to be evaluated for each run carried out.

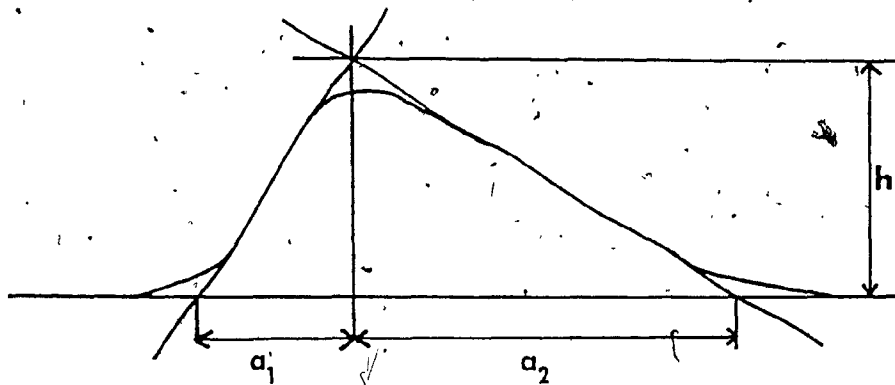
For each column listed in Table (6), at least duplicate runs were carried out with the ECD detector. Some, but not all the columns were tested with the FID detector, i.e., CG-AW, CG-HP, CP-AW, CP-AW-DMCS, C-104 and Ultra-bond 20m columns were not tested using FID detection.

2.7.0 INTERPRETATION OF PEAK SHAPES

On the seventeen columns evaluated, three different kinds of peak shapes were observed (Figure (13)). There were peaks that were almost symmetrical (i.e., on CG-NAW) and whose areas were calculated using the isosceles triangulation method described in the introduction (Figure (9B), Chapter 1). There were peaks that had a sharp front and a diffuse tail (Figure (13A)). The area of these peaks was evaluated by dropping a perpendicular from the vertex of the peak to the baseline of the peak, and then using the resulting two right

A

$$\text{AREA} = \frac{1}{2}(a_1 h) + \frac{1}{2}(a_2 h)$$

B

$$\text{AREA} = \frac{1}{2}(a_1 h) + \frac{1}{2}(a_2 h)$$

FIGURE (13) : Area Evaluation of Peaks:

A) Sharp Front, Diffuse Tail.

B) Diffuse Front and Diffuse Tail.

triangles, to determine the area. The third kind of peaks had diffuse fronts and even more diffuse tails (Figure 13B)). The area of these peaks was evaluated in the same way as for the peaks in Figure (13A).

The assumption was made that the peak area was proportional to the concentration of solute [53,54]. This means, the higher the area the more solute that had been eluted and the less adsorption that took place on the column. Using this argument, a more adsorptive column would generally give a smaller peak area than a less adsorptive column.

2.8.0 THERMOGRAMS

When the average area for each component at each column temperature was evaluated and a plot of average peak area versus temperature was made, a thermogram was produced. A thermogram indicates the response of the column in the column temperature range studied. The smaller the area under the thermogram the greater the adsorptive effects, or the bleeding of liquid phase, or the priming of the support, or the oxidation of the liquid phase, etc., and vice versa. In this thesis, thermograms were obtained under conditions given in Tables (7) and (8) for experiments using the ECD and FID detectors, respectively.

CHAPTER

3

RESPONSES FOR PESTICIDES USING THE FID

AND THE ECD DETECTORS

3.1.0 OBSERVATIONS AND RESULTS

The responses obtained in the study of the four pesticides by GLC are discussed in terms of the thermograms for each column tested and in terms of a comparison of the peak areas measured at selected temperatures.

3.1.1 THERMOGRAMS OBTAINED USING THE ECD DETECTOR

The thermograms for the second run on thirteen supports obtained using the ECD detector are presented in Appendix (I). All thermograms were plotted on the same scale to facilitate comparison between columns. The area under the curves ranged from zero to four thousand square millimetres in the temperature range of 140 to 230 deg C. It should be noted that peak areas were determined as well as at 130 deg C but because of the limitation of space on the graph, this temperature was not included, as it did not in any way change the results and conclusions to be derived from the thermograms.

The three compounds represented in these thermograms were Phorate, Disyston, and Malathion. In some of the thermograms Malathion was completely adsorbed and no peaks were obtained for it. Where no Malathion peaks were seen, the thermogram carries the notation 'Malathion adsorbed'.

The thermograms for Phorate, Disyston, and Malathion are represented by curves A, B and C, respectively.

Some thermograms indicated zero peak areas at low temperatures (i.e., 140 deg C on thermogram 2C), especially those thermograms for Malathion. This meant that a chromatographic peak was not observed at that temperature under the detector sensitivity conditions used.

At the higher temperatures some thermograms do not have any area indicated. This means that the peak went off scale on the recorder, and a determination of the peak area could not be made. Attempts to use a lower sensitivity (increase in attenuation from 16×10^2 to 32×10^2) to bring these chromatographic peaks on scale were not encouraging because of the uncertainty of relative response at different attenuations (thermograms 3A, 3B and 3C).

A summary of the ranking of the thermograms based on relative areas obtained with different columns is given in Table (11).

1.2 THERMOGRAMS OBTAINED USING THE FID DETECTOR

Thermograms for the second run of eight supports tested with the FID detector are presented in Appendix (II). The area under the curves ranged from zero to eight hundred

TABLE (11) : Ranking of Supports Based on Relative Areas under the Thermograms for Phorate, Disyston and Malathion Obtained Using the ECD Detector.

<u>RANK IN TERMS</u>	<u>OF AREA</u>	<u>PHORATE</u>	<u>DISYSTON</u>	<u>* MALATHION</u>
1		CG-HP	CP-AW	CW-HP
2		CP-W	CG-HP	CW-AW
3		CG-AW	CG-AW	CG-AW-DMCS
4		CG-AW-DMCS	CG-AW-DMCS	CG-HP
5		CW-HP	CP-AW-DMCS	CW-AW-DMCS
6		CW-AW	CW-AW	CP-NAW
7		CG-NAW	CW-HP	CG-AW
8		CW-AW-DMCS	CG-NAW	**Ultra-Bond 20m
9		CP-AW-DMCS	CP-NAW	
10		CW-NAW	CW-NAW	
11		CP-NAW	CW-AW-DMCS	
12		C-750	C-750	
13		Ultra-Bond 20m	Ultra-Bond 20m	

* - Malathion did not show up at a sensitivity of 16×10^2 for the following supports : CP-AW, CW-NAW, CG-NAW, C-750, and CP-AW-DMCS

** - An attenuation of 2×10^2 (sensitivity eight times greater than at attenuation 16×10^2) was used for the Ultra-Bond 20m columns.

square millimeters in the temperature range of 130 to 220 deg C. A temperature study was also done at 230 deg C for each support, but the results were not included in the graphs because of the limitations of space, and because their omission in no way changed the results or conclusions.

The compounds studied were Phorate, Disyston and Malathion. In all of the runs with FID detection, peaks for Malathion were observed, which was not always the case in the ECD detector tests reported in Appendix (I).

Curves A, B and C represent Phorate, Disyston and Malathion, respectively.

The explanation for the non-existence of peak areas in some cases, at low and high temperatures as the case may be, in thermograms, is the same as was given for the work with the ECD. At high temperatures the chromatographic peaks were off scale, and at low temperatures no peaks were observed at the sensitivity used.

It should be noted that only one run was done for CG-AW-DMCS. Thermogram (8) in Appendix (II) is therefore a first run result.

A summary of ranking of supports based on relative areas of the thermograms obtained with different columns is given in Table (12).

TABLE (12) : Ranking of Supports in Terms of Comparison of Relative Areas Under the Thermograms for Phorate, Disyston and Malathion Obtained Using the FID Detector.

<u>RANK IN TERMS</u>	<u>PHORATE</u>	<u>DISYSTON</u>	<u>MALATHION</u>
1	CW-HP	CW-HP	CW-HP
2	CG-AW-DMCS	CG-AW-DMCS	C-750
3	C-750	C-750	CG-AW-DMCS
4	CW-NAW	CW-NAW	CW-AW-DMCS
5	CW-AW	CG-NAW	CW-NAW
6	CG-NAW	CP-NAW	CW-NAW
7	CP-NAW	CW-AW	CP-NAW
8*	CW-AW-DMCS	CW-AW-DMCS	CG-NAW

* - Only one run was done with this column.
This is therefore a first run result.

3.1.3 QUANTITATIVE COMPARISON OF EFFECTS OF SUPPORTS AND PESTICIDE CONCENTRATIONS ON RESPONSE

Using the thermograms in Appendices (I) and (II), peak areas were evaluated at column temperatures of 150 and 180 deg C, and at the temperature where a maximum in the thermogram was obtained. These values were rounded off to whole numbers and ranked relative to one another in order to determine which column (support) gave the best response. Data at three concentration levels are reported. Tests with the FID detector are labelled 'High concentration', and with the ECD, 'Moderate concentration' or 'Low concentration' as the case may be. Results are tabulated in Appendix (IV).

CHROMOSORB W

The FID thermograms in Appendix (II) were used to obtain Tables (13), (14) and (15) which give areas for the five W supports at 'High Concentrations' (Appendix (IV)). For each pesticide at each temperature the greatest peak area observed was arbitrarily assigned a value of 10, and the areas of the remaining four supports were expressed as a ratio relative to 10. For example, at a column temperature of 150 deg C, Disyston has areas of 740, 490, 620, 590 and 680 square millimetres on the supports HP, DMCS, NAW, AW and 750, respectively. HP was assigned a value of 10, while DMCS, NAW, AW and 750 were then 6.6 ($490/740 \times 10$), 8.4 ($620/740 \times 10$), 8.0 ($590/$

740x10) and 9,2 (680/740x10), respectively (Table (13)), The same process was repeated at 180 deg C (Table (14)) and the peak maximum (Table (15)). From the ratios in these tables the supports could be ranked in terms of responses. Table (16) gives the Score and Rank for the three temperatures for the five W supports.

The same process was repeated for the 'Moderate Concentrations' using the thermograms in Appendix (I) to obtain the peak areas at 150 and 180 deg C, and at the peak maximum. Tables (17), (18), (19) and (20) represent these data (Appendix (IV)).

Table (21) has the ranking of the supports for the 'Low Concentrations' of pesticides. The data was taken from Table (22).

Table (23) represents the Score and Rank for the supports at various sample concentrations.

CHROMOSORB G

Chromosorb G's were ranked only for 'Moderate' and 'Low' concentrations of pesticides. Few tests were done at 'High Concentrations' for Chromosorb G or P.

Repeating the above process for Chromosorb G at 150 and

TABLE (22) : Response of Low Concentrations of Disyston and Malathion
on Columns With Different Supports at a Column
Temperature of 180 deg C.

<u>COLUMNS</u>	<u>13.76 µg DISYSTON</u>		<u>2.11 ng MALATHION</u>	
	<u>PEAK</u>	<u>PEAK</u>	<u>PEAK</u>	<u>PEAK</u>
	<u>AREA ***</u>	<u>HEIGHT **</u>	<u>AREA ***</u>	<u>HEIGHT **</u>
C-750	31.2	6.3	72.6	8.1
CG-HP	46.5	6.2	143.6	9.7
CW-AW	59.6	5.5	151.1	18.7
CW-NAW	62.0	16.3	277.3	36.3
CG-AW-DMCS	68.9	6.3	149.2	6.9
CW-AW-DMCS	69.5	18.3	186.3	27.9
CG-AW	72.4	8.7	142.8	7.4
CW-HP	250.4	65.3	1171.5	172.3
*CP-AW-DMCS	-	-	-	-
*CP-AW	-	-	-	-
*CP-NAW	-	-	-	-
*CG-NAW	-	-	-	-

* - No response on these supports

** - millimeter

*** - square millimeters

180 deg C, and at the thermogram maximum (Appendix (I)), the values in Tables (24), (25), (26) and (27) were obtained.

Table (28) represent the ranking with respect to 'Low Concentration' of pesticides, with data taken from Table (22).

CHROMOSORB P

Only one Chromosorb P support (CP-NAW) was tested with high concentrations of pesticides. On Chromosorb P supports, responses were not obtained for 'Low Concentrations' of pesticides. The responses on Chromosorb P support at 150 and 180 deg C, and at the thermogram maxima are given in Tables (29) and (30) in Appendix (IV).

3.1.4 RESPONSE ON DIFFERENT SUPPORTS FOR LOW CONCENTRATIONS OF PESTICIDES

From the thermograms in Appendix (I), the support that showed the lowest response towards Phorate and Disyston was chosen for use in the determination of the minimum amount of Disyston and Malathion that could be detected. This support was determined to be C-750 (Table (22)). Using the column containing this support, and the experimental conditions in Table (8), the sensitivity of the instrument was increased to the maximum possible at which the recorder baseline for

the chromatogram was still stable. At this sensitivity (attenuation 8×10^2), the concentrations of Disyston and Malathion were varied until the responses of the ECD at a column temperature of 180 deg C were just a little greater than twice the background noise level [53].

Suitable concentrations for Disyston and Malathion were found to be 13.76 picograms and 2.11 nanograms, respectively. Then, at a column temperature of 180 deg C, a sensitivity of 8×10^2 , and other conditions as specified in Table (8), the responses on all of the diatomaceous supports were determined for the above amounts of Disyston and Malathion. The peak area and peak height responses on these supports are listed in Table (22).

On the last four supports in Table (22) (CP-NAW, CP-AW, CP-AW-DMCS and CG-NAW) no response was obtained for the low concentrations of Disyston and Malathion used.

3.1.5 FURTHER OBSERVATIONS

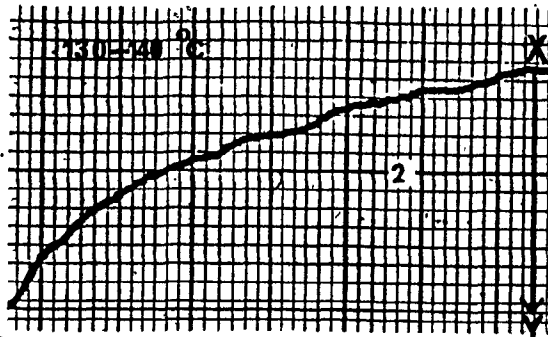
While thermograms did illustrate the relative responses of the supports studied, they gave no indication of the extra peaks that appeared on some chromatograms (peaks other than those for Malathion, Disyston and Phorate). They also gave no information about bleeding of the columns as was observed in work with the ECD (single column), or tailing of peaks, all of which effects are important in the comparative

study of support effects. Such information is given below.

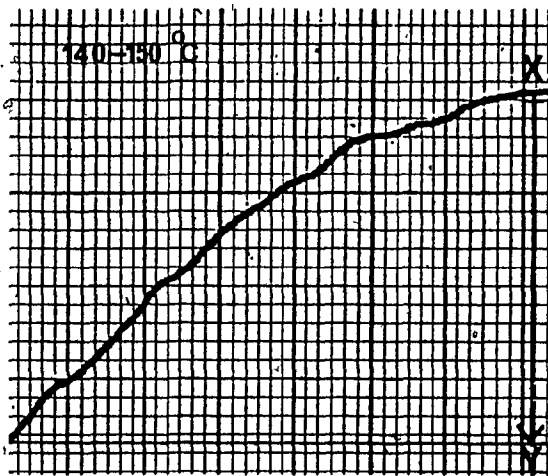
In the ECD study, every column showed bleeding. Figure (14) shows the bleeding observed from a glass column packed with coated CW-HP, using the conditions listed in Table (8). The following observations were made. At an isothermal column temperature of 130 deg C, a constant baseline was obtained after samples were injected. When the column temperature was changed to 140 deg C there was bleeding of the column and a baseline drift occurred. This drift was allowed to continue until a plateau was reached at which time the recorder pen was brought back to the original baseline. More samples were injection at a column temperature of 140 deg C and then the column temperature was raised to 150 deg C. On changing from column temperature 140 to 150 deg C more bleeding was observed. Again a plateau was reached and again the recorder pen was brought back to the original baseline (XY in Figure (14)). This process was repeated for all the temperature changes shown in Figure (14). The most intense bleeding occurred for the temperature change of 160 to 170 deg C in the case of the columns containing CW-HP.

In general, it should be noted that the temperature at which the most intense bleeding occurred was not fixed, but varied from run to run on the same column for the same solute and also from column to column for the same solute.

1



2



3

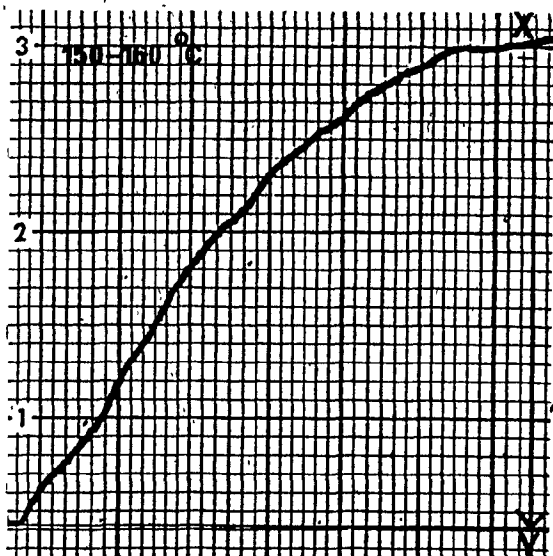


FIGURE (14A) :

Liquid Phase Bleed from
Glass Column Containing
Coated CW-HP₂

1 → bleed from 130-140°C.

2 → bleed from 140-150°C.

3 → bleed from 150-160°C.

Scale :

Vertical-10 Divisions =

10% Chart Scale.

Horizontal-10 Divisions =

1 Minute.

4

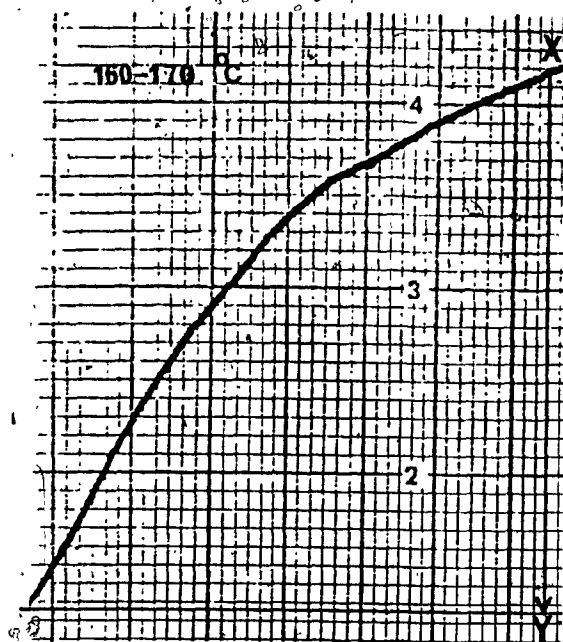


FIGURE (14B) :

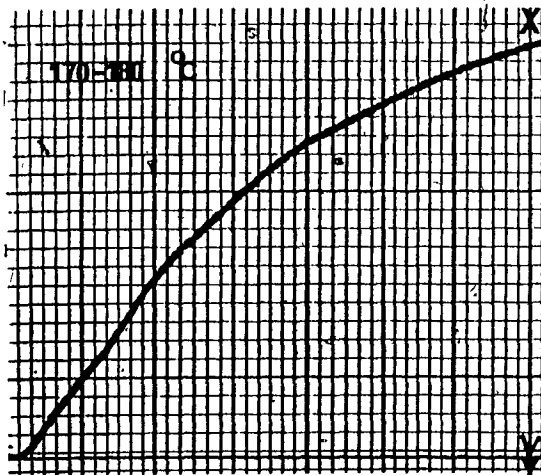
Liquid Phase Bleed from Glass Column Containing Coated CW-HP.

- 4 → bleed from 160-170°C.
- 5 → bleed from 170-180°C.
- 6 → bleed from 180-190°C.

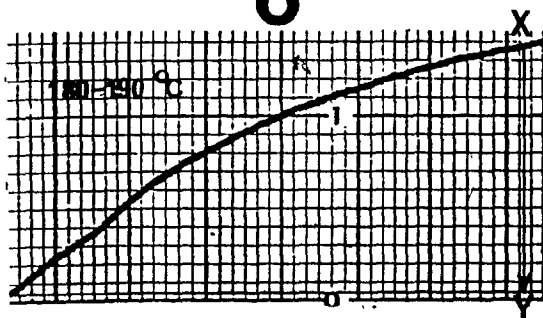
Scale:

Vertical-10 Divisions =
 10% Chart Scale.
 Horizontal-10 Divisions =
 1 Minute.

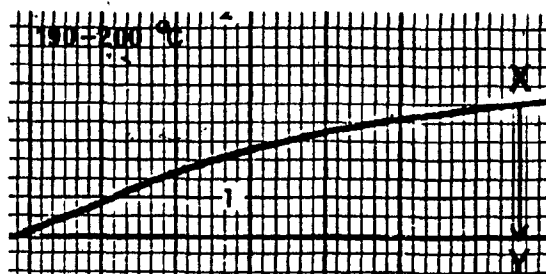
5



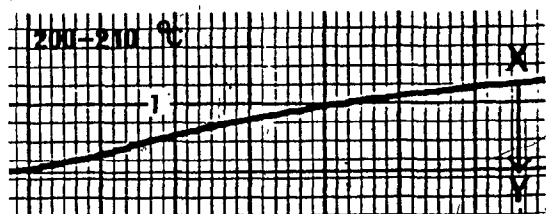
6



7



8



9

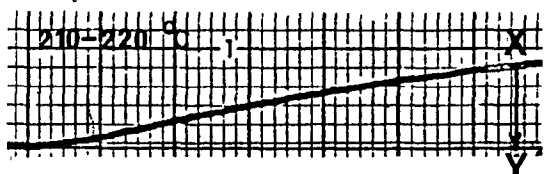


FIGURE (14C) :

Liquid Phase Bleed from
Glass Column Containing
Coated CW-HP.

7 → bleed from 190-200°C.

8 → bleed from 200-210°C.

9 → bleed from 210-220°C.

Scale :

Vertical-10 Divisions =

10% Chart Scale.

Horizontal-10 Divisions =

1 Minute.

All the columns showed decomposed product peaks when tested with the ECD detector. For the temperature range studied there were no interferences of these extraneous decomposition peaks with the pesticide peaks in most cases.

3.2.0 DISCUSSION OF RESULTS

3.2.1 ELUTION ORDER OF PESTICIDES

The order of elution of the organophosphorus pesticides

was observed to be according to their boiling points. The highest boiling compound, Malathion (b.p. 120 deg C), was eluted last on the chromatograms for the supports tested. Phorate, the lowest boiling compound (b.p. 100 deg C), was eluted first, while the elution time of Disyston (b.p. 113 deg C) was between that of Phorate and Malathion. Ewell et al [81] considers these pesticides as belonging to the Class II group because of their order of elution. A Class II group contains donor atoms (oxygen and sulfur) but does not contain any active hydrogen. The liquid phase OV-1 was considered as belonging to the Class D group [82,83]. A Class D group contains donor atoms (oxygen) but no hydrogen bonding capacity. When Class II compounds are eluted on a Class D liquid phase, then, the order of separation will be based on the boiling points - the lowest boiling compound will be the first to be eluted.

In the temperature range studied, 130 to 230 deg. C, all three compounds were well separated on the columns tested (Figure (21) Chapter 5). Therefore, evaluation of peak areas was an easy task.

3.2.2 REPRODUCIBILITY OF THERMOGRAMS

At least duplicate runs were done with each column with both detectors (ECD and FID). For no two replicate runs were the thermograms identical for any particular support. The

day to day performance of the same columns varied. The second run for some columns showed an increase in peak area over the first run, whereas for other columns a decrease in peak area was observed for the second run compared with the first. These results indicated that every run made on a column changed the physical and/or chemical properties of that column. The bleeding that was observed for every run indicated that the column properties must have been undergoing a change.

The same trend (Appendix (I)) was observed in all the thermograms obtained using the ECD detector, i.e., small peak areas at low temperatures, and a maximum at some middle temperature. Daniel et al [85] found a similar pattern in the thermograms for acetic acid, benzene and butanol, the only difference being that a plateau was reached at high temperatures, rather than a decrease in response being observed.

The patterns of thermograms obtained with the FID detector, Appendix (II), were different from those obtained with the ECD. There was a general decrease in peak area with temperature. Most FID thermograms showed two or more maxima.

The nature of the thermograms obtained with ECD and FID detectors could be explained by consideration of the

following four main factors :

(i) concentration effects (i.e., in FID tests, solutions 600 times more concentrated than in the ECD tests were used);

(ii) bleeding of the column which changed the physical and chemical properties of the column continually and thus led to many maxima in the same run because of priming and de-priming effects (e.g., in the case of FID tests),

(iii) decomposition of the pesticides because of heating, together with catalytic effects of the tubing and supports.

(iv) reaction of the pesticides with the liquid phase on the column.

3.2.3 RESULTS OBTAINED WITH THE ECD DETECTOR

Figure (15) shows the thermogram obtained on CG-AW-DMCS support using the conditions given in Table (8). All three pesticides showed a maximum at about 180 deg C, in the first run. The decrease in area above a temperature of 180 deg C can be explained by any of the four reasons given above.

Section 1.7 of Chapter 1 described some typical reactions that can take place with pentavalent phosphorus compounds.

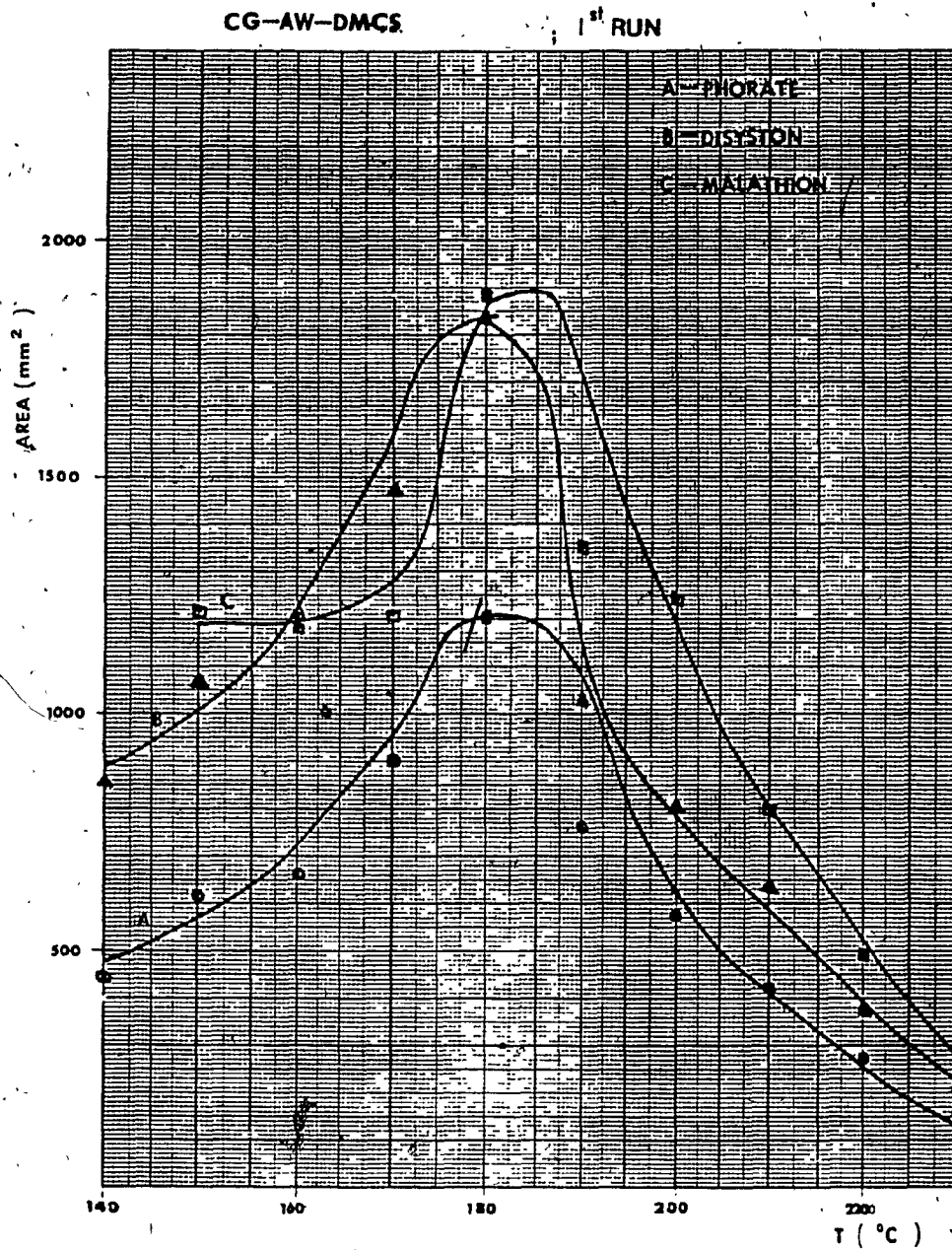


FIGURE (15) : Thermogram for the First Run on a Column Containing Coated CG-AW-DMCS Support Using the ECD Detector.

Reactions (12) and (13) described how the liquid phase (OV-1) could interact with phosphorus pesticides in the temperature range studied. If oxygen is present in the GLC system the thiophosphoryl group of the pesticides can be replaced with oxygen (reaction (16)). The thioether groups of the pesticides can be oxidized to sulfoxide and then to sulfones (17)). Heating can cause organophosphorus pesticides to decompose as was observed for trans-Dioxathion (reaction (18)). Heating can also cause these pesticides to isomerize as was the case for Parathion (reaction (19)). No attempts were made to prove which of these reactions occurred in this study, but the conditions (temperature of the column, silicone liquid phase, and the presence of trace amounts of oxygen) that were present in the GLC columns tested were those necessary for some of these reactions to take place. The actual extent of reaction of the pesticides that occurred with columns can be assumed as being small because of the small response observed for decomposed products. It is possible, however, that the pesticides reacted with the liquid phase and were retained on the column giving the small response observed for the decomposed products. However, the more likely explanation for the trends observed on the ECD thermograms was in terms of column bleed, and this is discussed below.

3.2.3a EFFECT OF COLUMN BLEED ON ECD RESULTS

When the XY shifts were added together for the nine temperature changes carried out on the CW-HP column (Figure (14)) they amounted to almost three full scale deflections on the recorder. This must have reduced the sensitivity of the detector, as was discussed in Chapter 1, Section 1.11.2. As reported by Devaux et al [69] the bleed rate of liquid phases increases exponentially with temperature. This meant that the eluted pesticides were competing with the bleeding liquid phase for the fixed amount of electron population present in the detector. With increase in column temperature, bleeding of the liquid phase increased, and therefore response for a given constant amount of pesticide would have been expected to decrease.

Novak [84] describes the ECD detector as mass sensitive rather than concentration sensitive. For a mass sensitive detector the peak area of an eluted component is proportional to the total mass of the component in the detector sensing element. Therefore, if there were two or more components eluted with the same relative retention times, then the peak area would represent a sum of the total masses present in the ECD detector sensing element. It should be noted that a mass flow detector is independent of the carrier gas flow rate. In contrast, for a concentration detector, the peak area is inversely proportional to the carrier gas flow rate, as for

example for the thermal conductivity detector.

The first run results with the CW-HP (glass tubing) column were used to produce bleeding data in Figure (14). The thermogram for this run, Appendix (III) (thermogram 2), had no maximum, but instead, decreased exponentially with an increase in column temperature. The second run on this column, Appendix (III) (thermogram 3), had maxima at about 140 deg C for the curves of Disyston and Phorate. The possible reason why the first run did not show any maxima was because the column was already bleeding badly at 130 deg C. The response of the ECD detector towards the pesticides was therefore decreasing continuously from 130 deg C onwards to 230 deg. C. The second run of the CW-HP (glass tubing) column had less bleed at 130 than the first run. The response was higher for all three pesticides. From a column temperature of 150 deg C upwards to 230 deg C in the second run (Appendix (III), thermogram 3) the bleed rate of the column was intense. Hence, the decrease in response of the pesticides. It was experimentally observed that the column bleed at 130 to 140 deg C was about 30 times more for the first run when compared to the second run.

The general shape of the ECD thermograms as illustrated in Figure (15) for Run 1 on the CG-AW-DMCS column can generally be explained in terms of adsorption of the pesticides from a column temperature of 140 to 180 deg C,

and bleeding of the liquid phase from a column temperature of 180 to 230 deg C. As the column temperature was increased from 140 to 180 deg C the pesticides were less adsorbed on the support and hence a higher response was observed with increasing column temperatures. However, at a column temperature of 180 deg C the bleeding of liquid phase from the column began to compete with the pesticides for the electron population in the detector, hence reducing the response of the ECD towards the pesticides. The response of the pesticides, therefore, decreased from 180 to 230 deg C because of increasing column bleed as column temperatures increased. Loss of injected pesticides because of priming of active sites which were exposed as a result of liquid phase bleeding also contributed to a decrease in response observed at the higher column temperatures. This effect is discussed in detail in the section on FID thermograms (Section 3.2.4). Of significance in Figure (15) is the temperature at which the maximum response occurred, i.e., 180 deg C, for each of the three thermograms shown. Since the decrease in response began at the same temperature, this was a strong indication that bleeding of the column leading to reduced detector sensitivity was the primary cause of the reduction of response. As can be seen from the thermograms in Appendices (I) and (II), in most cases, on any given column, the thermogram maxima occurred at the same temperature (\pm or $-$ 5 deg C) for Phorate and Disyston. Malathion showed unusual behavior which is discussed in

Section 3.2.4. Table (31) gives the column temperatures at which the thermogram maxima occurred for the first and second runs on the columns tested with the ECD detector.

3.2.3b. ULTRA-BOND 20m AND CHROMOSORB 104

All the results obtained for the diatomaceous earth supports (Chromosorb W, G, P and 750) were under identical ECD conditions, and generally comparable results were obtained. However, experimental conditions required modification for tests with the bonded support, Ultra-Bond 20m, and the porous polymer support, Chromosorb 104. Both gave results that were different from those for the diatomaceous earth supports.

In testing the column packed with Ultra-Bond 20m, a sensitivity sixteen times higher than that listed in Table (8) was required. The column made with the support Chromosorb 104 did not resolve the three pesticides peaks at the column temperatures listed in Table (8).

ULTRA-BOND 20m

Ultra-Bond 20m is a diatomite support which has the liquid phase Carbowax 20m bonded on its surface. The column containing this support was used with a high purity helium carrier gas (containing less than 0.5 ppm of oxygen). Under

TABLE (31) : Column Temperatures at which Thermogram Maxima Occurred for the 1st and 2nd Runs on Diatomaceous Supports Using the ECD Detector.

<u>SUPPORT</u>	<u>PHORATE</u>		<u>DISYSTON</u>	
	<u>1st Run</u>	<u>2nd Run</u>	<u>1st Run</u>	<u>2nd Run</u>
CW-NAW	170	200	170	200
CW-AW	180	170	185	170
CW-AW-DMCS	190	200	200	200
CW-HP	190	170	190	160
C-750	210	230	210	210
CP-NAW	160	180	160	180
CP-AW	200	160	180	160
CP-AW-DMCS	220	190	200	200
CG-NAW	170	190	170	190
CG-AW	180	200	190	200
CG-AW-DMCS	180	210	180	200
CG-HP	200	180	210	180

the conditions listed in Table (8) no response was observed. However, when the sensitivity was increased by a factor of sixteen, a reasonable response was observed.

The decreased response for the three pesticides on this column can be attributed to the change in carrier gas from nitrogen to helium. In work done by Locke et al [86] it was shown that nitrogen as a carrier gas has a greater capacity to deactivate the active sites on a support material than helium. Hence, the better response on columns that use nitrogen as a carrier gas and the poorer the response observed on the Ultra-Bond 20m column using helium carrier gas.

Guild et al [87] showed that when nitrogen was used as a carrier gas, a steady state was reached very quickly, i.e., the composition of the carrier gas entering the column soon equaled the composition of the carrier gas leaving the column. However, with helium, an extremely long time was required to reach a steady state.

As seen from Appendix (I), thermogram 13, Ultra-Bond 20m had the least overall area of all columns, for the three pesticides. The above explanation may be the reason for the small area observed.

CHROMOSORB 104

The column made with this support did not resolve the three pesticides under the conditions listed in Table (8).

The only logical explanation for this loss of resolution is that the liquid phase (3.5% (W/W) OV-1) did not coat the support effectively, and hence the column was packed with uncovered Chromosorb 104. If the liquid phase was actually coated on the support material, then resolution similar to that observed on other columns should have been obtained. The reason for the liquid phase not coating the surface of the C-104 support is that the surface energy of the liquid phase is far greater than the surface energy of the support [37,38] (see Section 1.6.1 of Chapter 1).

3.2.3c COMPARISON OF STAINLESS STEEL AND
GLASS AS COLUMN TUBING MATERIALS,
USING THE ECD DETECTOR

The claim by Egan et al [74], and Bevenue et al [76], that glass tubing is better than stainless steel tubing for the analysis of organophosphorus pesticides was confirmed (Appendices (I) and (III)). For the same experimental conditions the supports packed in glass tubing generally showed a higher response (Appendix (III)) than those packed in stainless steel tubing (Appendix (I)), at the lower

column temperatures, regardless of the packing contained. The likely reason why the response of the glass tubing columns decreased drastically at higher temperatures was because of the greater amount of liquid phase present in the columns (15 and 16 of Table (6)), especially the CW-HP column. The greater the amount of liquid phase in the column the more the bleeding of the column, and the greater the reduction in sensitivity of the detector towards the pesticides. Also, the greater the amount of liquid phase in the column the lower the column temperature at which bleeding becomes significant and the detector response decreased. This fact is immediately evident in the thermograms in Appendix (III) for the glass columns. The CW-AW column which had 0.20 gm OV-1 liquid phase gave a better response than the CW-HP column which had 0.331 gm OV-1. Also, the rate of decrease of response with increase in temperature was less with the CW-AW column than with the CW-HP column, again indicating more liquid phase bleed with the latter.

3.2.4 RESULTS OBTAINED WITH THE FID DETECTOR

The response of the FID detector was not directly affected by the bleed of the column because of the use of a dual column system which compensated for liquid phase bleed.

Budzinowicz et al [89] in their study of barbiturates compared the behavior of ECD and FID detectors. Less than

0.1 ug of barbiturate was used for the ECD detector, and greater than 0.1 ug of barbiturate was used for the FID detector. They found that the differences in concentrations used for the two detectors led to quite a difference in the results obtained. Similarly, in this thesis, response results were found to be much affected by the concentrations of the pesticides, and different shape thermograms were obtained using the FID and ECD detectors.

Gudzinowicz et al also found that their FID results showed a displacement effect in which one material adsorbed by the active sites on the support was replaced by another compound until it reached equilibrium on the column.

From the results of tests in this thesis with the ECD it was known that column bleed occurred as the column temperature was increased. Hence, new active sites on the support were continuously exposed. Based on this fact, and the fact that the FID tests were carried out with pesticide concentrations far greater than those used for the ECD tests (1000 times more for Malathion, 266 times more for Disyston and 400 times more for Phorate) the different shapes in the FID thermograms (Appendix (II)) compared to the ECD thermograms can be explained.

The thermograms obtained using a column packed with coated CW-HP support (Column 4 of Table (6)) are shown in

Figure (16). The shapes of these thermograms are typical of all those obtained with the FID detector, except for differences in rate of change of response with column temperature (Appendix (II)). The multimaxima in the FID thermograms were indirectly related to the bleeding of the liquid phase in the column as its temperature was raised. They can be explained for Figure (16) as follows. At the lower temperatures, the column had been primed by prior injection of the pesticides, and a gradual increase in response as the column temperature increased to 130 deg C. was observed because of decreasing adsorptivity of the support. Above 130 deg C, the response from the detector decreased up to a column temperature of 150 deg C. This decrease in response can be attributed to strong adsorption of injected pesticides to prime new active sites on the support that had been exposed because of the bleeding of the liquid phase at these temperatures. From a column temperature of 150 to 165 deg C there was an increase in response because the priming effect was complete and more of the injected pesticide was eluted. From a column temperature of 165 to 200 deg C the response of the detector decreased drastically. The rate of liquid phase bleed was probably the greatest in this temperature range resulting in maximum exposure of new active sites on the support, requiring the greatest amount of priming by the pesticides, and hence leading to smaller responses being given by the detector.

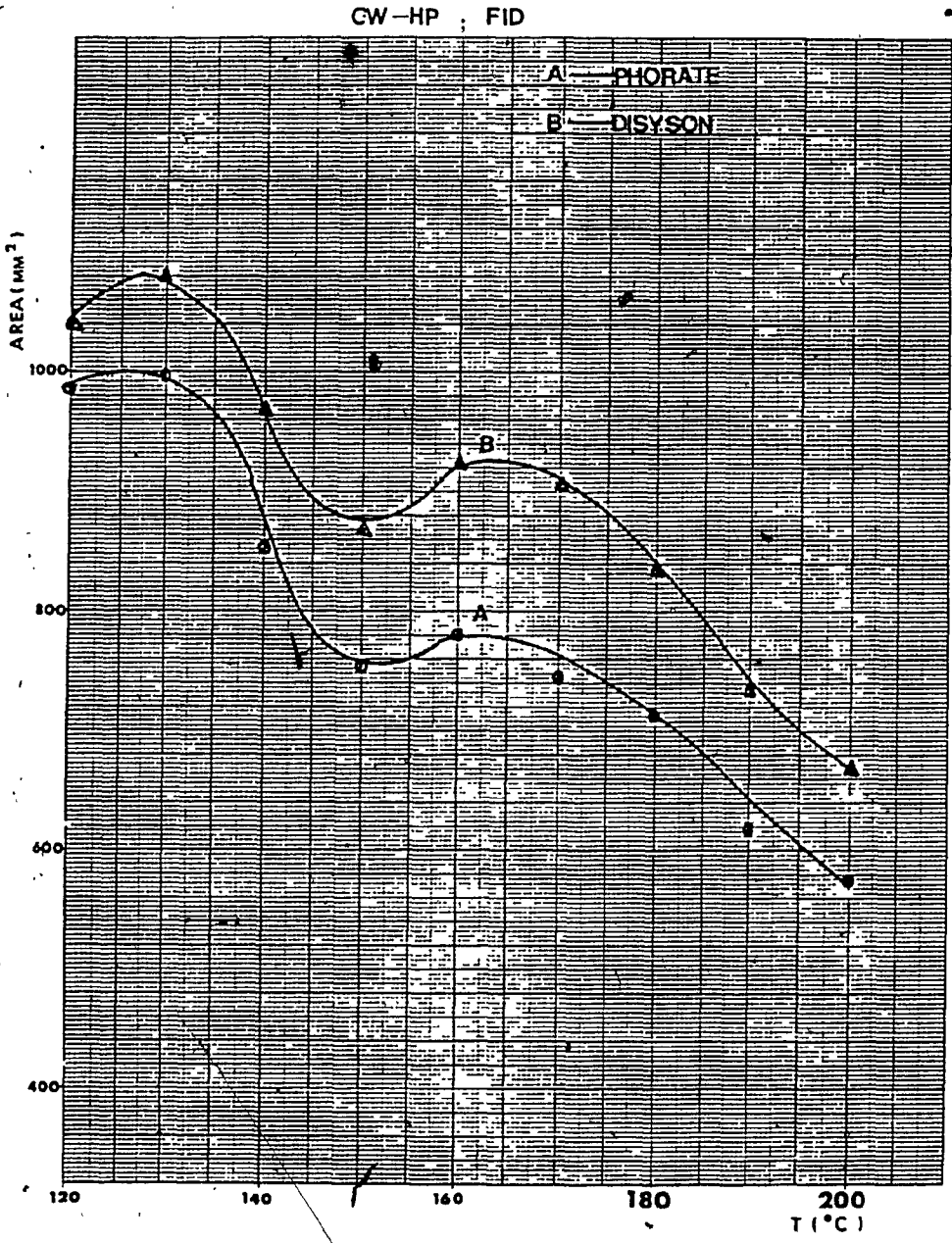


FIGURE (16) : Thermograms for Column Containing Coated CW-HP support Using the FID Detector

In contrast, two factors acted to give the decrease in response with increase in column temperature observed at higher temperatures with the ECD detector. The bleeding of the liquid phase reduced the sensitivity of the detector, and when the column bled the pesticides injected were used up in priming the newly exposed active sites, hence, decreasing the amount of pesticides reaching the detector. Only the latter of these reasons contributed to the decrease observed with the FID detector. It is, therefore, not surprising that the FID thermograms showed a smaller decrease in response with an increase of column temperature than was observed with the ECD thermograms.

Also, because the FID detector is less sensitive than the ECD detector, bleeding and priming effects would not be expected to cause as drastic changes in the FID detector response when compared to the ECD detector response.

Comparing the ECD and FID thermograms, one can conclude that the trends for the Phorate and Disyston curves were almost identical in all cases, whereas the trend for the Malathion curves were different. This difference can be correlated with the structure of the compounds which have different physical properties. Section 1.3 of Chapter 1 described the structure of these pesticides. Phorate and Disyston have similar structures and hence similar physical and chemical properties, whereas Malathion has a structure

quite different from that of the other two pesticides, and hence the difference in properties.

In a paper published by Lindgren et al [36] it was mentioned that organophosphorus pesticides can diffuse through the OV-1 liquid phase that coats the support material, and interact with the support's active sites. From the ECD and FID thermograms in this thesis, there was a strong indication that Malathion had a slower mass transfer through the OV-1 liquid phase than do Phorate and Disyston. Because of its slower diffusivity, due to structural effects, through the liquid phase, Malathion interacted to a greater extent with the support material and hence was susceptible to more adsorption. The higher adsorption for Malathion by the support materials was evident in the ECD thermograms (Appendix (I)). There were smaller responses, or even no responses observed on the columns tested. Seven of the support materials (CW-AW, CW-AW-DMCS, CW-HP, CP-NAW, CG-AW, CG-AW-DMCS and CG-HP) gave some response for Malathion, while the other five supports (CW-NAW, C-750, CP-AW, CP-AW-DMCS and CG-NAW) completely adsorbed Malathion.

3.2.5 LINDANE RESULTS

In the study of the chlorinated pesticide, Lindane, it was found that both FID and ECD experiments gave thermograms with similar shapes (Figure (17)). The thermograms for

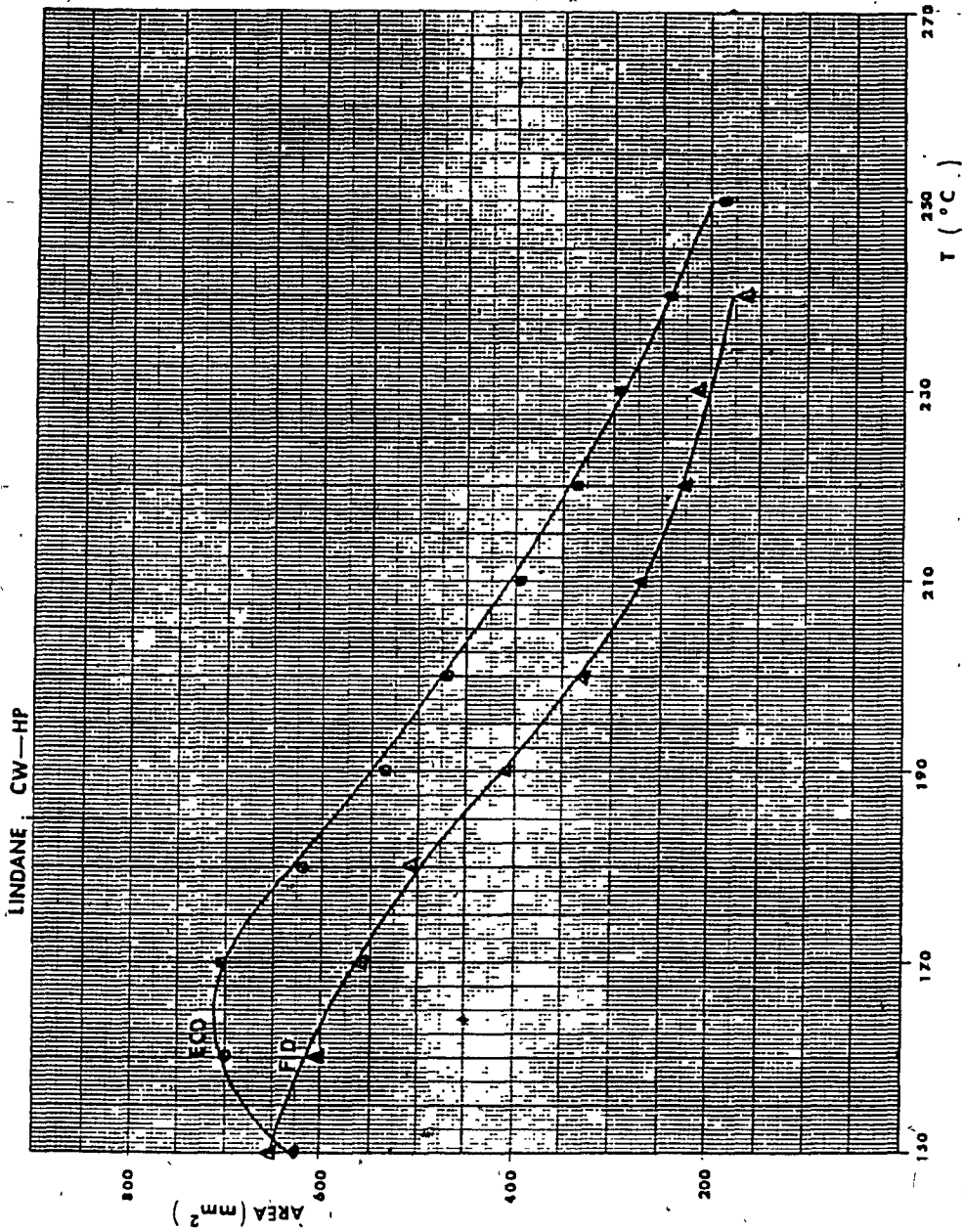


FIGURE (17) : Thermograms of Lindane for a Column Coated With CW-HP Support Using both FID and ECD Detectors.

Lindane were similar because it was possible that this pesticide reacted with the liquid phase OV-17 to a great enough extent such that this effect overwhelmed any liquid phase bleeding effect on the detectors.

Baiulescu et al [34], and Trash [90], strongly suggested that chlorinated compounds react with silicone liquid phases such as OV-17.

The trend in the thermograms of Figure (17) showed that as the column temperature increased, the response for Lindane with both detectors decreased. This could mean that at higher column temperatures the reaction between the liquid phase, OV-17, and Lindane increased. Of experimental significance was the fact that there were no extraneous peaks observed in the chromatograms for Lindane. This was a strong indication that the reaction product(s) between Lindane and the liquid phase were strongly retained on the column.

3.3.0 CONCLUSIONS

In this part of the thesis, an attempt was made to survey all the possible factors that could affect the response obtained for the pesticides studied using ECD and FID detectors. The three main contributing factors were found to be as follows:

(a) Liquid phase bleed decreased the sensitivity and, therefore, the response of the ECD detector directly.

(b) Liquid phase bleed decreased both the ECD and FID responses indirectly, i.e., through additional priming by pesticides being required on new active sites that were created through bleeding of the liquid phase.

(c) Adsorption of the pesticides by support material in two ways. (i) Onto exposed surfaces of the support material, and, (ii) by diffusion of the pesticides through the liquid phase followed by interaction with the support material.

It is not possible, therefore, to classify detector response on the basis of any one of the above three reasons alone, but all of them must be considered. To obtain a true comparison between the actual adsorptivity of a support material and detector response it would be necessary to study the support materials without any liquid phase coated on them, which would eliminate possible interferences due to liquid phase bleed. However, peak tailing should give an indication of the actual adsorptivity of a support material and this has been considered in Chapter 5.

Conclusions for the three main classes of diatomaceous earth supports (Chomosorbs W, G and P) are given below. The names of the supports in the columns were used to identify

the columns so as to make reading of the thesis more comprehensible. It should be remembered, however, that it was the detector responses for the different columns listed in Table-(6) that were compared, and that these were affected both by the support adsorptivities and by other factors such as liquid phase bleed.

CHROMOSORB W

For 'High Concentrations' (FID results) of pesticides tested, the decreasing order of response for the Chromosorb W columns was :

CW-HP > C-750 > CW-AW > CW-NAW > CW-AW-DMCS

The order of decreasing response for 'Moderate Concentrations' of pesticides was :

CW-HP > CW-AW > CW-AW-DMCS > CW-NAW > C-750.

The order of decreasing response for 'Low Concentrations' of pesticides was :

CW-HP > CW-AW-DMCS > CW-NAW > CW-AW > C-750

The overall average order for the three sample concentrations was :

CW-HP > CW-AW-DMCS > CW-AW > CW-NAW > C-750

CHROMOSORB G

The decreasing order of responses for 'Moderate Concentrations' of pesticides was :

CG-HP > CG-AW > CG-AW-DMCS > CG-NAW

For the 'Low Concentrations', the decreasing order of responses was :

CG-AW-DMCS > CG-AW > CG-HP > CG-NAW

The overall average for the low and moderate concentrations was :

CG-AW > CG-HP > CG-AW-DMCS > CG-NAW

CHROMOSORB P

The order of decreasing response for 'Moderate Concentrations' of pesticides was :

CP-AW > CP-NAW > CP-AW-DMCS

From the thermograms in Section 3.1.1 the columns that gave the best response for 'Medium Concentrations' of pesticides at all the column temperatures studied were :

CG-HP for Phorate,
CP-AW for Disyston,
and,
CW-HP for Malathion.

From the thermograms in Section 3.1.2, the best columns for use with pesticides at 'High Concentrations', at all the column temperatures studied were :

CW-HP for Phorate,
CW-HP for Disyston,
and,
CW-HP for Malathion.

The column that, overall, give the best response for all the different concentrations of pesticides studied in this project, using both ECD and FID detectors, was CW-HP.

CHAPTER

4

EFFECT OF REPEATED RUNS ON CHROMOSORB W-AW

COLUMN LIFE

A study was made of the effect of repeated chromatographic analysis of organophosphorus pesticides on the life time of a CW-AW column. (Column 2 of Table (6)).

4.1.0 OBSERVATIONS AND RESULTS

Seven consecutive runs were done on the CW-AW column using the ECD detector, and six consecutive runs were done using the FID detector. A different column containing the same kind of coated CW-AW support was used for tests with each detector. The FID results were not useful for the present interpretation. No significant tailing effects or changes in relative retention times were observed, presumably because of the high pesticide concentrations used. The following, therefore, represents data obtained with the ECD detector.

The relative retention times for Phorate, measured from the solvent peak, are given in Table (32) for the first, third and sixth runs on the column packed with coated CW-AW support. Similar results were obtained with Disyston and Malathion. It was observed that with each run on the column, the relative retention times of all three pesticides (Phorate, Disyston and Malathion) increased. Also, as the number of runs increased for the CW-AW column, the tailing of chromatographic peaks obtained increased, the bleeding of the liquid phase decreased, the recorder baseline became erratic. For the later runs (5th, 6th and 7th) it was observed that no

TABLE (32) : The Relative Retention Times (RRT) for the 1st, 3rd and 6th Runs for Phorate on the CW-AW Column Using the ECD Detector.

<u>COLUMN**</u>	<u>RRT OF</u>	<u>RRT OF</u>	<u>RRT OF</u>
<u>TEMPERATURE</u>	<u>1st RUN***</u>	<u>3rd RUN***</u>	<u>6th RUN***</u>
130	261.0	293.0	*adsorbed
140	179.0	196.0	*adsorbed
150	122.0	135.0	246.5
160	87.0	95.0	148.0
170	64.8	69.0	94.5
180	47.0	51.4	61.0
190	36.0	40.0	44.0
200	28.2	31.0	33.0
210	22.8	24.2	26.2

* → Phorate was completely adsorbed at these temperatures for the 6th run

** → deg C

*** → millimetres.

response were obtained at the lower column temperature (i.e., at 130, 140 and 150 deg C).

Appendix (V) represent the thermograms obtained for six runs done with the ECD detector for the CW-AW column. These thermograms showed that with an increase in the number of runs the maximum response generally shifted to higher column temperatures.

4.2.0 DISCUSSION OF RESULTS

The shift in the thermogram maximum (T.M.) observed in the thermograms for the three organophosphorus pesticides (Appendix (V)) can be explained in terms of the bleed of the liquid phase off the CW-AW column, and the adsorptivity of the support in the column.

4.2.1 INTERPRETATION OF THE THERMOGRAM TRENDS FOR THE REPEATED RUNS ON THE CW-AW COLUMN

Figure (18) shows the thermograms for the first, third and sixth runs for the pesticides Phorate, Disyston and Malathion. All three compounds showed a similar pattern for their thermograms, i.e., as the number of runs increased the T.M. shifted to higher and higher column temperatures. This trend in the thermograms can be indirectly related to the bleeding of the liquid phase off the column. As mentioned

in Section 1.6.2 of Chapter 1 the PDMS liquid phases have a wide range of molecular weights and the lower the molecular weight of the PDMS liquid phase the earlier the column temperature at which bleeding will occur. Once bleeding occurs, the ECD detector will decrease in sensitivity towards the pesticides tested (Section 3.2.3a). The first runs for all three pesticides gave thermogram maxima at relatively lower column temperatures, while the sixth run for all pesticides showed T.M. at relatively higher column temperatures. The reason for this is that there occurred a greater liquid phase bleeding during the first run because there were more lower molecular weight polymers present in the OV-1 liquid phase at this stage, than during the second to the sixth runs. This being the case, the ECD detector was responding to a high liquid phase bleed at a relatively low column temperature during the first run (the lower the molecular weight of OV-1 polymer present, the lower the column temperature at which it was volatilized off the column). As the column temperature was increased during the first run, higher and higher molecular weight polymers making up the OV-1 liquid phase were volatilized off causing an additive bleeding effect. This effect caused a reduced ECD response towards the pesticides.

When the second and third runs were carried out on the column with the CW-AW support there were still polymer fractions in the OV-1 liquid phase that had molecular weights

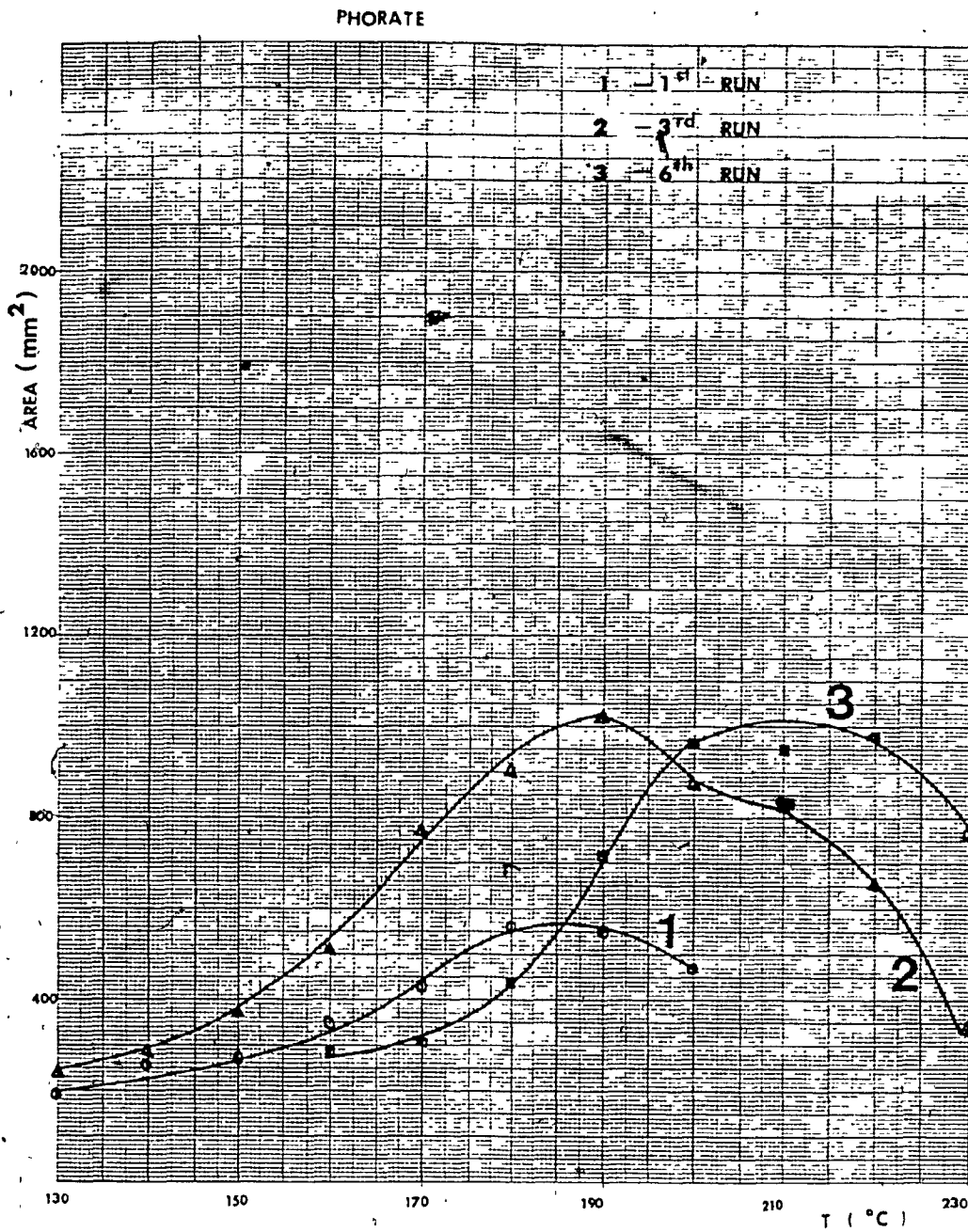


FIGURE (18X) : Thermograms for Phorate on a Column Containing Coated CW-AW Using the ECD Detector.

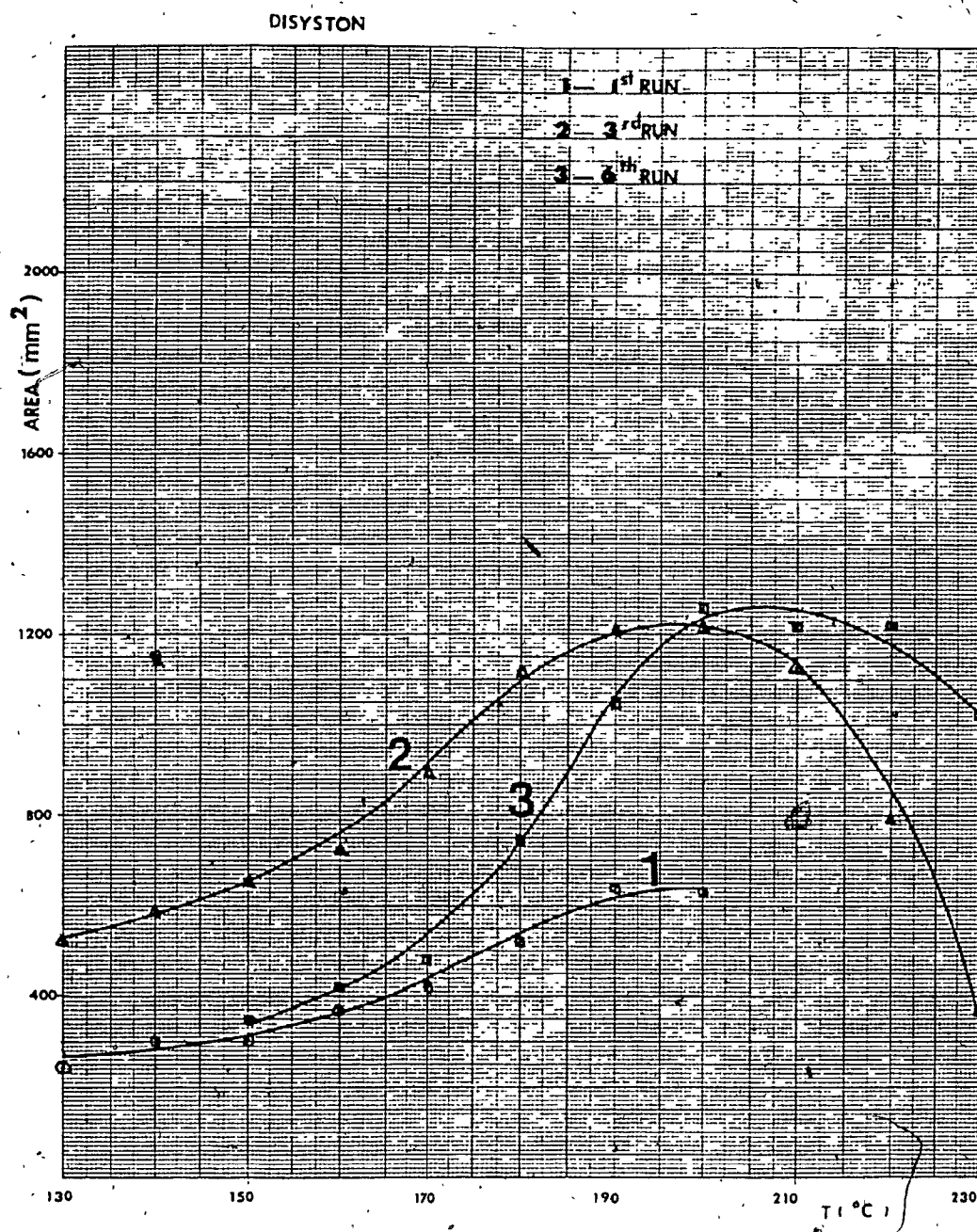


FIGURE (18Y) : Thermograms for Disyston on a Column Containing Coated CW-AW Using the ECD Detector.

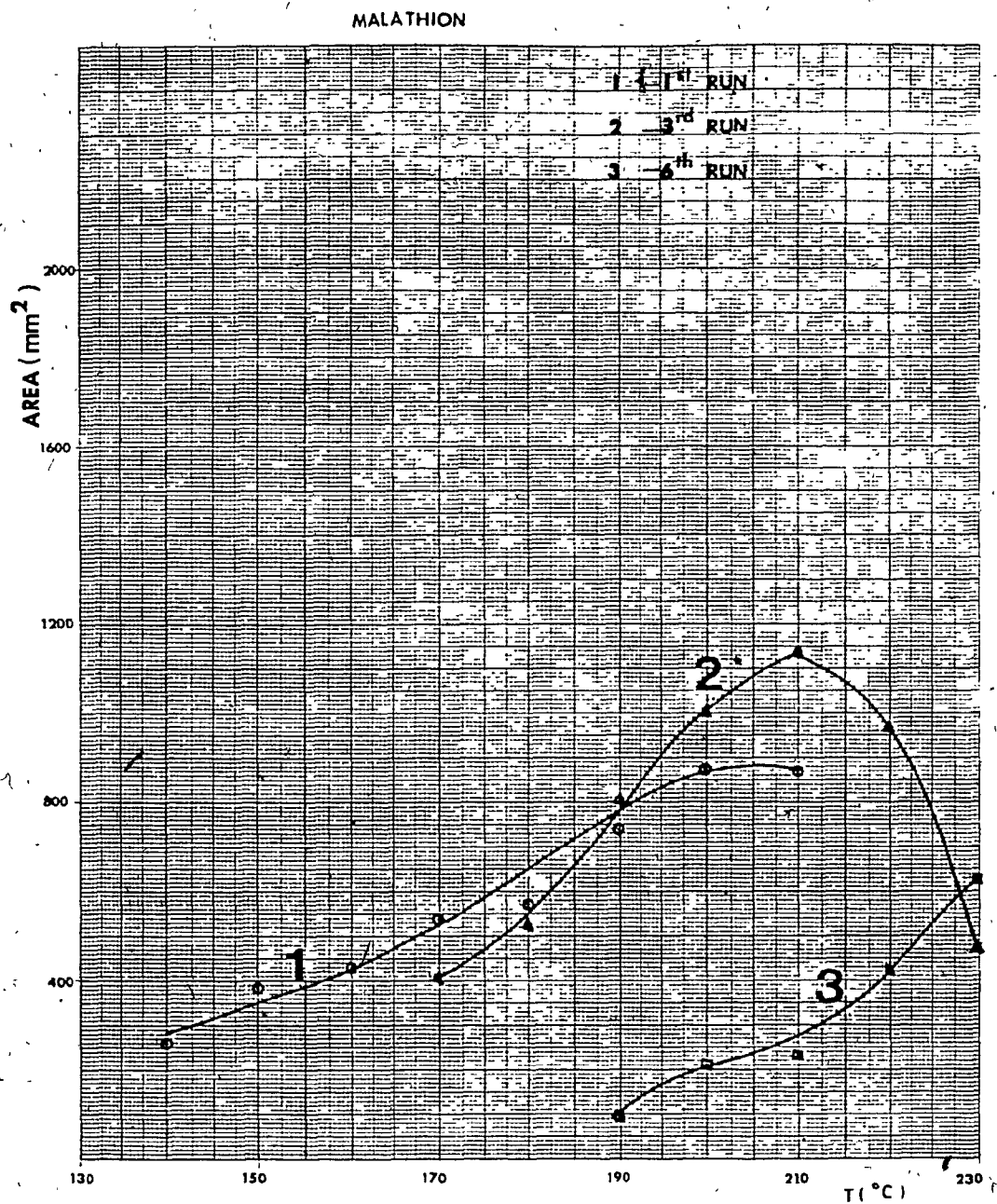


FIGURE (18Z) : Thermograms for Malathion on a Column Containing Coated CW-AW Using the ECD Detector.

similar to what existed during the first run. However, the amount of low molecular weight polymers remaining in the liquid phase was smaller than in the first run, so that less bleeding occurred at the lower column temperatures, and a higher detector response was initially obtained for Disyston and Phorate. The T.M. for the third run was shifted, therefore, to a higher temperature.

By the time the sixth run (Figure (18)) was carried out, the low molecular weight polymers that were initially present in the OV-1 liquid phase had been completely removed from the column. This meant that only high molecular weight polymers remained on the column. Therefore, bleeding of the liquid phase could only take place at higher column temperatures. This was what was observed for the sixth run on the column packed with CW-AW (Figure (18)). From Appendix (V), the T.M. for Phorate for the 4th, 5th and 6th runs were 195, 210 and 210 deg C, respectively. It seemed that during the 5th run and 6th run on the CW-AW column, bleeding of the same molecular weight fractions occurred since the T.M. was approximately fixed at 210 deg C for both the Phorate and Disyston.

The thermograms in Appendix (V) also indicated that the CW-AW column deteriorated as the number of runs carried out increased. The detector response at lower column temperatures was generally lower for later runs. For

example, for Malathion the responses at a column temperature of 170 deg C were 530.0 sq.mm, 400.0 sq.mm, and 0.0 sq. mm for the first, third and sixth runs, respectively (Figure (18Z)). The explanation for this is that as the liquid phase was lost from the column through bleeding, more and more support surface became exposed to the pesticides. The pesticides then interacted with the active sites on the support and were adsorbed. Malathion, because of its greater adsorptive property, showed a greater amount of adsorptivity toward the CW-AW support. No Malathion was seen until a column temperature of 190 deg C was reached for the sixth run (Figure (18Z)). Consideration of results with Phorate and Disyston led to similar conclusions as for Malathion (Appendix (V)).

Another indication that the CW-AW column became more adsorptive with the number of runs carried out was demonstrated in Table (32). The relative retention times increased from one run to the next at all column temperatures studied. The increased retention times were related to increased tailing observed for each subsequent run. For example, at a column temperature of 150 deg C the RRT for the first, third and sixth runs were 122.0, 135.0 and 246.5 millimeters, respectively.

4.2.2 TAILING EFFECTS

Using the relationship $10(a/2b)$ as a measure of

tailing, as described in Section 1.8, Chapter 1, the tailing factors for the chromatographic peaks obtained at a column temperature of 150 deg C were calculated. Figure (19) is a plot of the tailing of the peaks versus the number of runs for each pesticide tested on the column packed with CW-AW. For all three pesticides there was a gradual increase in tailing of their peaks with each subsequent run. In this figure a value of ten was considered to represent a truly symmetrical peak. Values greater than ten were considered to represent assymetrical peaks. Up to the third run there was almost no indication of change in the column behaviour towards the pesticides because the peak shapes remained almost the same. However, from the fourth run to the seventh run, tailing of the pesticide peaks gradually increased. Malathion was completely adsorbed by the support material during the sixth and seventh runs at a column temperature of 150 deg C. Phorate and Disyton showed drastic increases in tailing for the sixth and seventh runs.

The increased tailing of the sixth and seventh runs for all three pesticides was a strong indication that the column had lost most of the OV-1 liquid phase. There was increased interaction between the support surfaces and the pesticides during the last three runs (Figure (19)).

However, the thermograms for Phorate and Disyton (Appendix (V)) showed an increase in response at higher

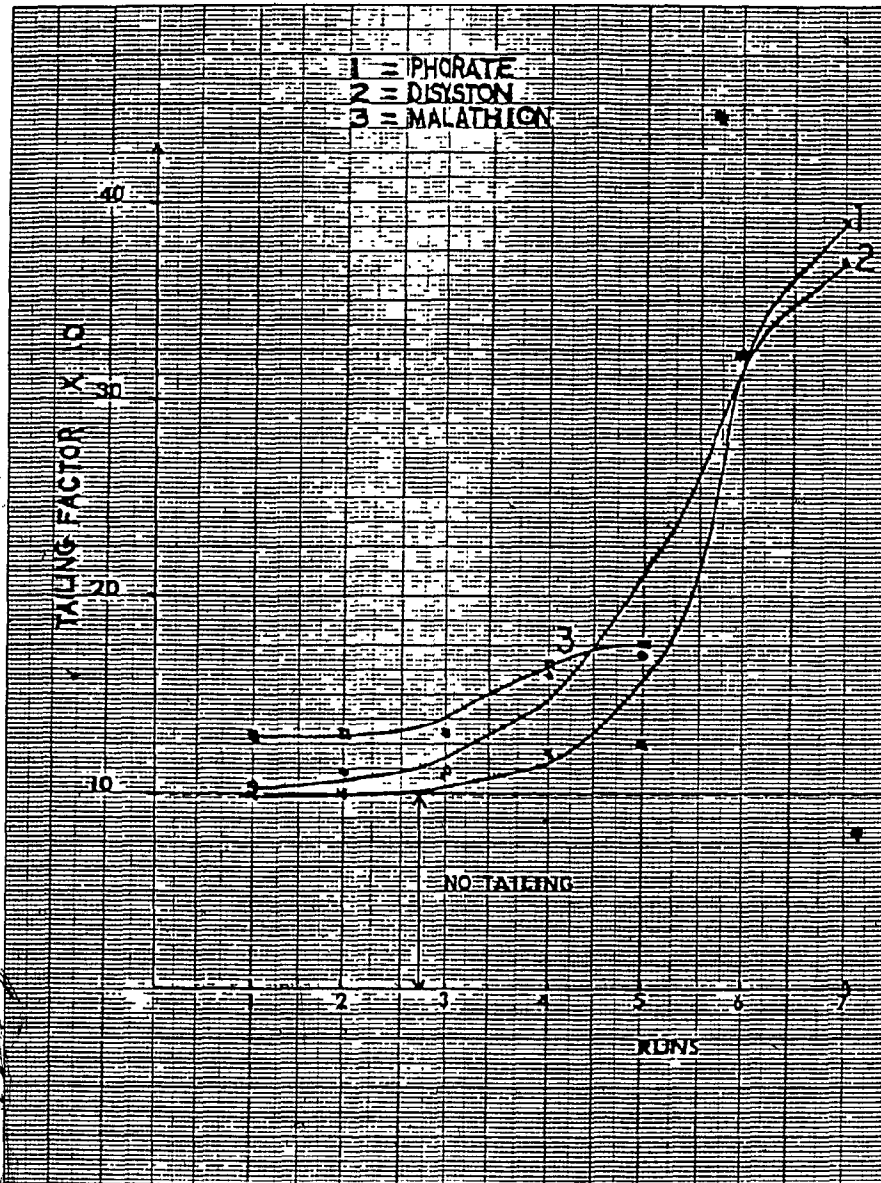


FIGURE (9) : The Degree of Tailing of Chromatographic Peaks Versus the Number of Runs at a Column Temperature of 150 deg C, Using the CW-AW Column

column temperatures for the later runs (i.e., the 5th and 6th). This higher response for the pesticides at higher column temperatures for the later runs was due to a decrease in the liquid phase bleed and hence an increase in ECD detector response. Therefore, even though peak tailing had increased for the later runs (increased pesticide adsorption) there was better response for the pesticides at higher column temperatures. Malathion showed more tailing than the other two pesticides during the first three runs. If the concept of the slower diffusivity of Malathion through the OV-1 liquid phase is true [102], then the greater tailing of Malathion for the first three runs is explained, i.e., the slower the diffusivity through the liquid phase the greater the interaction with the support material and hence the larger the tailing that will be observed.

Another reason why Malathion showed a greater tailing effect at low temperatures compared to Phorate and Disyston was because of its structure (Section 1.3, Chapter 1). Malathion is a much more polar compound than Disyston and Phorate because it has more active oxygen atoms present in it than the other two pesticides. It is known [18] that the presence of oxygen in a compound increases the possibility of hydrogen bonding with the $-Si-OH$ group of the support. Hence, the greater tailing and adsorption of Malathion that was observed.

The explanations given above for liquid phase bleeding in this project correspond well with the results reported by Guild et al [87], and Graham [88], in their study of Apiezon L grease as a liquid phase. These authors found that the first run with Apiezon L liquid phase gave intense bleeding at lower column temperatures. Repeated runs on the Apiezon L column caused the column bleeding to be shifted to higher and higher column temperatures until a column temperature (180 deg C) was reached where bleeding always occurred. The bleeding during early runs was attributed to the presence of low molecular weight polymers, whereas, the bleeding that always occurred at a column temperature of 180 deg C was attributed to vaporization of higher molecular weight polymers. These polymers had a small molecular weight range compared to OV-1.

Keppler et al [91] showed that poor quality silicone polymers (those that contained a reasonably high quality of low molecular weight polymers) bleed at a rate of about 8 mg per hour at a column temperature of 210 deg C.

4.2.3 EXTENSION OF COLUMN LIFE

The life time of OV-1 coated diatomaceous support columns could be extended if a column temperature of 160 deg C or less was used for the pesticides tested. At such column

temperatures only low molecular weight silicone polymers would bleed off the column leaving the higher molecular weight polymers on the support surface. Subsequently, repeated runs up to a column temperature of 160 deg C would show less and less liquid phase bleeding, and higher and higher ECD detector response for the pesticides. The choice of a column temperature limit of 160 deg C was based on the data given in Table (31). From this table it was clear that the lowest column temperature at which any thermogram showed a maximum was just over 160 deg C. At column temperatures just over 160 deg C there was observed, normally, intense bleeding of the OV-1 liquid phase.

The graphs in Figure (20) demonstrate the performance of CW-HP support in the case where the 1st run was restricted to a maximum column temperature of 180 deg C. This figure showed that the response of the second run was increased by a factor of about two and half times over that of the first run. The reason for this increase of response was because there was less bleeding of the liquid phase in the second run than in the first run and also there was a priming effect during the first run. This same phenomenon was observed for the first and second runs on the column packed with CW-AW (Appendix (V)), where the first run was restricted to a maximum column temperature of 200 deg C.

PHORATE

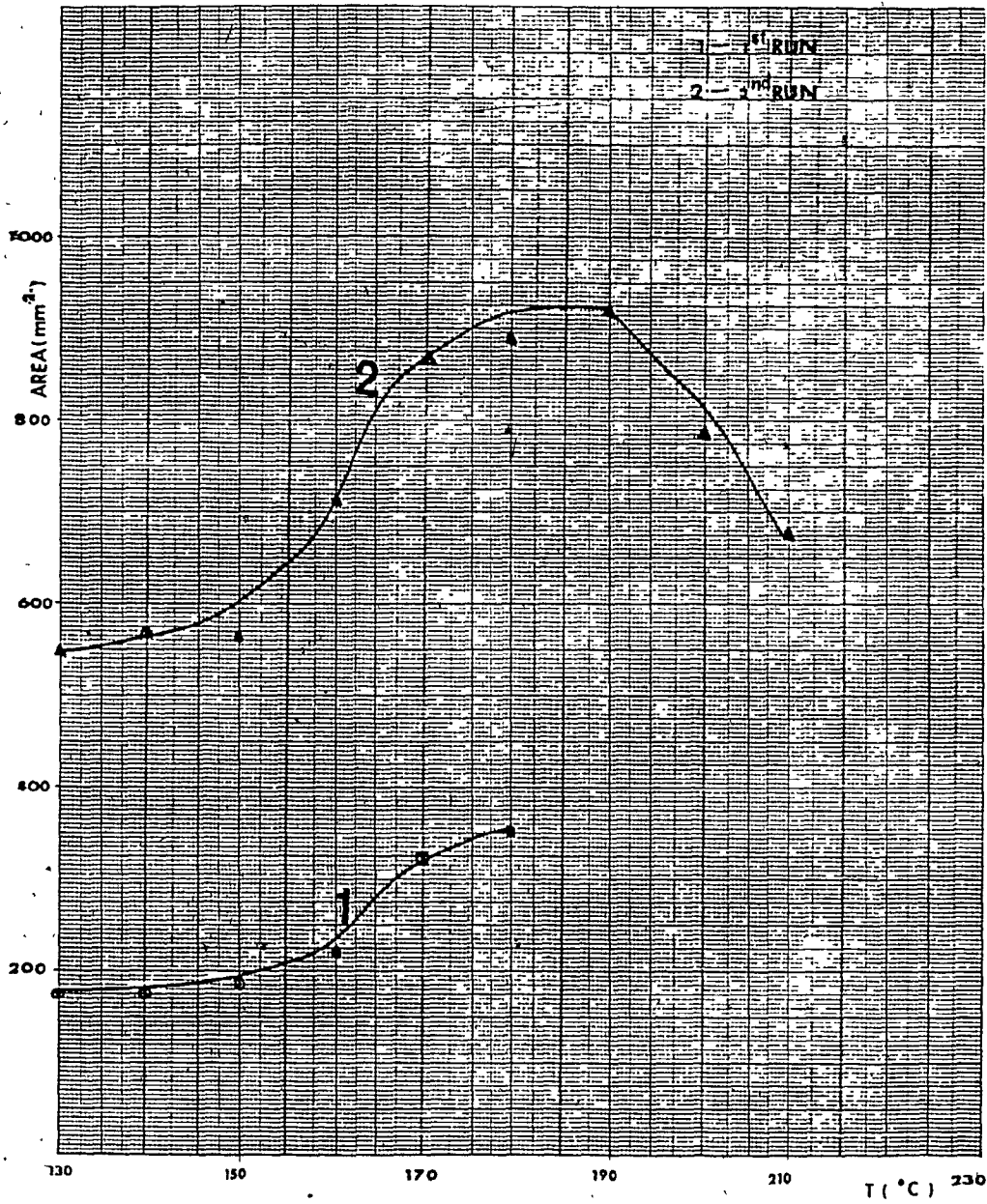


FIGURE (20A) : Thermograms for Phorate for a Column Packed with CW-HP Using the ECD Detector

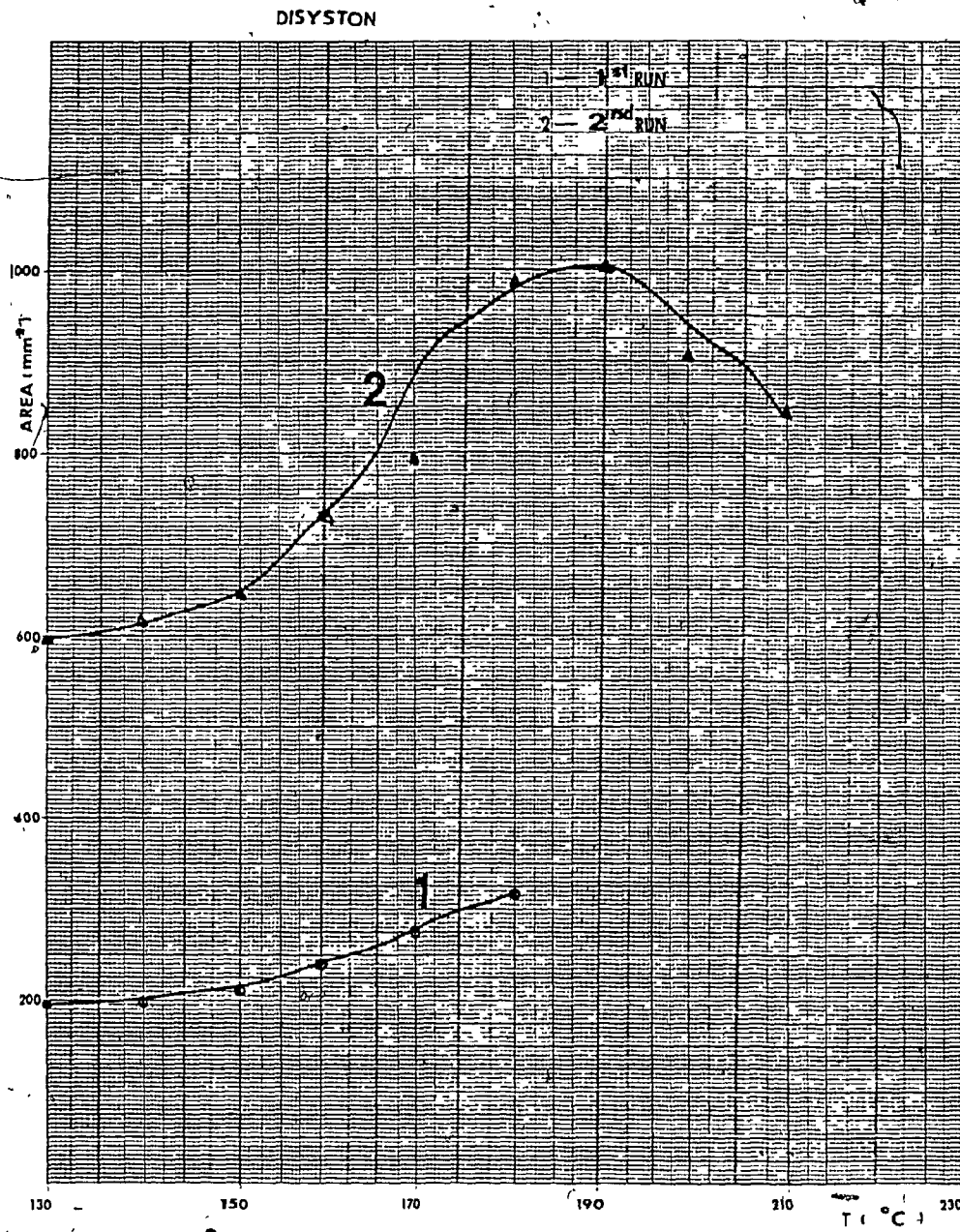


FIGURE (20B) : Thermograms for Disyston for a Column Packed with CW-HP Using the ECD Detector

4.3.0 CONCLUSIONS

The CW-AW column studied repeatedly with the ECD detector in the column temperature range of 130 to 230 deg C showed signs of deterioration after the third run was carried out with the organophosphorus pesticides. The bleeding of the OV-1 liquid phase off the column was the main reason for the increase of relative retention times and increased tailing of the pesticides.

The shift of the thermogram maxima to higher column temperatures for each subsequent run on the columns studied was due to the removal (during earlier runs) of lower molecular weight polymers from the liquid phase in the columns.

Deterioration of the columns tested could be partially reduced by use of lower column temperatures, i.e., a column temperature of 160 deg C should not be exceeded for the OV-1 liquid phase. A priming effect was obtained during repeated runs when the column temperature was not allowed to surpass 180 deg C for the column packed with CW-AW.

CHAPTER

5

COLUMN PERFORMANCE (MODERATE CONCENTRATION

ANALYSES WITH THE ECD DETECTOR)

5.1.0 OBSERVATIONS AND RESULTS

The relative retention times (RRT) for the three organophosphorus pesticides were determined as indicated in Figure (21) on a column with CW-AW-DMCS support and a column temperature of 180 deg C.

Using equation (23) of Section 1.9 in Chapter 1 the efficiencies of the columns used in this study were calculated (Table (33)). Using equation (25) of Section 1.9 in Chapter 1 the resolutions of the columns were calculated.

Most of the columns studied showed tailing at lower column temperatures and symmetrical peaks at higher column temperatures for the organophosphorus pesticides. Figure (22) shows the change in peak shape as the column temperature was increased for the column with C-750 support. The symbol, T.F., in Figure (22) means 'tailing factor'. The tailing factor was obtained from the relation $10 \times (a/2b)$ which was described in Section 1.8 of Chapter 1. Figure (23) shows a plot of tailing factor versus column temperature of three columns with CP-AW, C-750 and CG-HP supports, using the compounds Phorate and Disyston. The CG-HP column represents a column with small tailing. The C-750 column represents a column with medium tailing. And

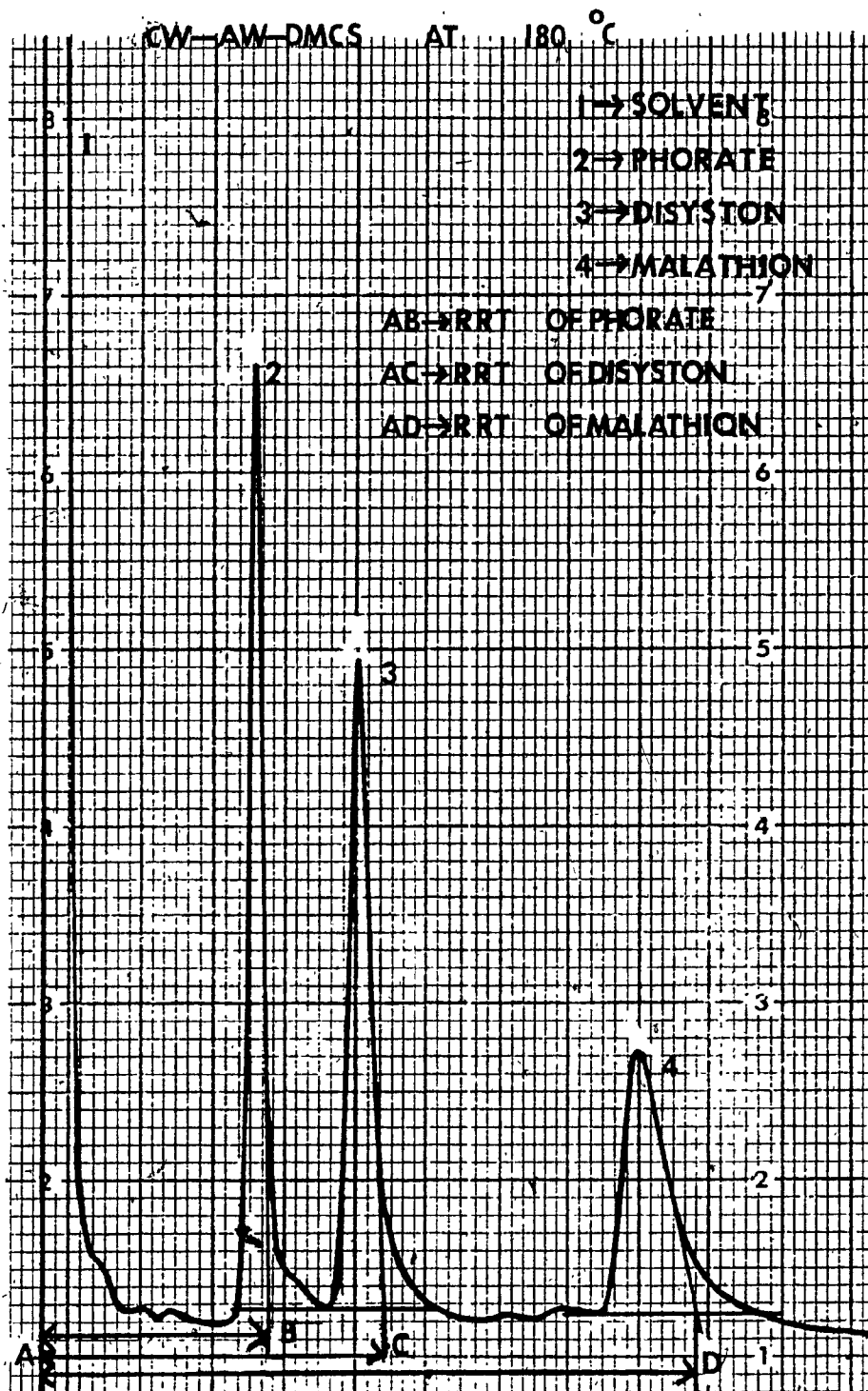


FIGURE (21) : Determination of the Relative Retention Times (RRT) for Phorate, Disyston and Malathion on a Column With CW-AW-DMCS, and at a Column Temperature of 180 deg. C.

TABLE (33) : Efficiency and Resolution of Columns
 at a Column Temperature of 190 deg C
 for the Pesticide Phorate.

<u>COLUMN</u>	<u>COLUMN EFFICIENCY (THEORETICAL PLATES)*</u>	<u>COLUMN RESOLUTION</u>
CW-NAW	968	3.05
CW-AW	1133	3.63
CW-AW-DMCS	420	2.22
CW-HP	476	2.21
C-750	1024	4.51
CG-NAW	970	3.18
CG-AW	1225	3.19
CG-AW-DMCS	1600	3.85
CG-HP	420	2.01
CP-NAW	888	1.24
CP-AW	632	2.20
CP-AW-DMCS	619	2.55
Ultra-Bond 20m	1024	3.56

* → efficiency per eight foot of column

the CP-AW column represents a column with large tailing. A tailing factor of 10 represents a symmetrical peak.

5.2.0 DISCUSSION OF RESULTS

The solid support in GLC plays a vital role in column performance. The physical characteristics of the support, such as surface area, pore volume, pore size distribution, particle size and packing characteristics, determine the extent of peak broadening [93].

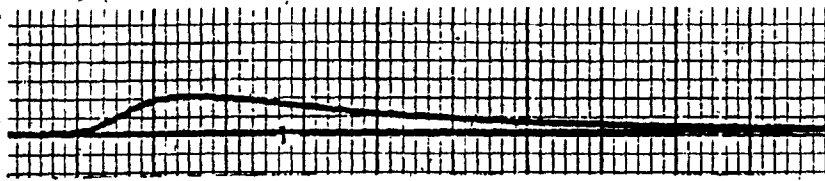
5.2.1 COLUMN EFFICIENCY AND RESOLUTION

EFFICIENCY

The efficiency of a column depends directly on the RRT and inversely on the base width (spreading) of the chromatographic peak. The RRT of an eluted peak depends mainly on the amount of liquid phase present in the column and on the degree of adsorption of the solute on the support [94]. The higher the liquid phase loading on the support, the longer the RRT. Also, the greater the adsorption of the solute on the support, the longer the RRT (Section 1.9.3 of Chapter 1).

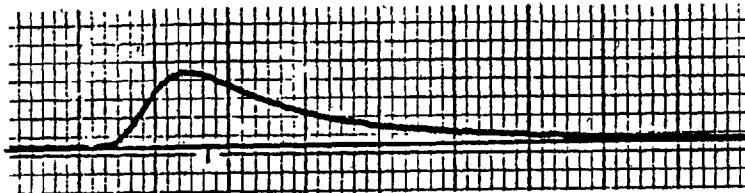
The width at the base of an eluted peak depends on the time the solute spends on the column. The longer the RRT

130 °C DISYSTON



T.F - 34.6

140 °C



T.F - 31.8

150 °C



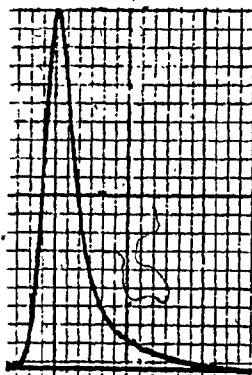
T.F - 28.6

160 °C



T.F - 23.3

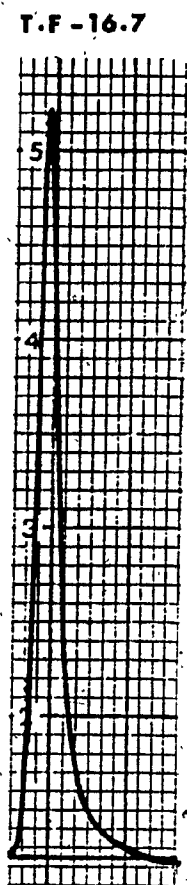
170 °C



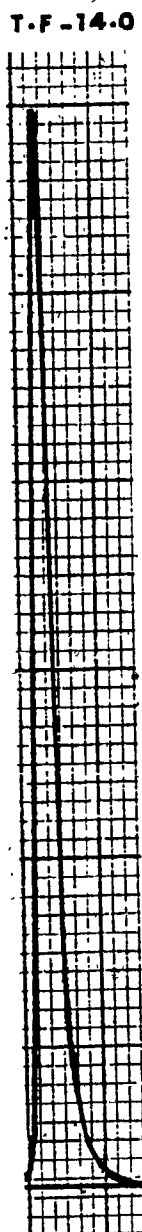
T.F - 20.0

FIGURE (22A) : Changes in Peak Shape as the Column Temperature was Increased from 130°C to 170°C for the Column with C-750. (T.F. equals Tailing Factor).

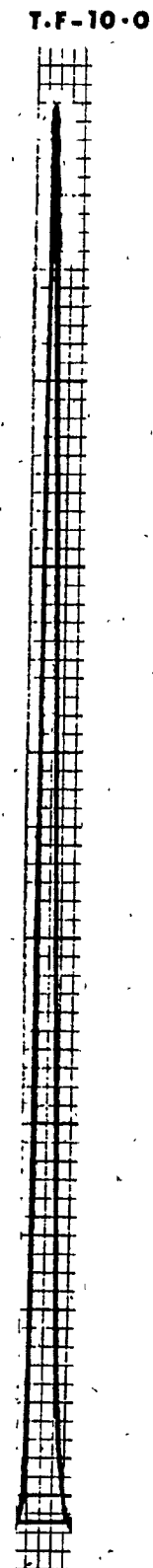
FIGURE (22B) : Changes in Peak Shape as the Column Temperature was Increased from 180°C to 200°C for the Column with C-750. (T.F. equals Tailing Factor).



180 °C



190 °C



200 °C

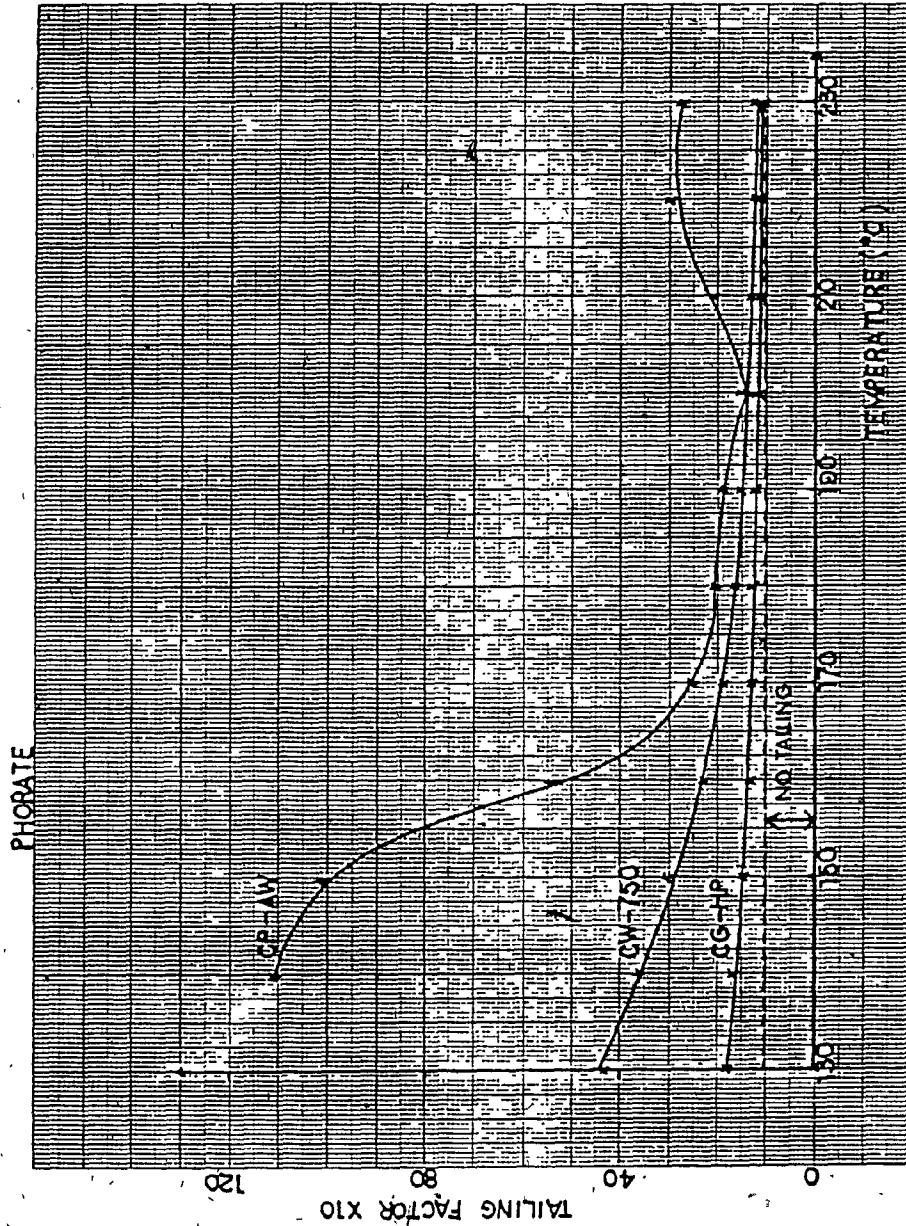


FIGURE (23A) : Graphs of Tailing Factor Versus Column Temperature for the Columns with CP-AN, C-750 and CG-HP Supports Using the Compound Phosphate.

PHORATE

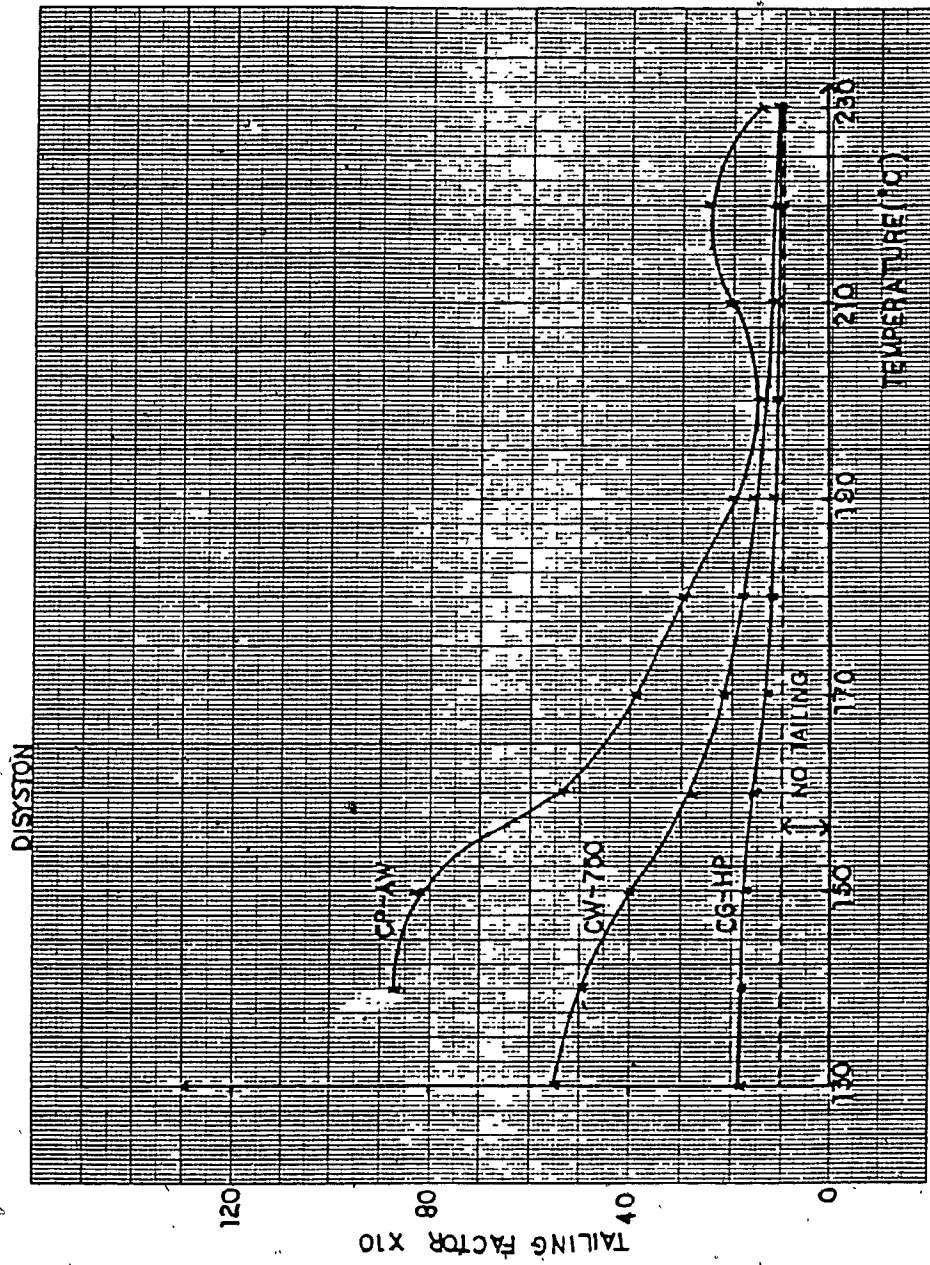


FIGURE (238) : Graphs of Tailing Factor Versus Column Temperature for the Columns With

CP-AW, C-750 and CG-HP Supports Using the Compound Disyston.

on the column the broader the peak width. It also depends on the porosity of the support [20,94,95,96]. The greater the porosity of the support the broader the eluted peak.

Based on Table (33), some of the most efficient columns were those with the Chromosorb G supports, i.e., CG-AW-DMCS had 1600 plates, CG-AW had 1225 plates, and CG-NAW had 970 plates. Some of the least efficient columns were those with Chromosorb W supports, i.e., CW-AW-DMCS had 420 plates and CW-HP had 476 plates. The Chromosorb P supports had intermediate efficiencies, i.e., CP-NAW had 888 plates and CP-AW had 632 plates. These results were indicative of the amount of liquid phase present in the columns. The Chromosorb G supports contained an average of 0.197 gm of OV-1. The Chromosorb P supports contained an average of 0.154 gm of OV-1. The Chromosorb W supports contained an average of 0.094 gm of OV-1. As mentioned before, the larger the amount of liquid phase in the column the larger the RRT and hence the greater the efficiency. Some of the inconsistencies in efficiencies seen in Table (33) (i.e., CW-AW and C-750 were much higher than other Chromosorb W columns, and CG-HP was lower than other Chromosorb G columns) can be accounted for when one takes into consideration the tailing of some of the eluted peaks. Tailing decreased the accuracy of estimating peak widths at the base, hence, an under-estimation of the column efficiency may have resulted. Another reason for the

inconsistencies in efficiencies could have been the way in which the columns were packed [93]. A poorly packed column gives a broad base width for an eluted peak whereas a properly packed column gives a small base width for the same eluted peak.

RESOLUTION

The columns that separated the three organophosphorus pesticides best were those with the supports C-750 (resolution of 4.51); CG-AW-DMCS (resolution of 3.85), Ultra-Bond 20m (resolution of 3.56) and CW-AW (resolution of 3.63). The three worst columns for separating the organophosphorus pesticides were those with the supports CP-NAW (resolution of 1.24), CG-HP (resolution of 2.01) and CP-AW (resolution of 2.20).

5.2.2 TAILING OF COLUMNS

All of the columns studied in this project showed some degree of tailing. Figure (22) gives the shape of peaks for Disyston at eight column temperatures. The shapes of these peaks were typical of those on other columns that gave tailing peaks. Altenau et al [97], in their temperature studies with a Carbowax 20m column, found similar shape peak patterns to those shown in Figure (22), for the solute n-pentane. The increase in symmetry of the

Disyston peak on C-750, as the column temperature increased, can be attributed to a decrease of adsorption of the pesticide on the support material. Therefore, the adsorptivity of the support material can be evaluated by using the tailing factor of the pesticide peaks [98].

The columns studied in this thesis are classified according to the degree of tailing obtained at a column temperature of 150 deg C for the pesticides Phorate and Disyston (Table (34)). There were four main categories. Group (a) includes supports that had the largest tailing factors (T.F. greater than 30), i.e., CP-AW-DMCS, CP-AW and CP-NAW. Group (b) includes supports that had medium tailing factors (T.F. between 30 and 18), i.e., CW-AW-DMCS and C-750. Group (c) contains supports that had small tailing factors (T.F. between 18 and 12), i.e., CG-HP, CW-NAW, Ultra-Bond 20m etc. Group (d) includes supports that had negligible tailing factors (T.F. less than 12), i.e., CG-NAW, CW-HP and CG-AW-DMCS.

The large tailing of the Chromosorb P supports was expected because of the greater number of active sites [18], and the greater surface area of this support [22] compared to the Chromosorb W and G supports.

The Chromosorb W supports showed inconsistent tailing factors. CW-AW-DMCS and C-750 were predicted, from the

TABLE (34) : Classification of Columns According to the Tailing Factor, at a Column Temperature of 150 deg C, for the Pesticides Phorate and Disyston.

<u>COLUMNS</u>	<u>PHORATE</u> <u>(TAILING FACTOR)</u>	<u>DISYSTON</u> <u>(TAILING FACTOR)</u>
(a) Large Tailing		
(*T.F. > 30)		
CP-AW-DMCS	too large	too large
CP-AW	100.9	83.3
CP-NAW	31.7	47.0
(b) Medium Tailing		
(18 < T.F. < 30)		
CW-AW-DMCS	27.3	29.7
C-750	25.0	28.3
(c) Small Tailing		
(12 < T.F. < 18)		
CG-HP	14.5	17.9
CW-NAW	14.1	15.6
Ultra-Bond 20m	13.3	15.5
CW-AW	12.5	13.75
CG-AW	12.2	12.3
(d) Negligible Tailing		
(T.F. < 12)		
CG-NAW	11.0	11.5
CG-AW-DMCS	10.8	10.8
CW-HP	10.3	10.5

* --> T.F. means tailing factor

literature, to be more inert than the Chromosorb W-NAW and W-AW supports. However, this was not the case in this study. One explanation for the unexpected tailing of the Chromosorb W supports (other than W-HP) could be breakage of the support particles during packing and, hence, exposure of more active sites leading to the increased tailing of the pesticides. Another explanation for the unexpected tailing of the Chromosorb W supports could be incomplete coverage of the support surfaces with liquid phase (Section 1.6.1 of Chapter 1).

The Chromosorb G supports were, overall, as a family, the best supports for inertness towards the organophosphorus pesticides. These supports have low surface areas and few active sites compared to the Chromosorb P supports. Also, because of their high density, Chromosorb G supports accept a higher amount of liquid phase on their surfaces than the Chromosorb W supports (Table (2) of Chapter 1). The combined desirable qualities of the Chromosorb P and Chromosorb W supports built into the Chromosorb G supports made them more inert towards the organophosphorus pesticides.

The best single support for inertness towards the pesticides (Table (34)) was the CW-HP.

5.2.3 CONCENTRATION EFFECTS

The chromatographic peak shapes can vary with the concentration of pesticides injected into the column. In our study it was found that the pesticide concentrations used in the ECD study were small enough so as to make tailing evident (Table (34)). On the other hand, the pesticide concentrations used in the FID study were large enough to overwhelm tailing. This phenomenon is described as a concentration effect. Figure (24A) shows the chromatograms for Phorate at two column temperatures, i.e., 130 and 140 deg C. The peaks obtained with the ECD detector and the FID detector, with relatively low and high concentrations, respectively, were placed opposite each other for easy comparison of the degrees of tailing. The concentration of Phorate used for the ECD analysis was 8.76 nanograms, and the concentration for the FID study was 3.50 micrograms (about 400 times larger than that for the ECD tests). This difference in Phorate concentration caused the differences in peak shapes [89], i.e., large tailing of peaks observed with the ECD detector, and symmetrical peaks observed with the FID detector.

Because the amount of Phorate used for the ECD study was so small, the adsorption effects of the support material in the column were detected by the very sensitive ECD detector.

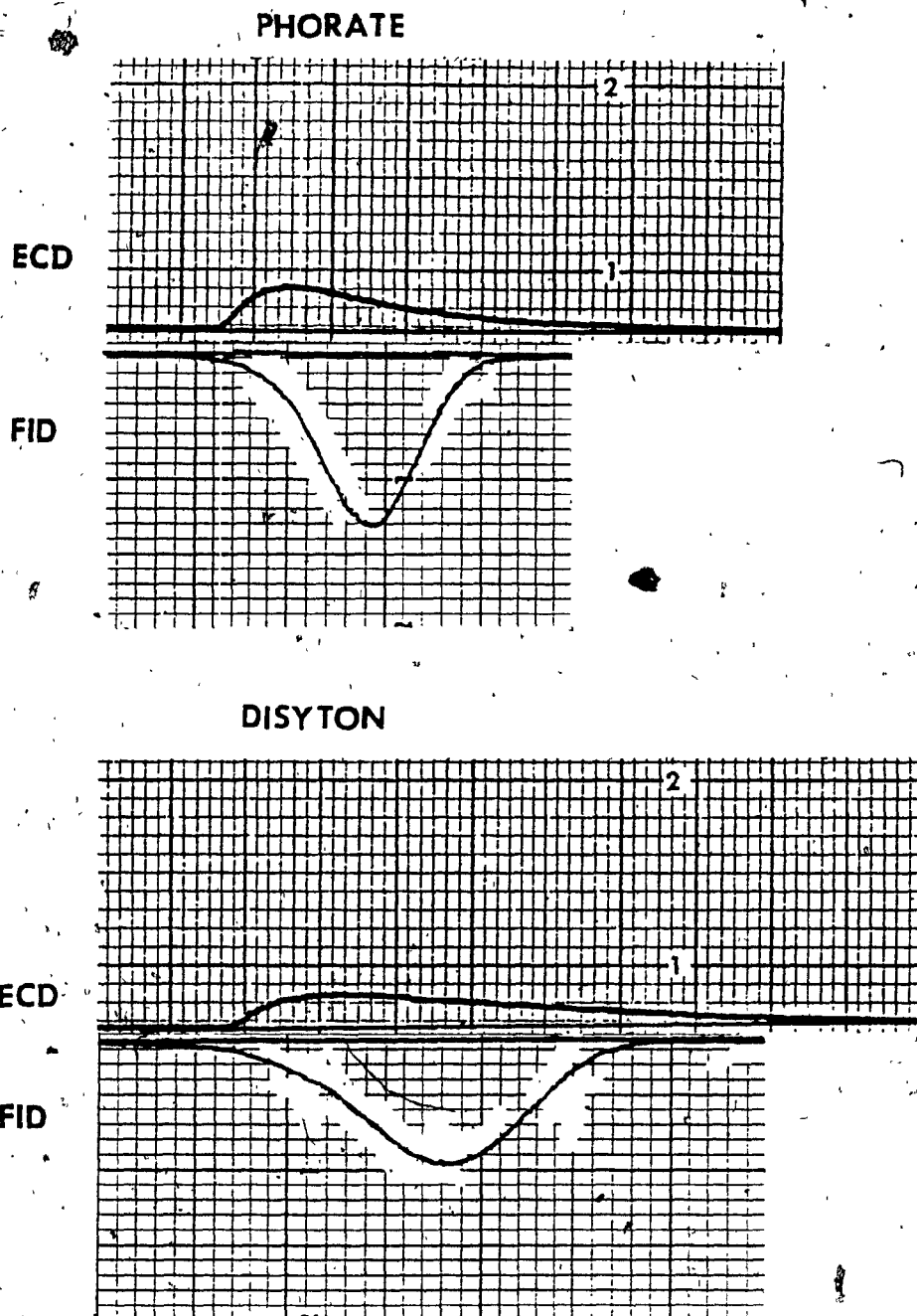
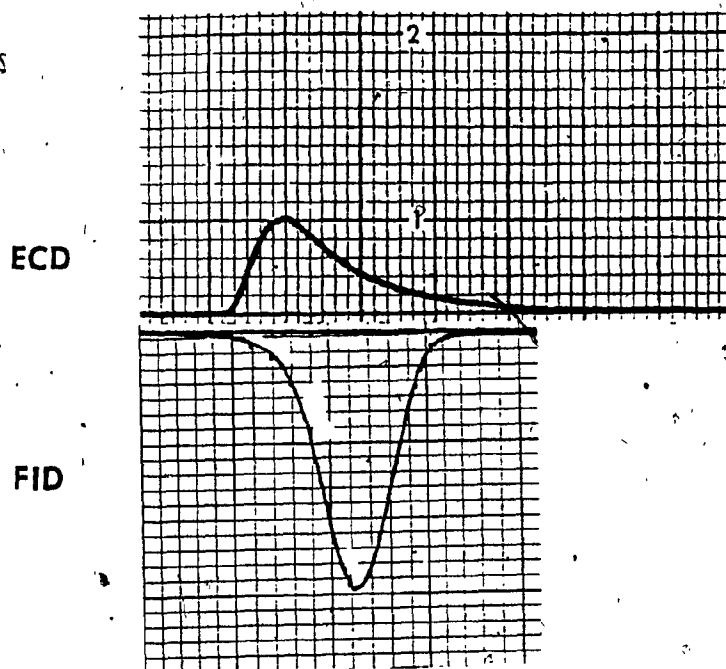


FIGURE (24A) : Chromatographic Peaks for Phorate and Disyston Showing Concentration Effects at a Column Temperature of 130 deg C. (8.76 ng/Phorate and 23.26 ng Disyston for the ECD Study; 3.50 μ g Phorate and 6.20 μ g Disyston for the FID Study.)

PHORATE

161



DISYSTON

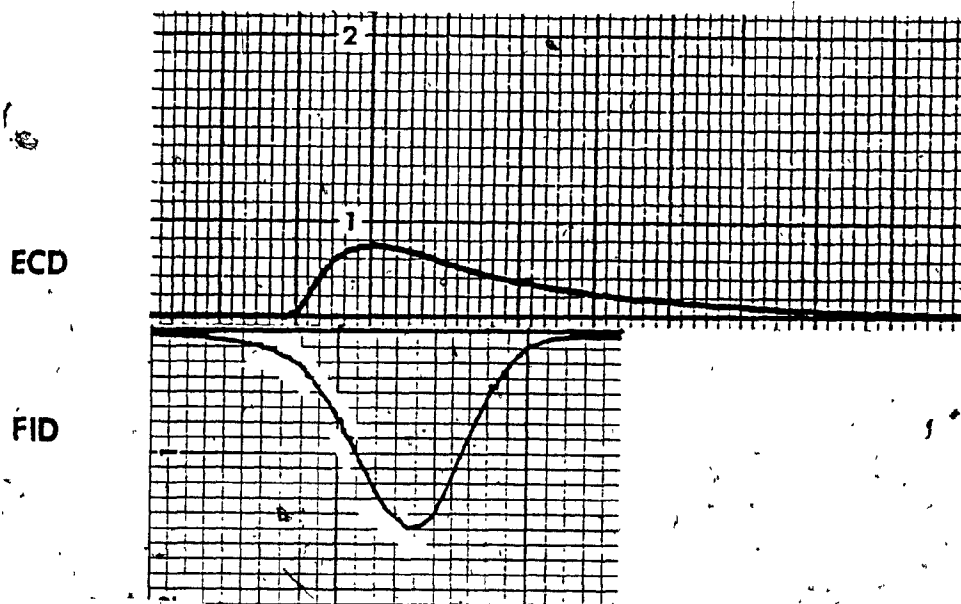


FIGURE (24B) : Chromatographic Peaks for Phorate and Disyston Showing Concentration Effects at a Column Temperature of 140 deg C. (8.76 ng Phorate and 23.26 ng Disyston for the ECD Study; 3.50 ug Phorate and 6.28 ug Disyston for the FID Study.

Knight, et al [98], found in their study of the chromatographic behaviour of water that the best way of reducing tailing was to avoid the concentration region where the adsorption isotherm is strongly curved. Also, undesirable tailing effects could sometimes be overcome by priming the column with compounds that were similar to the compounds to be analyzed. This factor could have decreased the tailing observed for the ECD results in Figure (24A) if it had been carried out.

A similar explanation holds for the chromatographic peaks for Disyston (Figure (24B)).

5.3.0 CONCLUSIONS

Only the results of analyses with the ECD were used to obtain a measure of the performances of the columns studied.

The two main factors that contributed to the performances of the columns were, (a) the amount of liquid phase present in the column, and (b) the way in which the columns were prepared and packed. The degree of tailing of peaks on the columns affected the accuracy of interpretation of results.

The category of supports that performed best overall were the Chromosorb G supports. These supports were among

the best in terms of good efficiency, good resolution, and small tailing. The best Chromosorb G support was the CG-AW-DMCS.

The support that individually performed the best was the CW-HP support. This support should be the first choice for the analysis of organophosphorus pesticides.

From this study the Chromosorb P supports should not be used for the analysis of organophosphorus pesticides because of the large tailing observed.

If the Chromosorb W supports are to be used for organophosphorus pesticide analysis, then, a better method should be used for packing these supports. Because of the high percentage of breakage of these supports during packing in the column, very inconsistent results were obtained with them. The CW-HP support was very good, while the other Chromosorb W supports were relatively poor according to T.F. data. One could conclude, then, that the CW-HP support is more friable than the other Chromosorb W supports.

CHAPTER

6

HEATS OF ADSORPTION

6.1.0 OBSERVATIONS AND RESULTS

The relative retention times for the pesticides chromatographed were obtained as described in Figure (21) in Chapter 5. Using these RRT the specific retention volumes (V_g) were calculated according to equation (12) of Section 1.9 in Chapter 1.

For each column studied a graph was plotted based on equation (31) of Section 1.10 in Chapter 1, i.e., $\log (V_g)$ versus the inverse of column temperature. Figure (25) represents a typical plot for the pesticide Phorate.

It can be seen from Figure (25) that there are two slopes in the graph. The slope AB was used to calculate the heat of adsorption (ΔH^{AB}) of Phorate on the column, between the column temperatures of 130 and 190 deg C. The slope BC was used to calculate the heat of adsorption (ΔH^{BC}) of Phorate on the column between the column temperatures of 190 and 230 deg C. Similar calculations were done for the other columns for the three organophosphorus pesticides. Table (35) lists the heats of adsorption for the twelve columns, and Table (36) list the heats of adsorption for the seven runs on the CW-AW column.

/ PHORATE

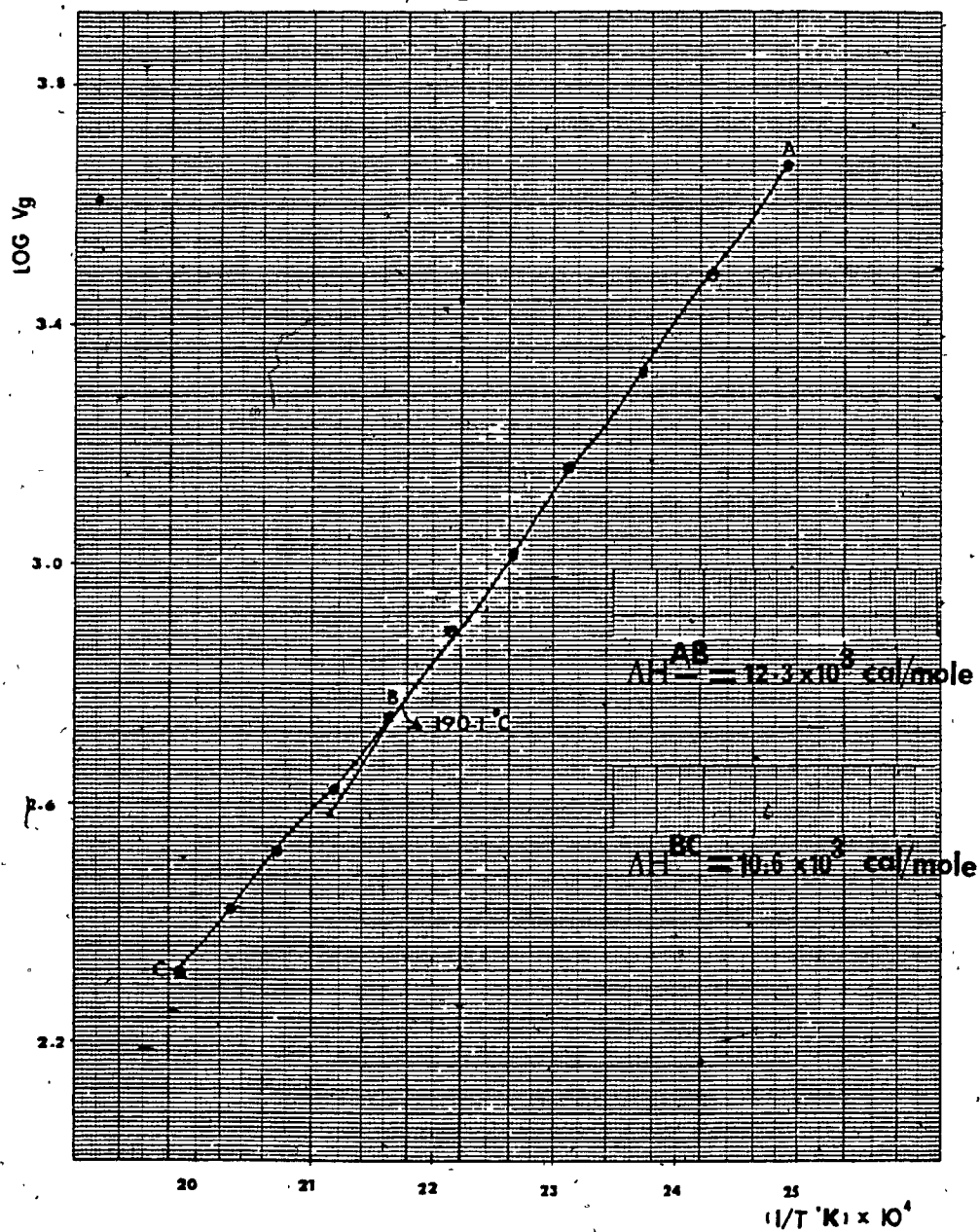


FIGURE (25) : A Plot of the Logarithm of V_g (ml/gm) Versus the Inverse of Column Temperature. (deg K) for Phorate Using the Column with CW-HP Support.

TABLE (35) : Heats of Adsorption (ΔH^{AB} and ΔH^{BC})* for Phorate, Disyston and Malathion.

COLUMN	PHORATE		DISYSTON		MALATHION	
	ΔH^{AB}	ΔH^{BC}	ΔH^{AB}	ΔH^{BC}	ΔH^{AB}	ΔH^{BC}
CW-NAW	13.0	10.9	14.4	12.1	a	a
CW-AW	13.1	11.1	14.3	12.5	16.8	14.5
CW-AW-DMCS	13.8	10.5	15.0	11.4	18.3	13.7
CW-HP	12.7	10.6	14.7	12.2	15.6	12.7
C-750	14.3	11.2	15.2	12.6	15.5 **	15.5
CG-NAW	13.8	12.1	14.6	12.8	a	a
CG-AW	13.8	12.0	14.3	13.5	a	a
CG-AW-DMCS	13.4	11.5	14.4	12.3	16.2	14.3
CG-HP	16.3	11.8	15.2	12.8	15.6 **	15.6
CP-NAW	14.4	12.2	16.8	13.0	14.0 **	14.0
CP-AW	16.1	11.9	17.7	13.0	a	a
CP-AW-DMCS	19.6	11.3	22.8	14.3	a	a

a → Completely Adsorbed - no peak

* → ΔH^{AB} and ΔH^{BC} values are negative with units of kcal/mole

** → No Change in Slope

TABLE (36) : Heats of Adsorption (ΔH^{AB} and ΔH^{BC})* for Phorate, Disyston, Disyston and Malathion on a Column With CW-AW Support (Seven Runs).

COLUMN	PHORATE		DISYSTON		MALATHION	
	ΔH^{AB}	ΔH^{BC}	ΔH^{AB}	ΔH^{BC}	ΔH^{AB}	ΔH^{BC}
1st Run	13.3	11.4	14.3	12.9	17.1	15.2
2nd Run	13.3	11.7	13.9	12.3	17.1	15.6
3rd Run	13.1	11.1	14.3	12.5	16.8	14.5
4th Run	13.5	11.1	14.6	11.7	19.2	14.3
5th Run	13.9	10.9	14.9	12.1	17.2	14.0
6th Run	18.0	11.2	19.2	12.4	19.9	19.9 **
7th Run	18.7	11.8	17.9	12.4	21.1	21.1 **

* \rightarrow ΔH^{AB} and ΔH^{BC} values are negative with units of kcal/mole \downarrow

** \rightarrow No Change in Slope

6.2.0 DISCUSSION OF RESULTS

The liquid phase, OV-1, used in this project was a solid both at room temperature and at elevated temperatures (310 deg C). For solid 'liquid phases', the slopes of the graph shown in Figure (25) are as expected [99,100,101]. Guran et al [101] found that when the solid, AgHgI_4 , was used as a support in GSC analysis, there was a solid-solid change, i.e., the AgHgI_4 solid changed from a yellow powder to an orange powder at 51 deg C. The change from one solid to another solid was usually accompanied by a point of inflection in the plot of $\log(V_g)$ versus inverse column temperature (e.g., point B in Figure (25)). Hradil [100] also observed plots similar to Figure (25) for the solid 'liquid phase' Poly(2-hydroxyethylmethacrylate). He attributed the inflection point of the plot to the glass transition temperature of the polymer. Purnell [99], in a general discussion, attributed the shape of graphs such as that in Figure (25) to the solid-solid transition of the stationary phase.

Since the pesticides were separated on a solid stationary phase (OV-1) there was adsorption taking place rather than partition. Hence, the heats calculated from Figure (25) were called heats of adsorption.

Figure (25) indicates that there was greater adsorption.

of the pesticides on the stationary phase at lower column temperatures (greater slope AB) than at higher column temperatures (smaller slope BC). At lower column temperatures the stationary phase OV-1 was a compact solid whereas at higher column temperatures it was a swollen solid. The change from a compact solid to a swollen solid can be the reason for the inflection point at B in Figure (25). Furthermore, the swollen solid would have more solution properties and less adsorption properties for the pesticides. Hence, the decreased slope for BC in Figure (25). The heat of adsorption for BC, (ΔH^{BC}) was always less than the heat of adsorption for AB, (ΔH^{AB}).

From Tables (35) and (36) it was clear that, generally, Malathion had the highest heat of adsorption, followed by Disyston and then Phorate. These results were not surprising since it was established in Chapter 4 that Malathion had the lowest diffusivity through the liquid phase, followed by Disyston and then Phorate [102]. This lower diffusivity of Malathion through the OV-1 liquid phase caused it to be retained longer on the column and hence it experienced greater adsorption by the support material.

No consistent correlation could be obtained between the detector response (peak areas) and the heats of adsorption in Table (35) for the columns studied using organophosphorus pesticides.

A plot of V_g versus column (Figure (26)) showed that the mechanism for retention volumes did not depend only on the stationary phase OV-1, but also on adsorption of the pesticide on the support material. If adsorption of the phase had been the only means by which the pesticides were retained on the column, then the specific retention volumes would have been the same for all the columns [94]. However, this was not the case and hence adsorption of the pesticides on the support material was also taking place. Tailing of all the columns, as discussed in Chapter 5 (Section 5.2.2), reinforces this fact.

The data in Table (36) for the seven runs of pesticides on the column with CW-AW support give a general indication that adsorption of the pesticides on the CW-AW support did occur. Adsorption was more pronounced for the 5th, 6th and 7th runs as shown by their increasing heats of adsorption, i.e., for Phorate the (ΔH^{AB}) for the 5th, 6th and 7th runs were 13.9, 18.0 and 18.7 kcal/mole, respectively. These increased heats of adsorption also corresponded with the increased tailing observed for the 5th, 6th and 7th runs on this column (Section 4.2.2 of Chapter 4). Also, the heats of adsorption for the first three runs on this column were almost constant. The average (ΔH^{AB}) for Phorate was 13.2 kcal/mole, for Disyston 14.1 kcal/mole, and for Malathion 17.0 kcal/mole. The tailing factors for the first three runs on this column were also approximately constant

(Section 4.2.2 of Chapter 4). These facts for the first three runs on this column indicate that there was not much change in the number of active sites which caused adsorption and tailing of the pesticides.

6.3.0 CONCLUSIONS

Of the three organophosphorus pesticides tested, Malathion showed the greatest amount of adsorption for the column supports, based on the (ΔH^{AB}) values. Disyston was adsorbed less than Malathion on the support materials, but more than Phorate.

The (ΔH^{AB}) values for each pesticide were not very different for the different columns (Tables (35) and (36)). Phorate had an average (ΔH^{AB}) of 11.4 kcal/mole, Disyston had an average value of 12.7 kcal/mole, and Malathion had an average value of (ΔH^{AB}) of 13.8 kcal/mole for the twelve columns in Table (35).

If the (ΔH^{AB}) values indeed give an indication of the amount of adsorption by a support for the pesticides, then the columns with the Chromosorb P supports were the most adsorptive. Table (35) shows that the Chromosorb P supports have unusually high (ΔH^{AB}) values. For example, for Phorate, the columns with CP-NAW, CP-AW and CP-AW-DMCS had (ΔH^{AB}) values of 14.4, 16.1 and 19.6 kcal/mole, respectively.

The average (ΔH^{AB}) for Phorate was 13.8 kcal/mole for the other columns in Table (35). Again the Chromosorb P supports proved to be poor for the analysis of organophosphorus pesticides.

CHAPTER

7

GENERAL CONCLUSIONS

The overall rank for the three sample concentrations tested ('High Concentration', 'Medium Concentration', and 'Low Concentration') of organophosphorus pesticides on the columns made with the diatomaceous supports were as follows:

(a) For the columns made with the Chromosorb W family of supports, the decreasing order of response was,

CW-HP > CW-AW-DMCS > CW-AW > CW-NAW > C-750

(b) For the columns made with the Chromosorb G family of supports, the decreasing order of response was,

CG-AW > CG-HP > CG-AW-DMCS > CG-NAW

(c) For the columns made with the Chromosorb P family of supports, the decreasing order of response was,

CP-AW > CP-NAW > CP-AW-DMCS

The column that performed the best when response, tailing, efficiency and resolution were taken into consideration, was the CW-HP column. The worst column based on the above considerations was CP-NAW.

The temperature study of organophosphorus pesticides showed that the factors that contributed to the variation of

detector responses that were observed were:

(a) the adsorption of the support materials,

(b) the priming of the columns with the pesticides used as test samples,

and,

(c) the bleeding of the stationary phase used (OV-1).

Using moderate concentrations of pesticides, all supports studied showed some degree of tailing. The Chromosorb P supports had the highest tailing factor, thus indicating that these supports had more active sites than the other two Chromosorbs (G and W). The Chromosorb G supports showed the least tailing and hence were the least adsorptive. Some of the specific supports that gave almost symmetrical peaks were CG-NAW, CG-AW and CW-HP.

Of the three organophosphorus pesticides tested, Malathion showed the highest degree of adsorption for the support materials used (the larger the tailing factor the greater the adsorption of the column). Disyston showed medium adsorption and Phorate showed the least adsorption. It could be suggested from these results that Malathion had the slowest diffusivity through the liquid phase (OV-1), and

hence, it resided longer on the support material and was therefore adsorbed the most.

Since tailing was observed for all of the columns tested with organophosphorus pesticides, there must have been at least three mechanisms contributing to the relative retention times and responses observed (i.e., (i) adsorption of the stationary phase (OV-1), (ii) adsorption on the support material, and (iii) interfacial adsorption). Therefore, the heats of adsorption (ΔH^{AB}) and (ΔH^{BC}) discussed in Chapter 6 could not be used to interpret adsorption on the support material only. Rather, this data must have been representative of three of the forms of adsorption.

The multimaxima observed in the FID detector thermograms can be attributed to bleeding of the liquid phase which created new active sites which were subsequently primed with the pesticide samples. With this detector, less adsorptive effects were evident compared to what was observed with the ECD detector since much more concentrated pesticides were used for the FID tests.

The response of the ECD detector was affected as well by the bleeding and repriming process described above for the FID tests. In addition, response of the ECD was reduced when liquid phase bleeding took place. The reduced response was attributed to a competitive removal of electrons

by the liquid phase and the pesticides in the detector cell. At column temperatures above that at which a response maxima was observed on the ECD thermograms, the liquid phase bleed increased almost exponentially with an increase in column temperature. Hence, exponential decreases in response for the pesticides after the thermogram maxima were observed.

No correlation could be obtained between the ECD and FID response data for organophosphorus pesticides. This was not surprising since these detectors operate on different principles and therefore varying experimental conditions affect them differently. However, the thermograms for Lindane had similar shapes with both detectors. This similarity in response can be explained if it is assumed that Lindane reacted with the liquid phase in the column, and if the OV-17 liquid phase did not bleed sufficiently at the column temperatures investigated to affect the ECD responses.

It was found that a column with 3.5% (W/W) QV-1 on CW-AW support began to deteriorate after about the fourth chromatographic run with the organophosphorus pesticides. Increased tailing factors and relative retention times were used as criteria for deciding when a column started to deteriorate. This conclusion should apply to the other columns studied in this thesis.

Theoretically, if all experimental variables are kept constant, and only the column temperature is changed, then, the peak area for a pesticide should be the same at all temperatures (irrespective of peak shape). However, this hypothetical situation was never realized in the GLC tests carried out in this project. The so called 'fixed experimental variables' were actually varying with temperature (e.g., column bleeding). Hence, the pesticides' peak area varied with column temperature.

CHAPTER

8

SUGGESTIONS FOR FUTURE RESEARCH WORK

In Chapter 3 it was concluded that one of the factors that reduced the ECD response for the organophosphorus pesticides was bleeding of the liquid phase. This reduction in response was argued to be due to a competition between the bleeding liquid phase and the pesticides for the electron population present in the detector. It is possible that if a greater electron concentration was present in the detector, sufficient electrons would be present for complete interaction with the pesticides leading to higher responses. This hypothesis could be tested by increasing the electron population in the detector perhaps by reduction of the time interval between pulses.

In projects where more than one kind of detector must be used because of instrument availability limitations, the same concentration of test compounds should be used in all cases. In this way effects due to differences in concentration will be eliminated and a better comparison will be obtained between results with different detectors. These detectors should be part of the same instrument so that the same extra-column effects will be encountered.

An investigation should be carried out to determine the amount of liquid phase actually lost from the type of column studied in this thesis. This could be done by preparing ten columns, doing one run on the first, two runs on the second, and so on. The packing from the first few

inches of each column should then be removed and the liquid phase recovered by extraction using a soxhlet apparatus. A plot of liquid phase loss versus the number of runs would give an indication of the rate of deterioration of the columns. The reason for testing the first few inches of packing is that liquid phase is lost at a faster rate from the inlet part of the column than from the outlet part of the column [103].

To determine if Lindane does in fact react with OV-17 liquid phase, an experiment could be carried out to extract the liquid phase from the packing after Lindane analysis. The residue from the extract should then be analyzed for traces of Lindane or its by-products.

The liquid phases OV-1, OV-101 and SE-30 are all polydimethylsilicones with different molecular weights. As the molecular weights of the polydimethylsilicones increases, their viscosity increases. OV-101 has the lowest viscosity, SE-30 has medium viscosity, and OV-1 is a solid. From this thesis and the publications by Lindgren et al [36], there are indications that the viscosity of the liquid phases determines how fast the organophosphorus pesticides diffuse into and out of them. The higher the viscosity of a liquid phase the slower the rate of diffusion through it. OV-1, therefore, should have the slowest rate of diffusion for the organophosphorus pesticides. The diffusion rates

for these three phases should be studied since the slower the diffusion rate, the greater the possibility for adsorption of the pesticides on the support. The tailing factor can be used to determine the degree of adsorption.

To obtain a true comparison of the adsorptive effects of different support materials, columns should be made with bare support (no liquid phase coated on the support). In this way a better correlation could be made between adsorption of supports and detector response of pesticides. Also, a better correlation could be obtained between tailing factor and adsorptive effects.

GLOSSARY OF SYMBOLS

- A - Area of a chromatographic peak
- A_i - Total Surface Area where Interfacial Adsorption Takes Place
- A_s - Total Surface Area where the Adsorption Takes Place on the Support.
- CG - Chromosorb G
- CG-AW - Chromosorb G Acid Washed
- CG-AW-DMCS - Chromosorb G Acid Washed and Dimethyldichlorosilanated
- CG-HP - Chromosorb G High Performance
- CG-NAW - Chromosorb G Non-Acid Washed
- CP - Chromosorb Pink
- CP-AW - Chromosorb Pink Acid Washed
- CP-AW-DMCS - Chromosorb Pink Acid Washed and Dimethyldichlorosilanated
- CP-NAW - Chromosorb Pink Non-Acid Washed
- CW - Chromosorb White
- CW-AW - Chromosorb White Acid Washed
- CW-AW-DMCS - Chromosorb White Acid Washed and Dimethyldichlorosilanated
- CW-HP - Chromosorb White High Performance
- CW-NAW - Chromosorb White Non-Acid Washed
- C-104 - Chromosorb 104
- C-750 - Chromosorb 750
- D - Dual Column

deg. C	- Degree Centigrade
deg. ^o F	- Degree Farenheit
ECD	- Electron Capture Detector
F_c	- Flow Rate of Carrier Gas
FID	- Flame Ionization Detector
f	- Correction Factor for the Pressure Gradient in the Column
GC	- Gas Chromatography
GLC	- Gas Liquid Chromatography
GSC	- Gas Solid Chromatography
H	- Height Equivalent to a Theoretical Plate
ΔH^{AB}	- Heat of Adsorption Between the Column Temperatures A and B
ΔH^{BC}	- Heat of Adsorption Between the Column Temperatures B and C
ΔH_a	- Heat of Adsorption
h	- Height of a Chromatographic Peak
I_0	- Standing Current of the Electron Capture Detector
k	- Coefficient of Electronic Adsorption
K_I	- Partition Coefficient for Interfacial Adsorption
K_s	- Partition Coefficient for the Solid Support
K_1	- Partition Coefficient
LD (50)	- The Dose of Pesticide Required to Kill 50% of the Population of Test Animals

- n - Number of Theoretical Plates of a Column
- ng - Nanogram
- o.d. - Outside Diameter
- PDMS - Polydimethylsilicone
- pg - Picogram
- psig - Pounds per Square Inch on Guage
- R - Resolution
- Response - Chromatographic Peak Area
- RRT - Relative Retention Time
- S - Single Column
- SS - Stainless Steel
- T_c - Column Temperature
- T.F. - Tailing Factor
- T.M. - Thermogram Maximum
- u - Recorder Chart Speed
- V - Retention Volume
- V_g - Specific Retention Volume
- V_L - Volume of Stationary Phase
- V_R^o - Net Relative Retention Volume
- W - Weight of Stationary Phase
- μg - Microgram
- μl - Microlitre

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APPENDIX (I)

Thermograms for the 2nd Run of Columns
Tested Using the Electron Capture Detector

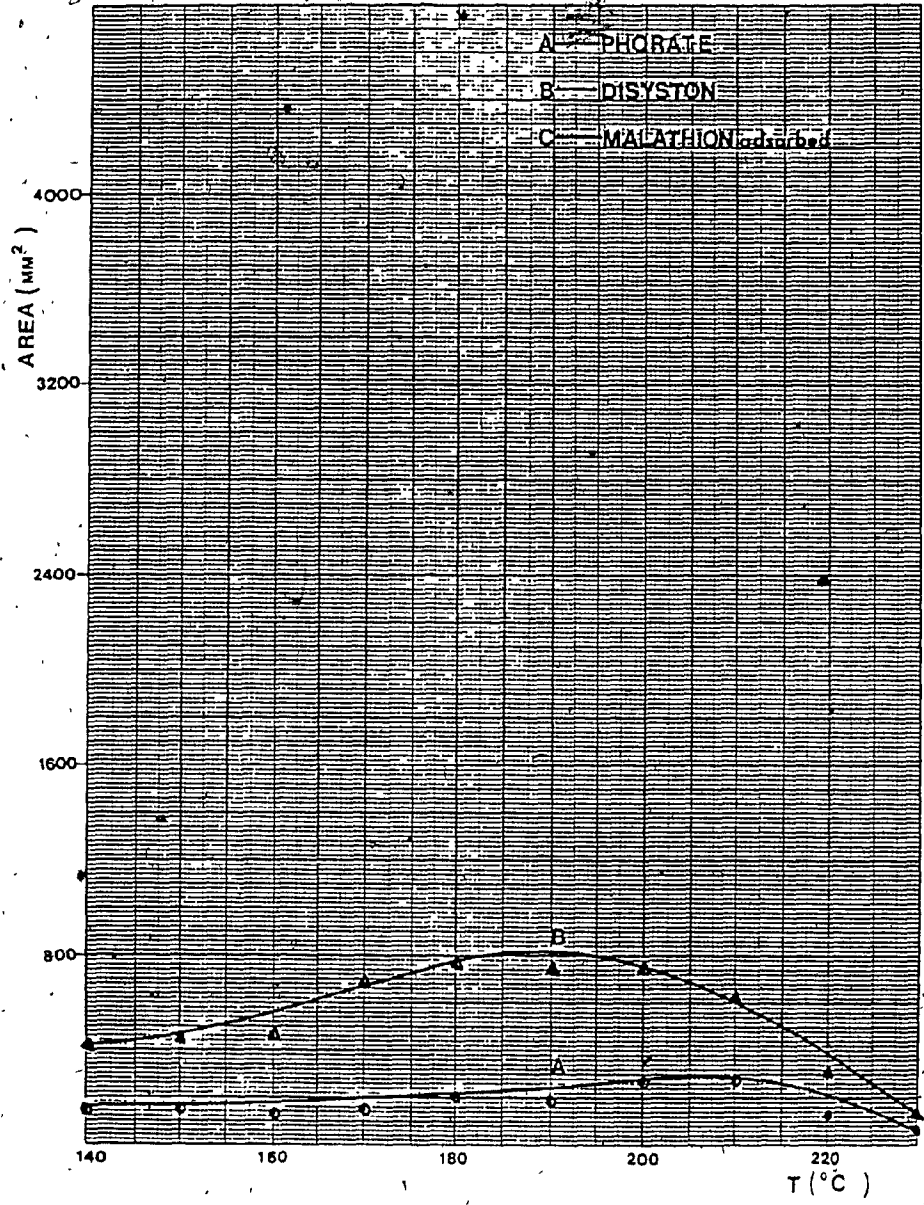
IDENTIFICATION OF THERMOGRAMS

- 1 - CW-NAW
- 2 - CW-AW
- 3 - CW-AW-DMCS
- 4 - CW-HP
- 5 - C-750
- 6 - CP-NAW
- 7 - CP-AW
- 8 - CP-AW-DMCS
- 9 - CG-NAW
- 10 - CG-AW
- 11 - CG-AW-DMCS
- 12 - CG-HP
- 13 - Ultra-Bond-20m*

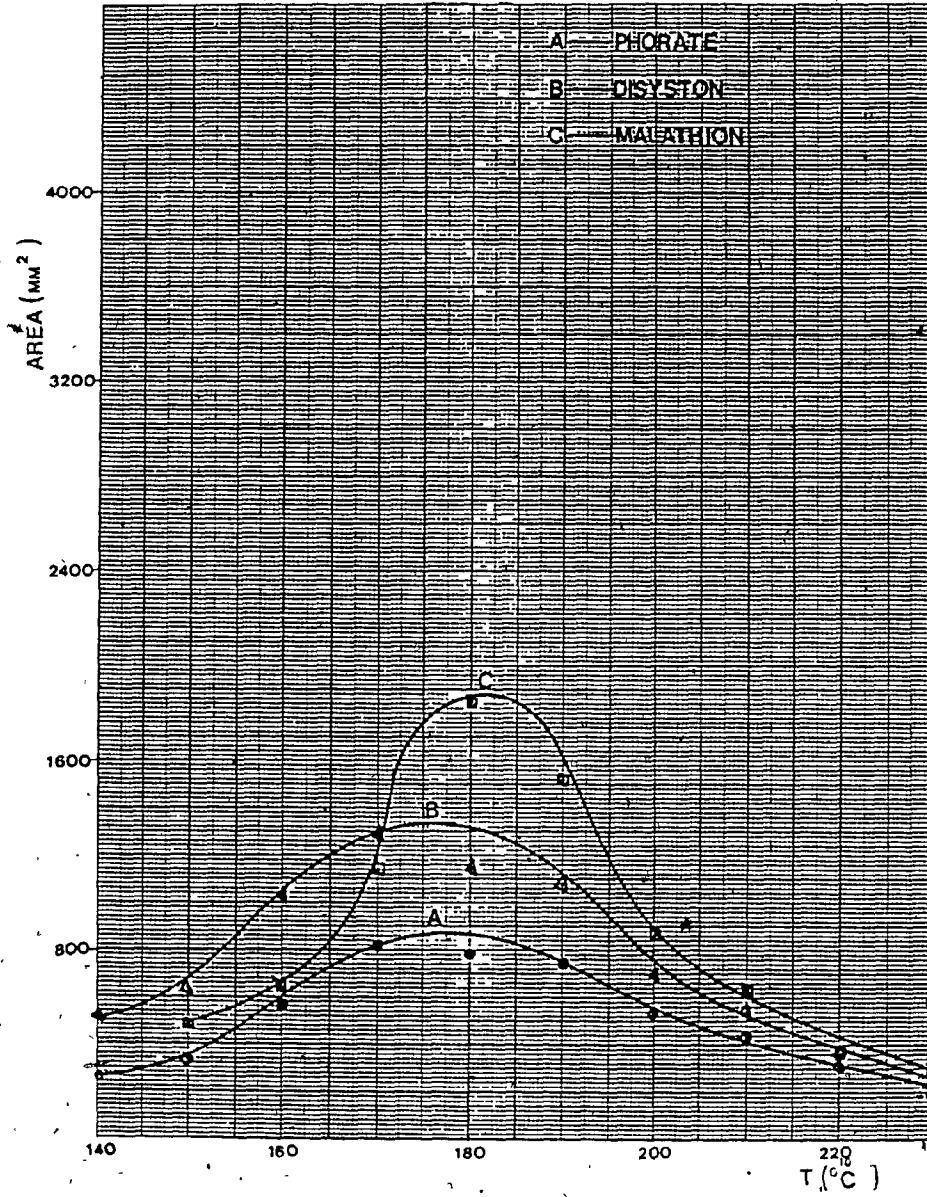
* --> not done to same scale as Thermograms 1 to 12

Note: The Curves A, B and C are the Thermograms for Phorate (8.8 ng), Disyston (23.3 ng), and Malathion (11.9 ng), respectively.

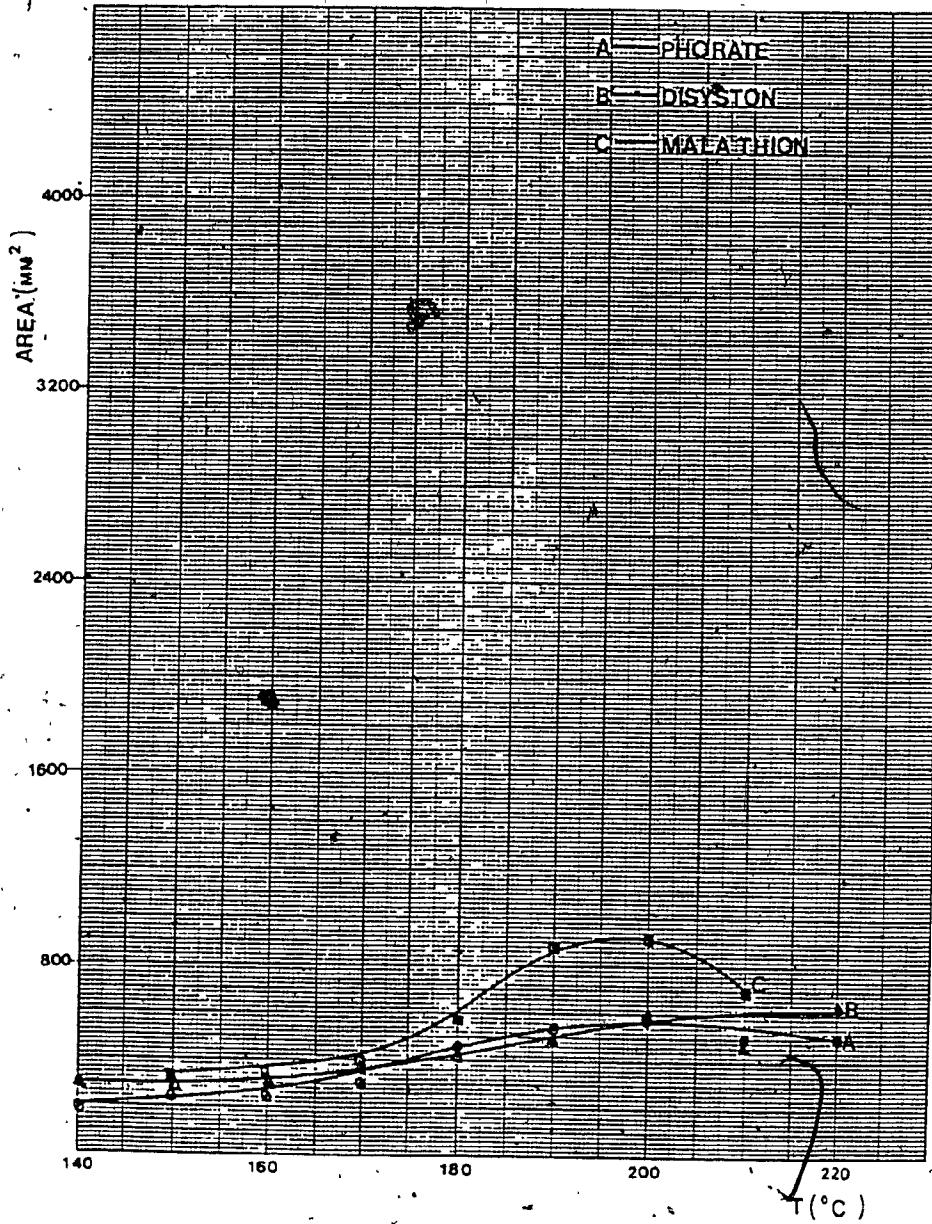
CW-NAW



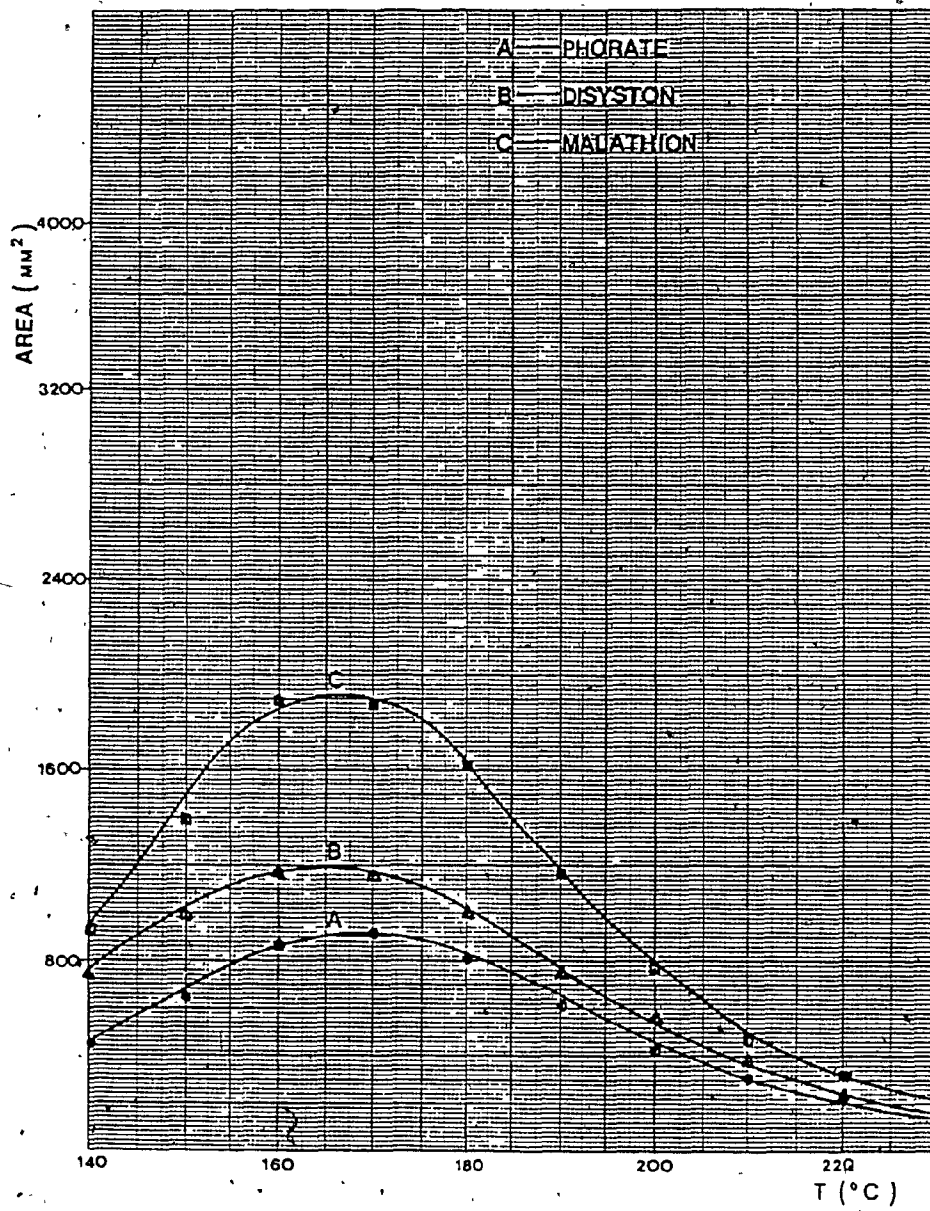
CW-AW



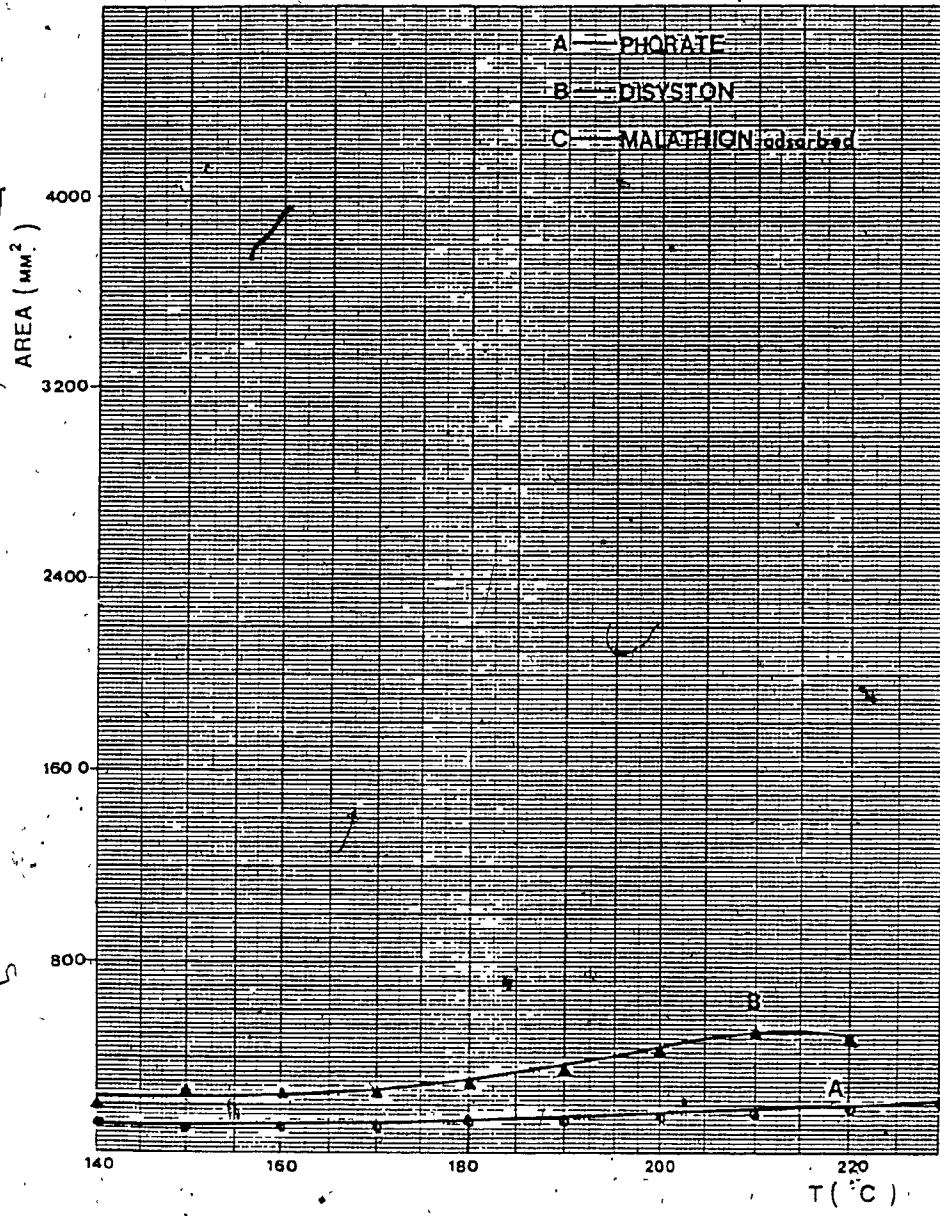
CW - AW - DMCS



CW-HP

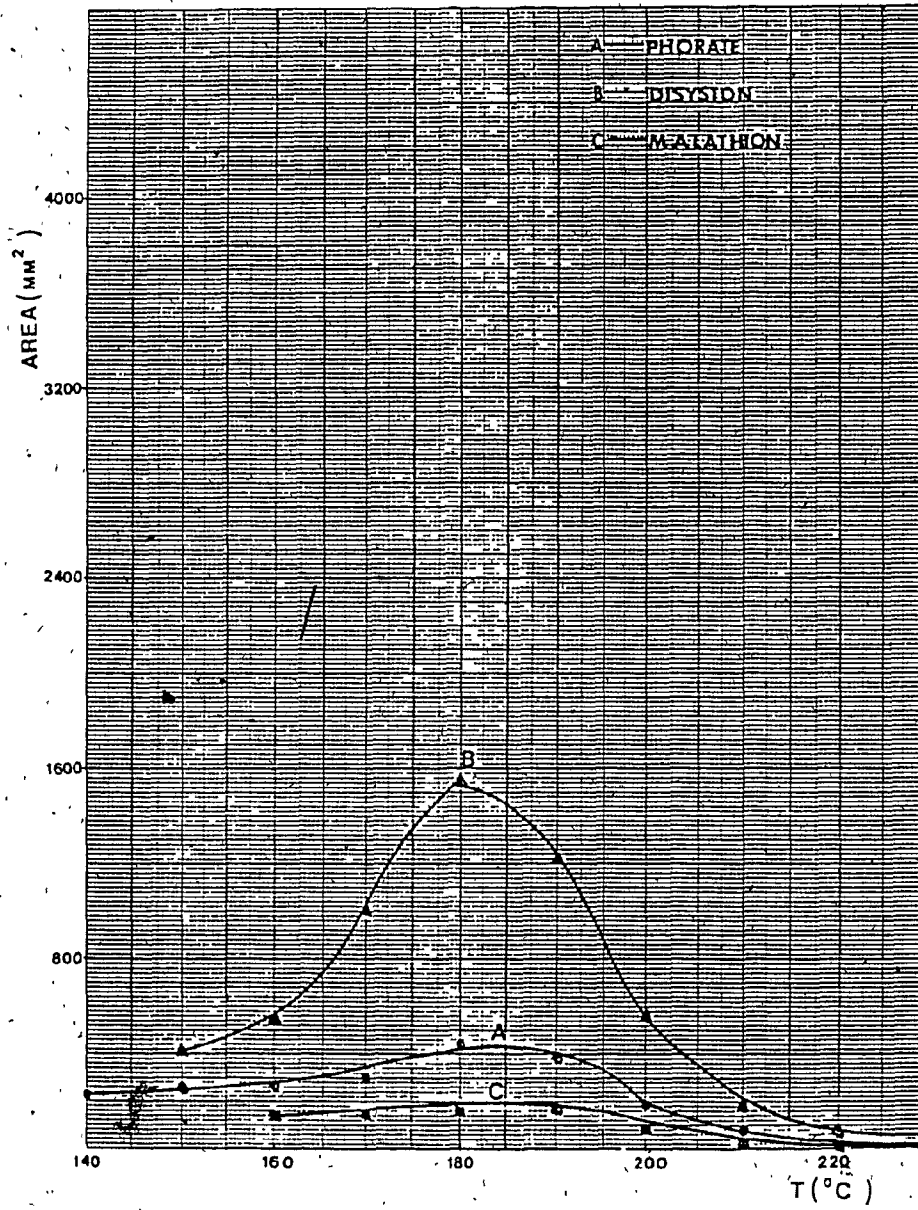


C-750

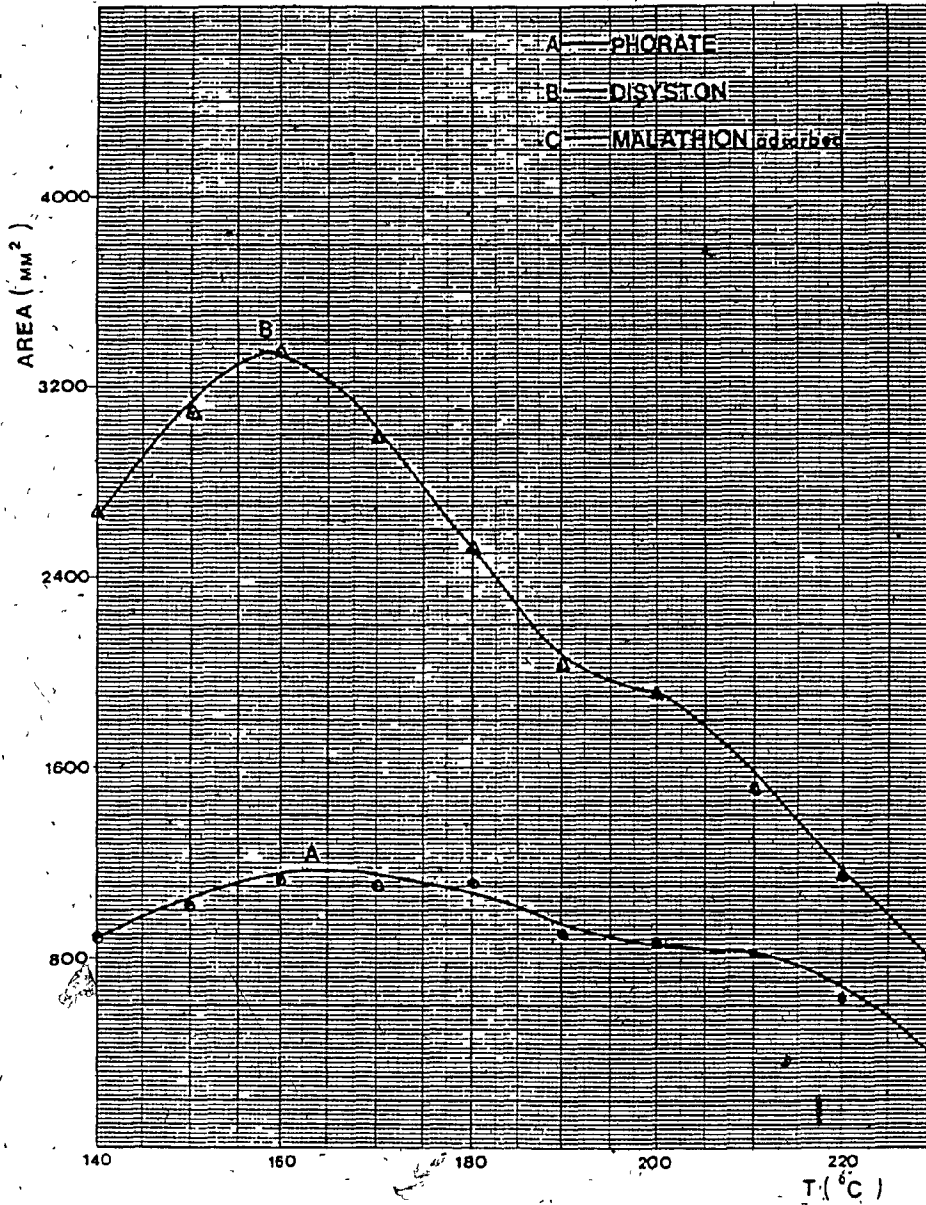


5

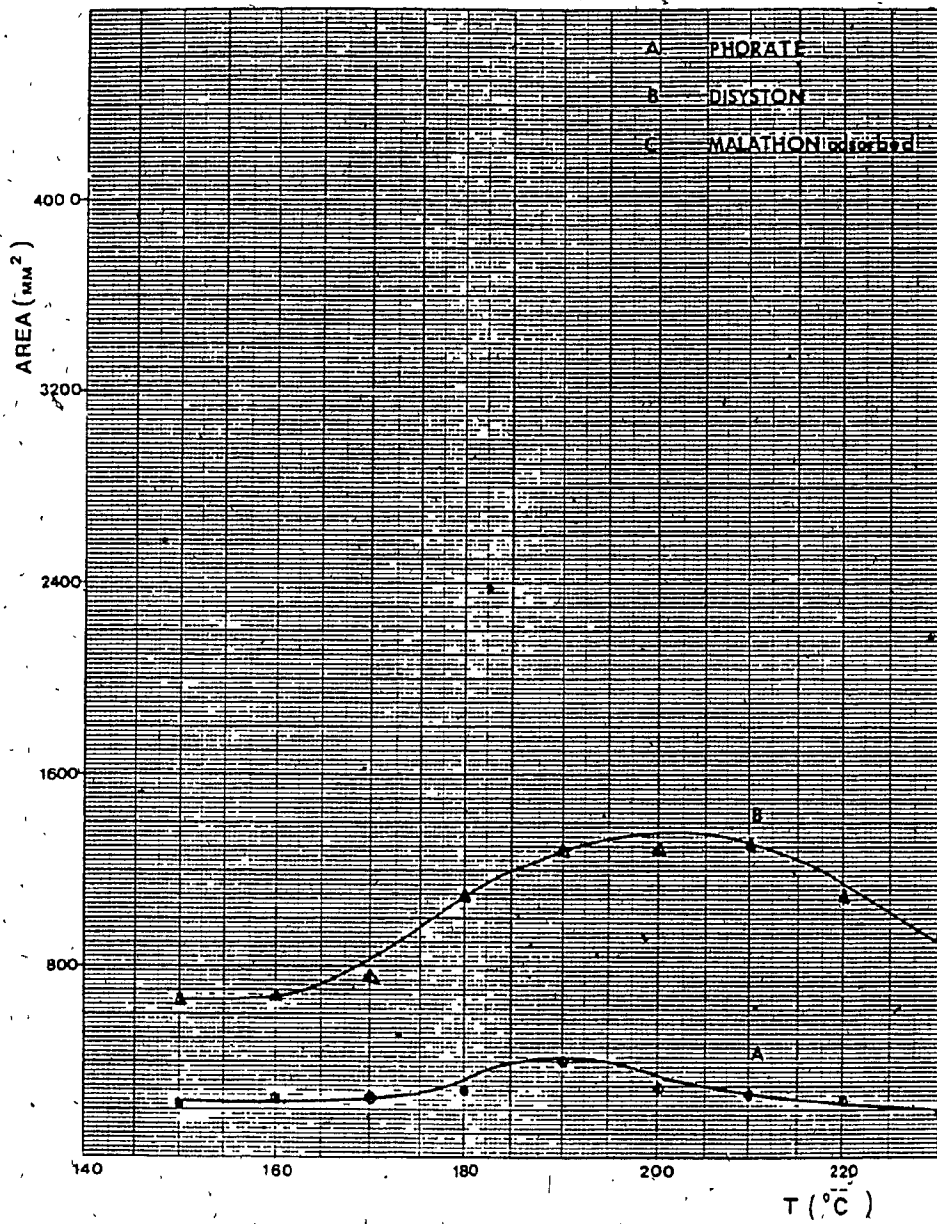
CP-NAW



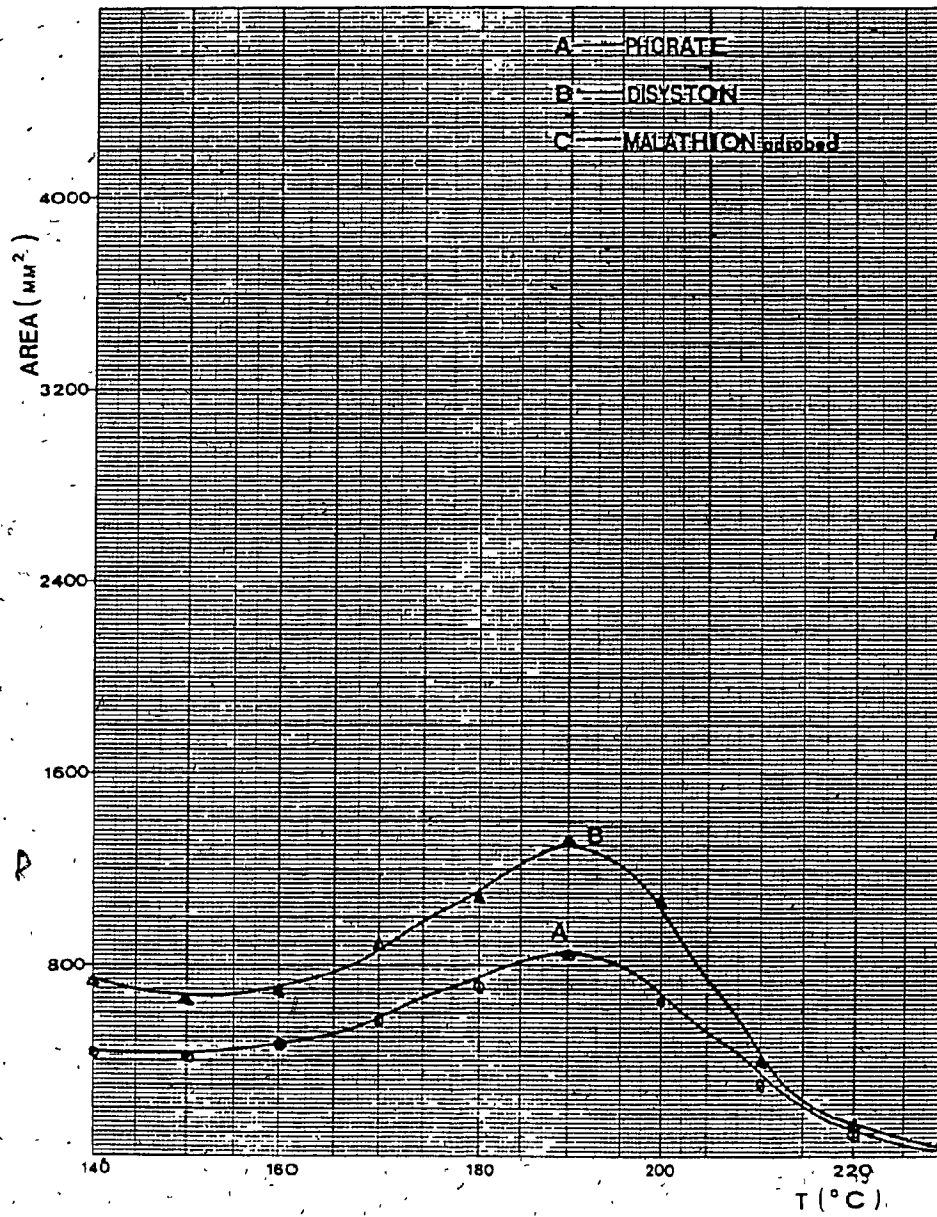
CP - AW



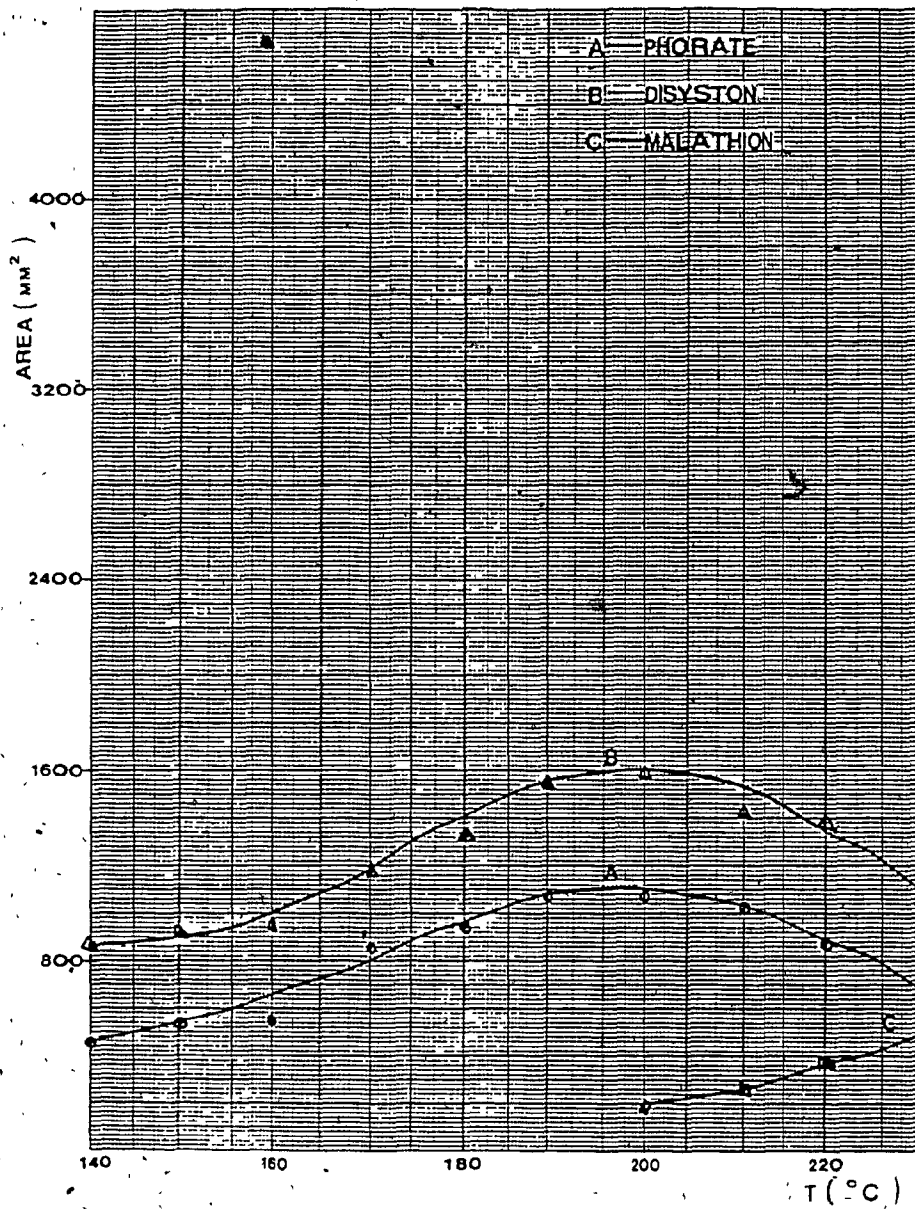
CP-AW-DMCS



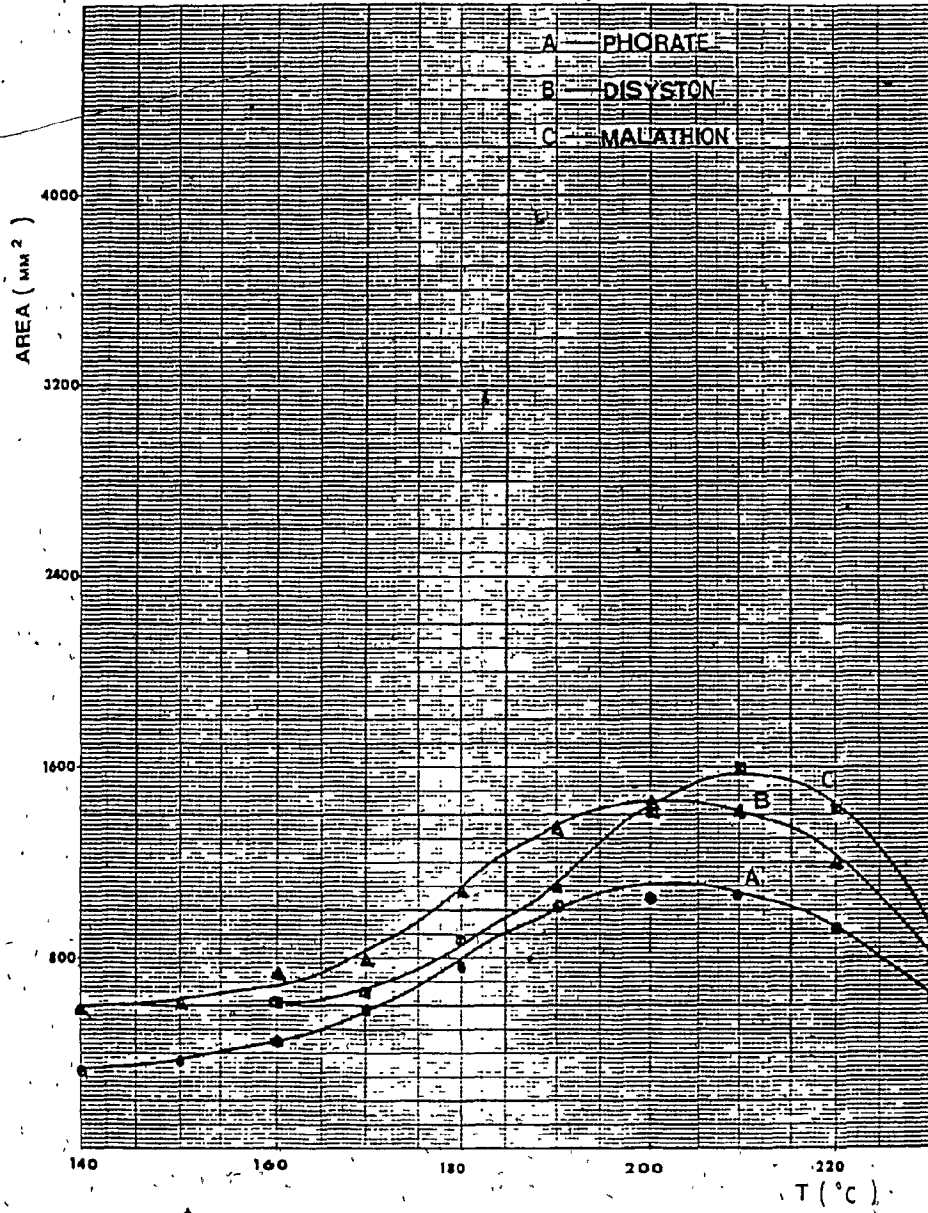
CG - NAW



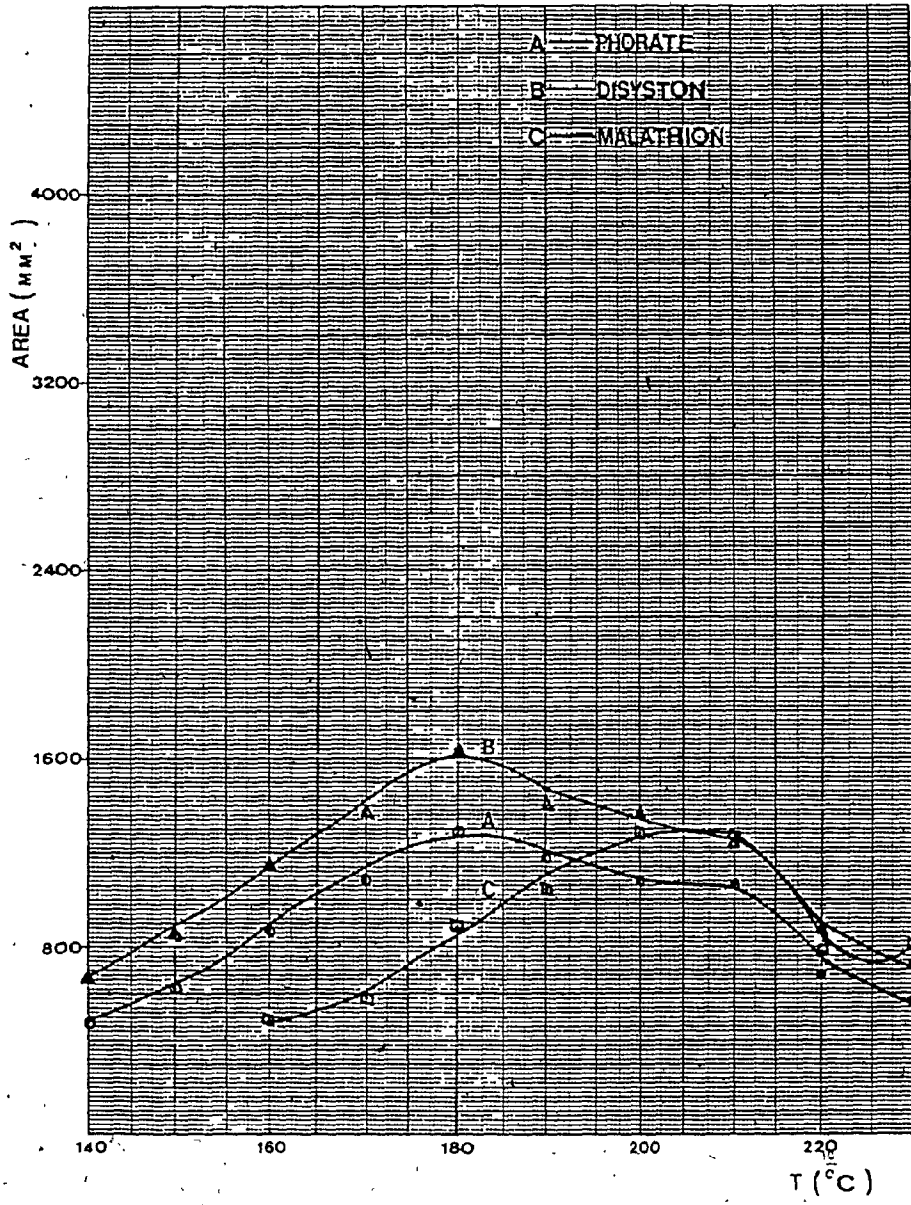
CG-AW

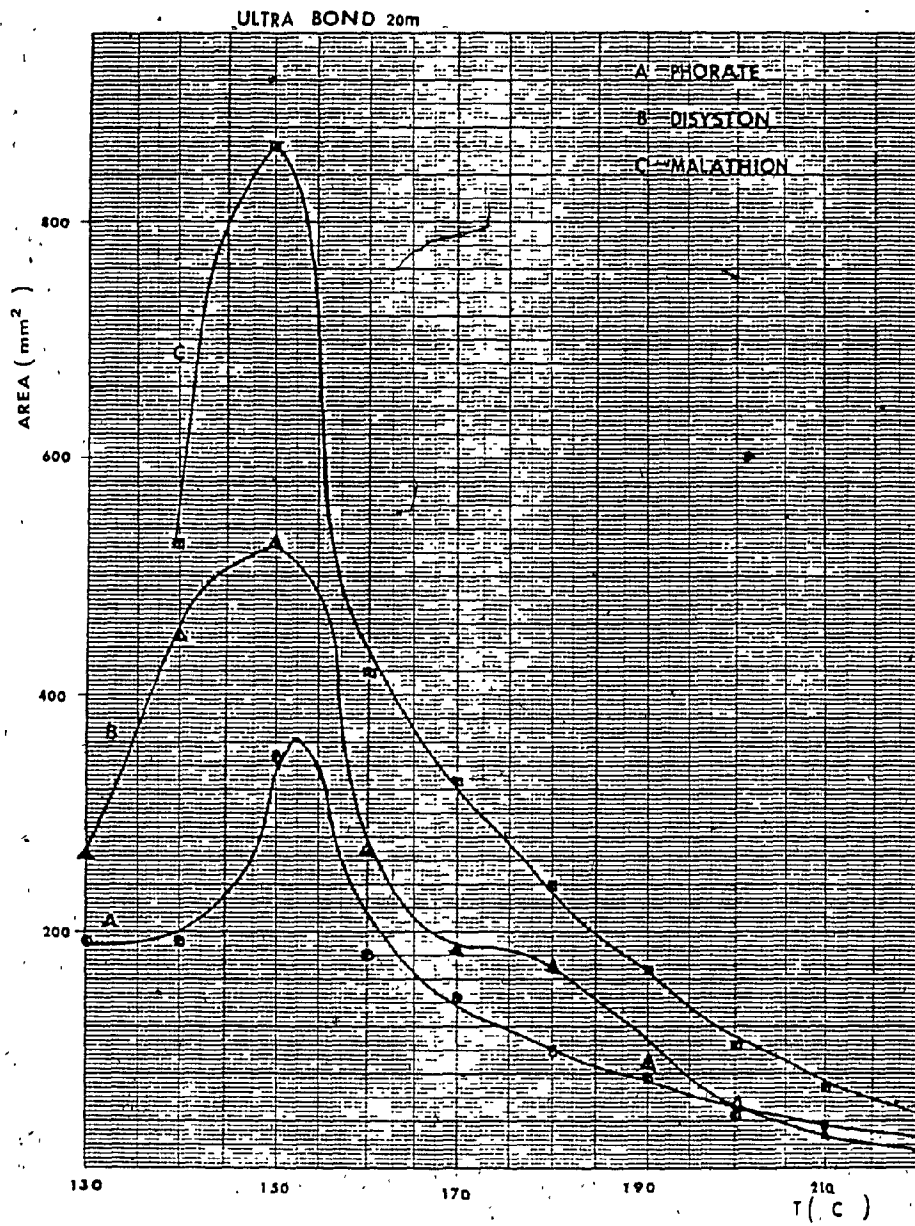


CG-AW-DMCS



CG - HP





APPENDIX (II)

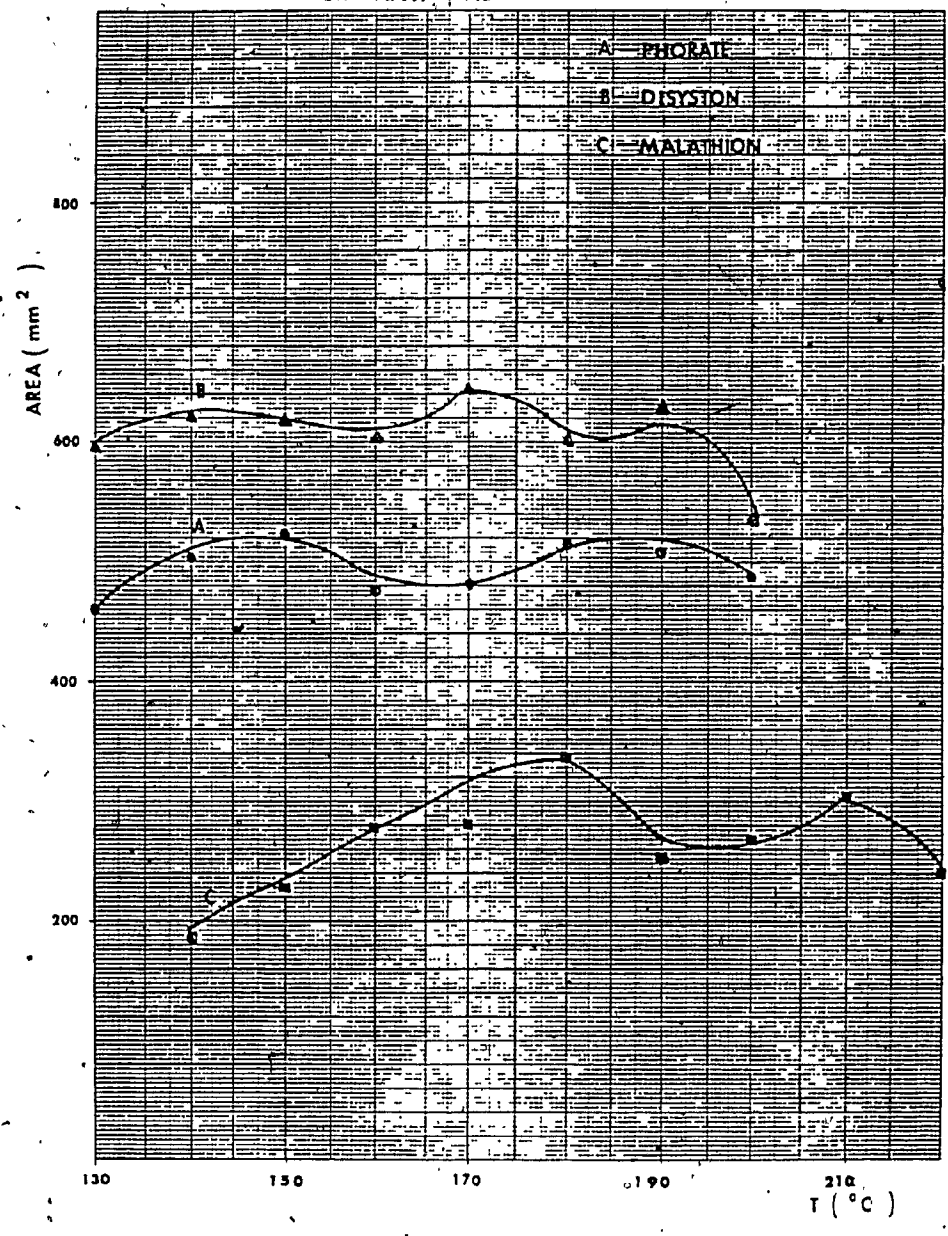
Thermograms for the 2nd Run of Columns Tested
Using the Flame Ionization Detector

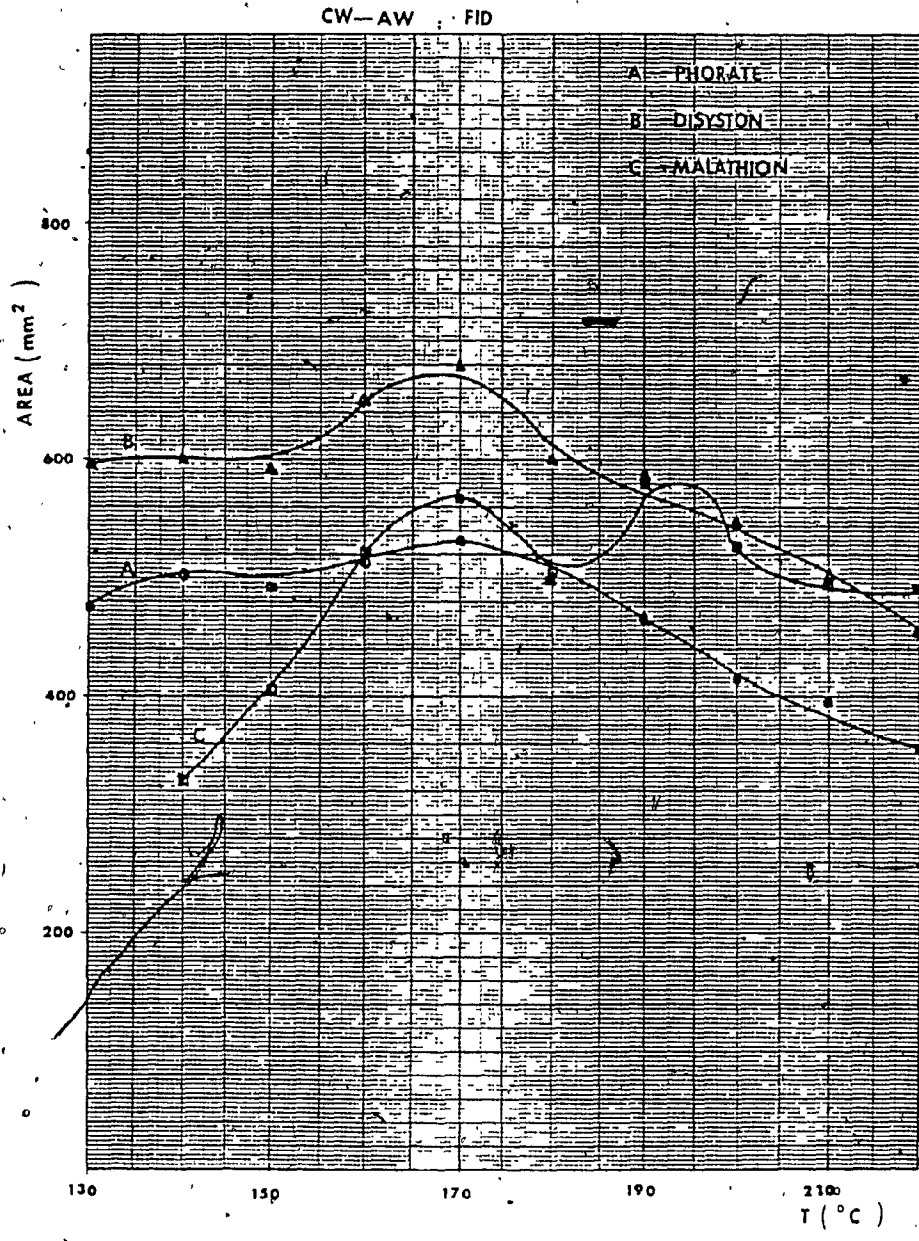
IDENTIFICATION OF THERMOGRAMS

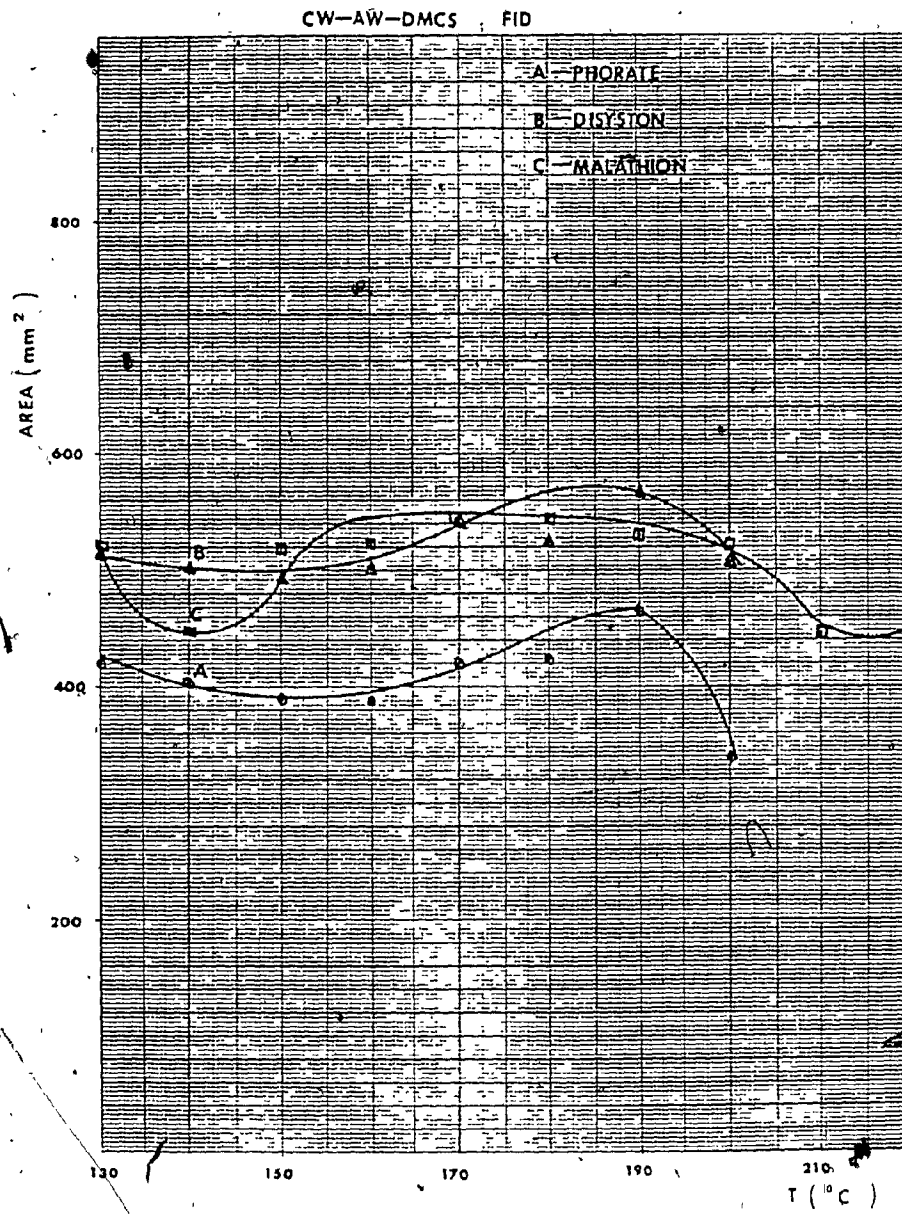
- 1 - CW-NAW
- 2 - CW-AW
- 3 - CW-AW-DMCS
- 4 - CW-HP
- 5 - C-750
- 6 - CP-NAW
- 7 - CG-NAW
- 8 - CG-AW-DMCS

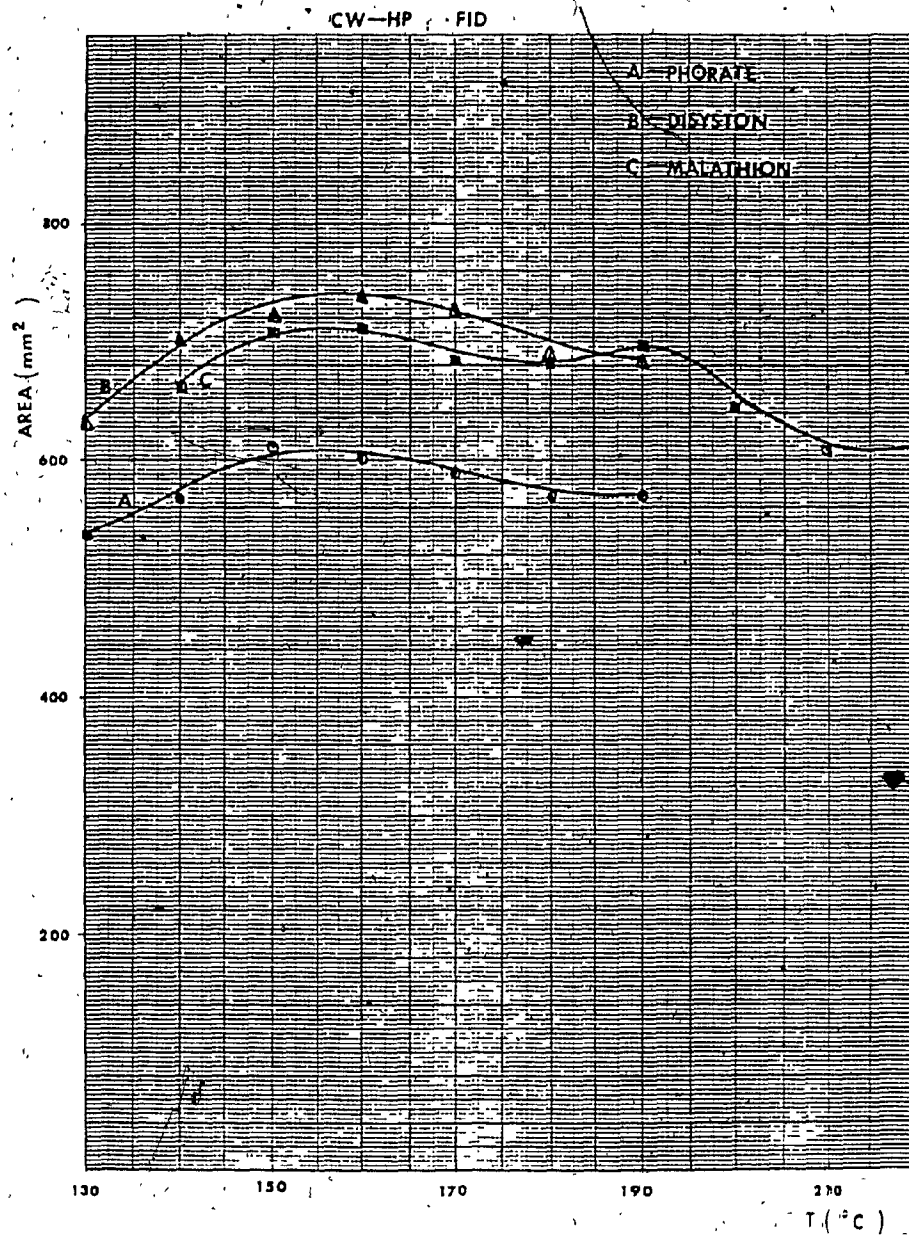
Note: The curves A, B and C are the Thermograms for Phorate (3.5 ug), Disyston (6.2 ug), and Malathion (11.9 ug), respectively. Numbers 1 to 7 are Second Run Results. Number 8 is a First Run Result.

CW-NAW FID

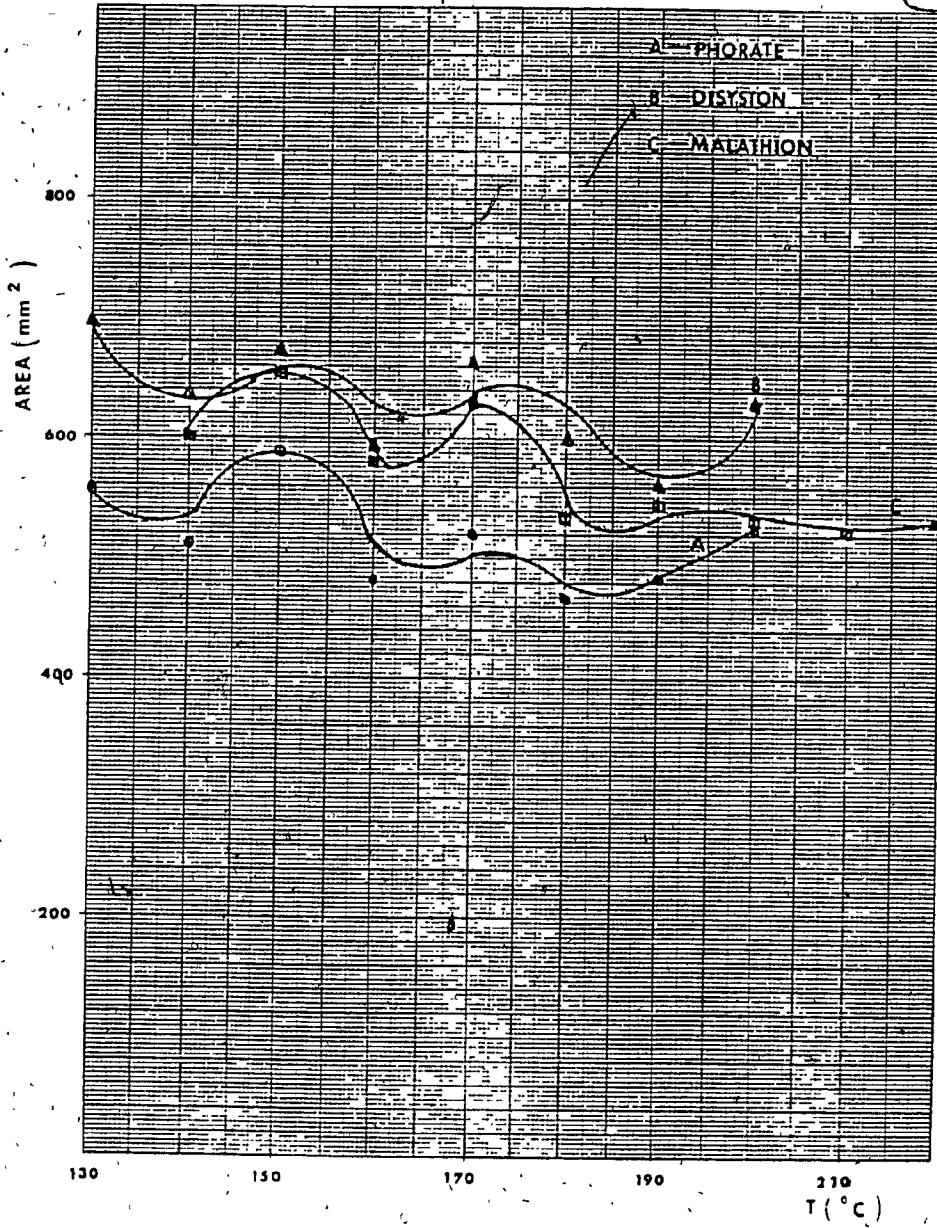




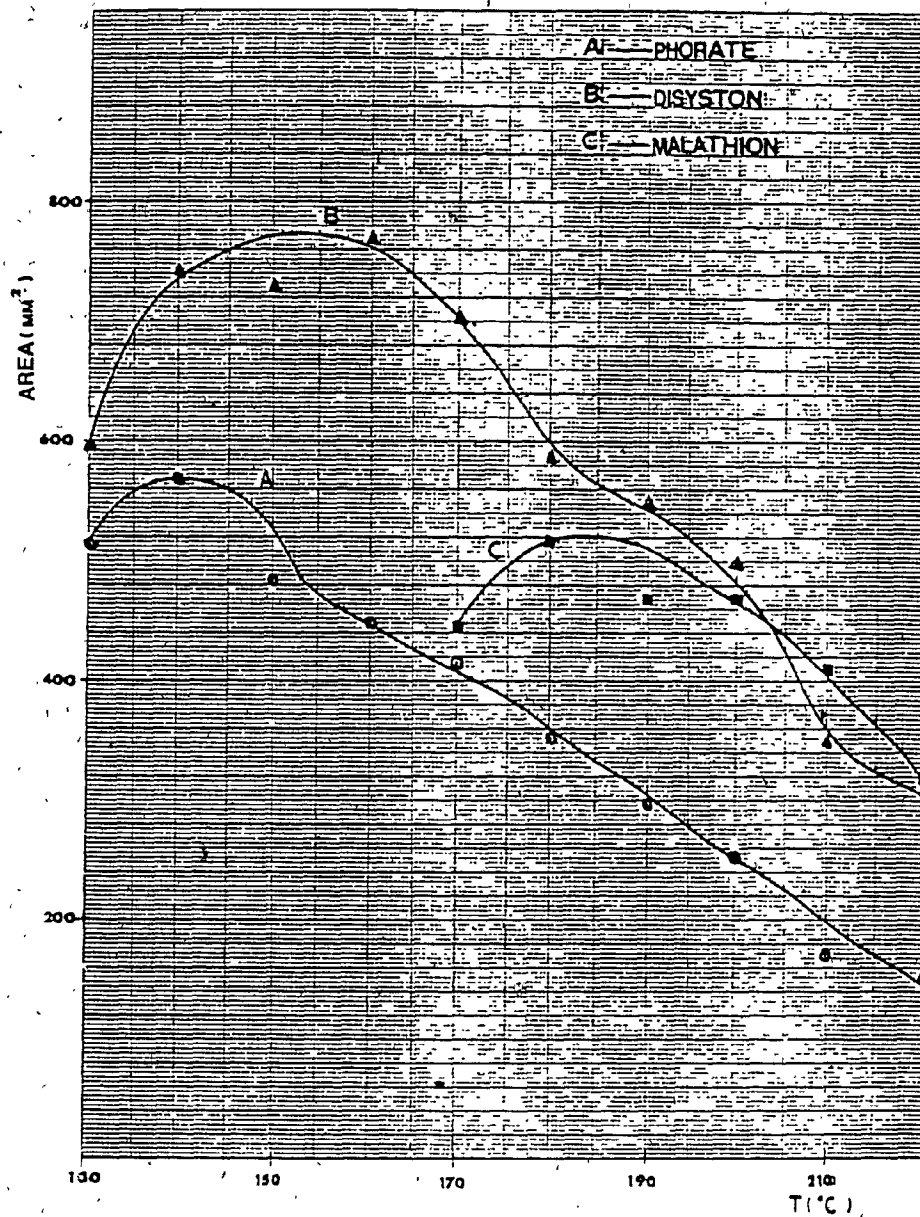


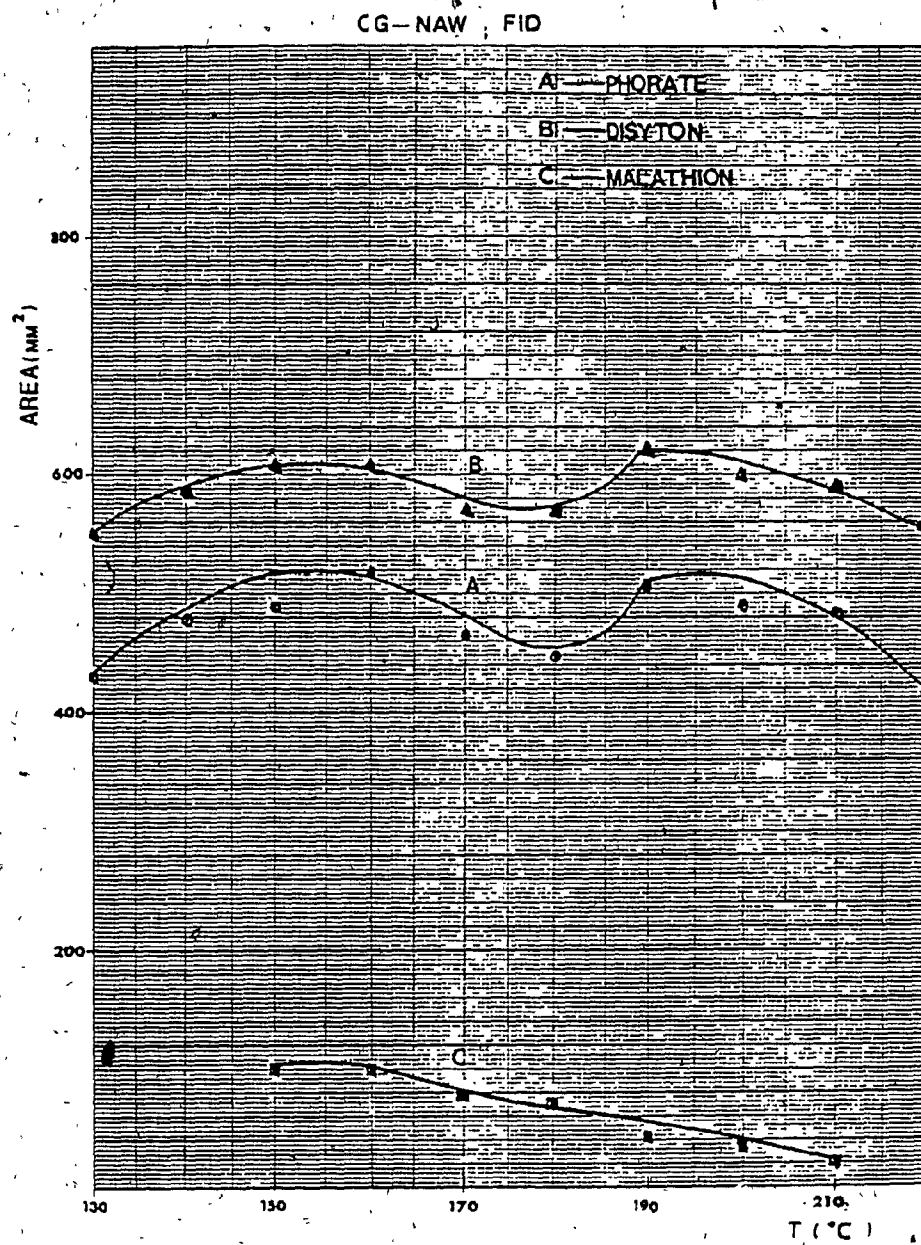


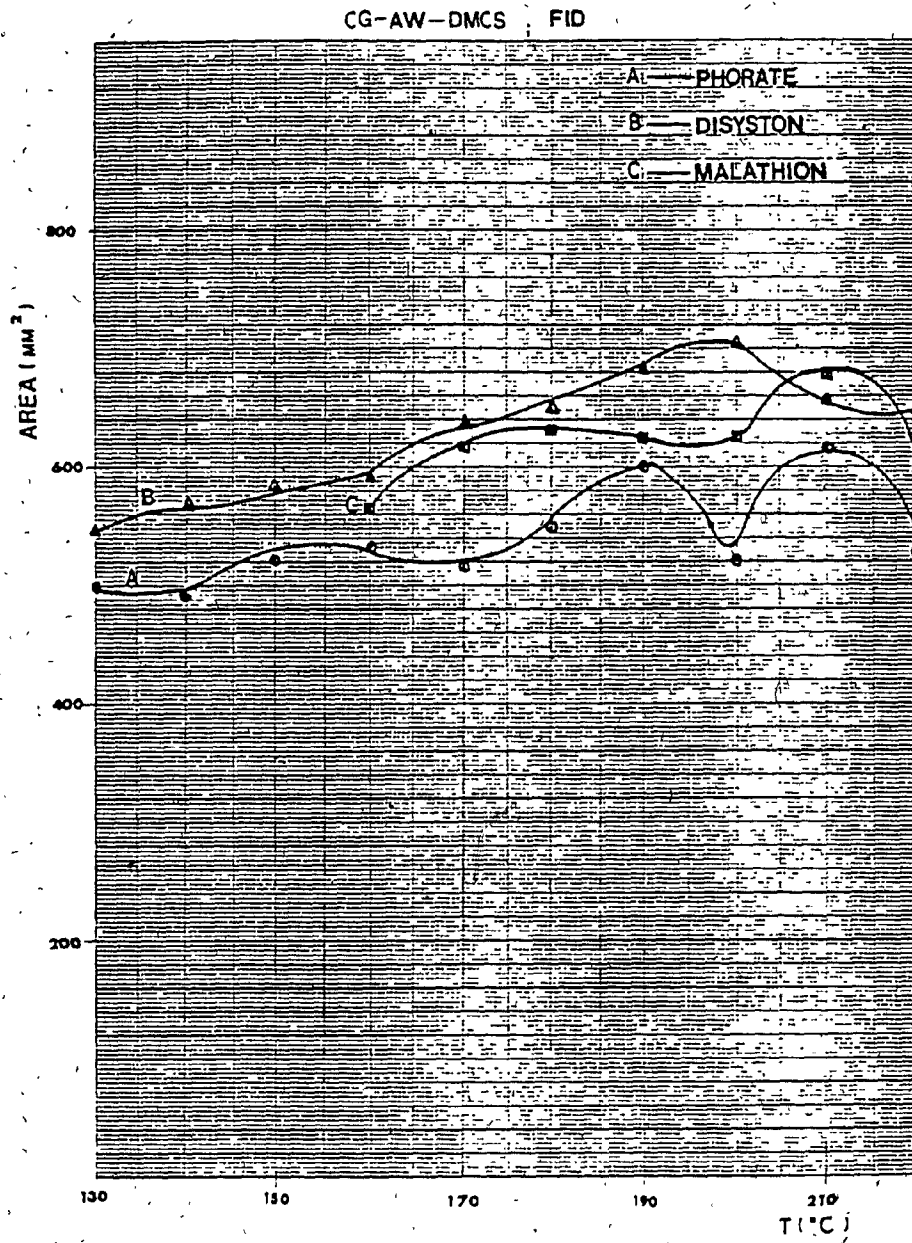
C-750 FID



CP-NAW FID







APPENDIX (III)

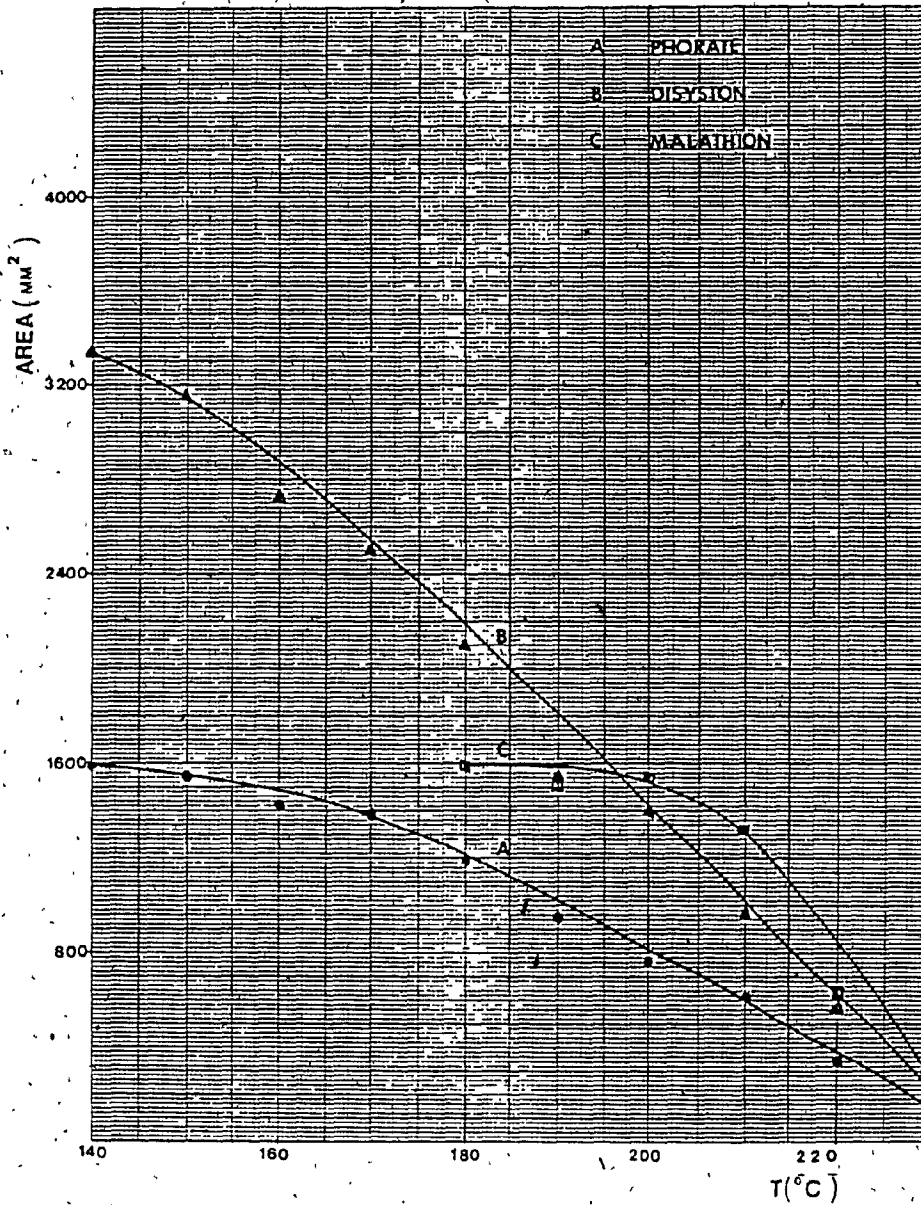
Thermograms for the Runs on Columns Packed
in Glass Tubing Using the Electron Capture Detector

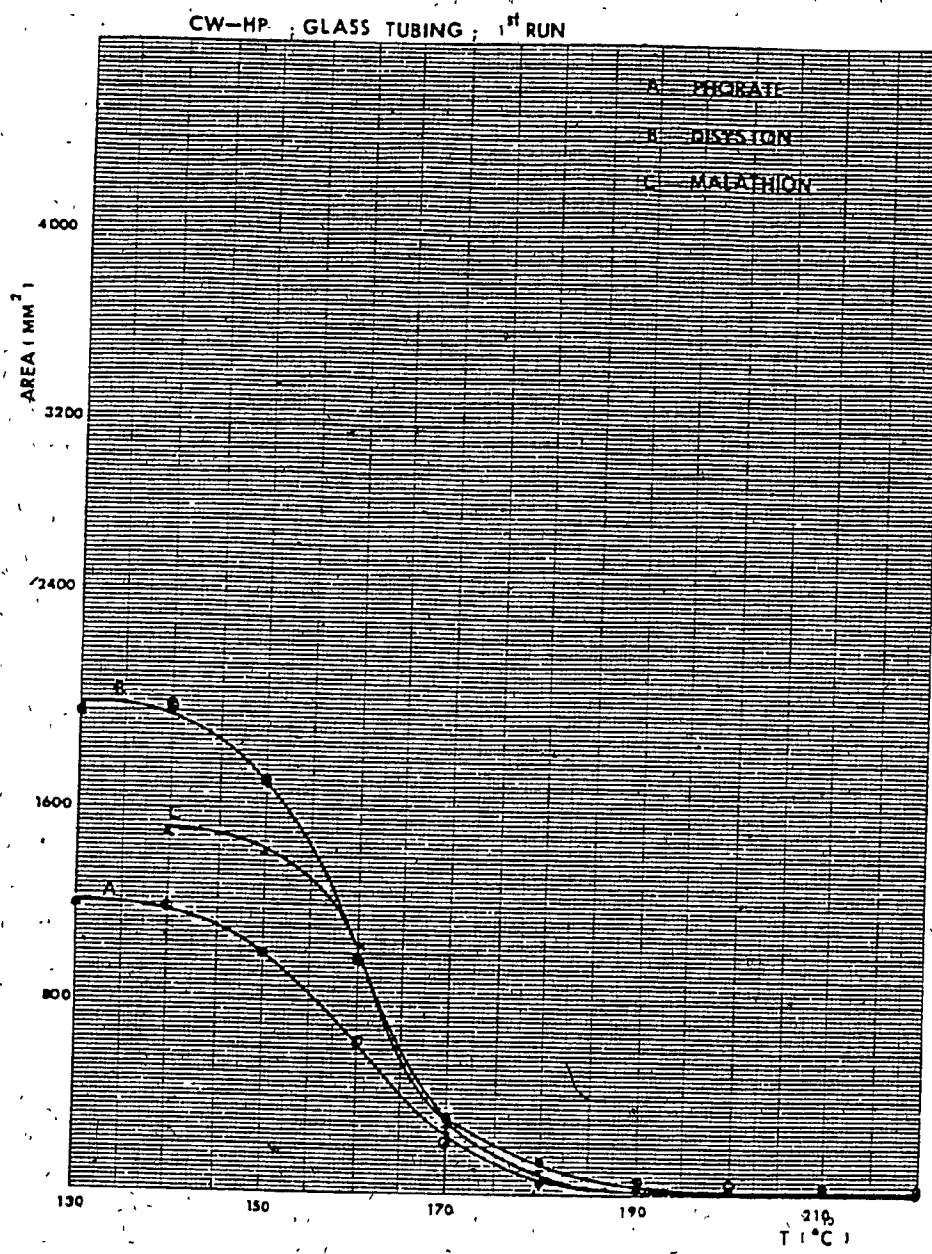
IDENTIFICATION OF THERMOGRAMS

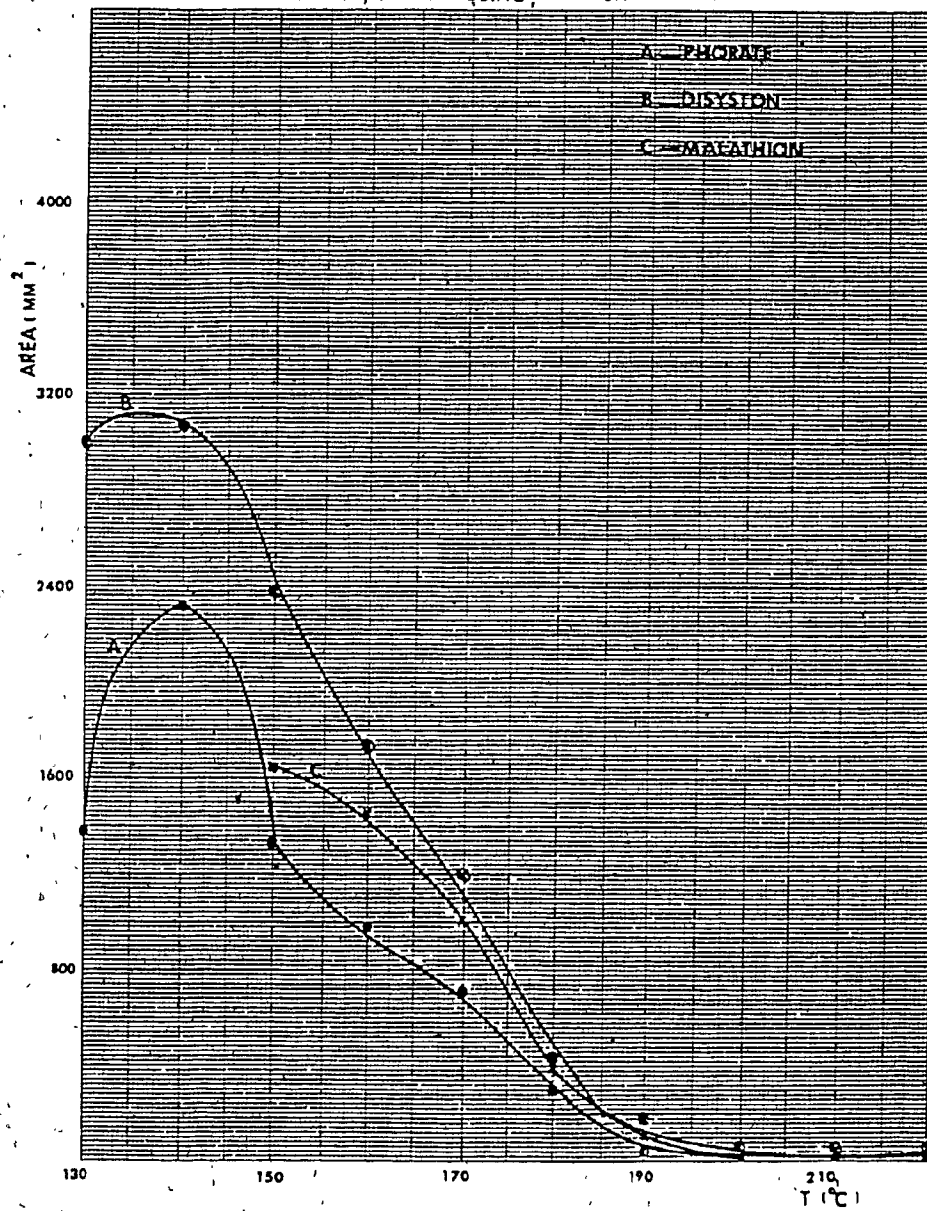
- 1 - 2nd Run on CW-AW
- 2 - 1st Run on CW-HP
- 3 - 2nd Run on CW-HP

Note: The Curves A, B and C are the Thermograms for Phorate (8.8 ng), Disyston (23.3 ng) and Malathion (11.9 ng), respectively.

CW-AW GLASS TUBING





CW-HP; GLASS TUBING; 2nd RUN

APPENDIX (IV)

Classification of Chromosorb Supports at
Specific Temperatures of 150, and 180 deg C and
at the Temperatures of Peak Area Maxima

TABLE (13) : Classification of Chromosorb W Supports
Using High Concentrations of Pesticides.
(Peak Area of 2nd Run at 150°C).

	<u>HP</u>	<u>QMCS</u>	<u>NAW</u>	<u>AW</u>	<u>750</u>
DISYSTON 6.2 UG	740	490	620	590	680
RATIO	10	6.6	8.4	8.0	9.2
PHORATE 3.5 UG	610	390	520	490	590
RATIO	10	6.4	8.5	8.0	9.7
MALATHION 11.86 UG	710	520	230	410	660
RATIO	10	7.3	3.2	5.8	9.3

TABLE (14) : Classification of Chromosorb W Supports,
Using High Concentrations of Pesticides.
(Peak Area of 2nd Run at 180°C).

	<u>HP</u>	<u>DMCS</u>	<u>NAW</u>	<u>AW</u>	<u>750</u>
DISYSTON 6.2 µg	690	530	600	600	600
RATIO	10	7.7	8.7	8.7	8.7
PHORATE 3.5 µg	570	420	520	510	470
RATIO	10	7.4	9.1	8.9	8.3
MALATHION 11.86 µg	680	550	340	510	540
RATIO	10	8.1	5.0	7.5	7.9

TABLE (15) : Classification of Chromosorb W Supports
Using High Concentrations of Pesticides.
(Peak Area of 2nd Run at Peak Area Maxima.)

	HP <u>AREA/T°</u>	DMCS <u>AREA/T°</u>	NAW <u>AREA/T°</u>	AW <u>AREA/T°</u>	750 <u>AREA/T°</u>
DISYSTON 6.2 UG	760/160°	570/190°	640/170°	680/170°	685/150°
RATIO	10	7.5	8.4	8.9	8.9
PHORATE 3.5 UG	610/150°	470/190°	520/150°	530/170°	590/150°
RATIO	10	7.7	8.5	8.7	9.7
MALATHION 11.86 UG	710/160°	550/180°	340/180°	580/190°	660/150°
RATIO	10	7.1	4.8	8.2	9.3

TABLE (16) : Classification of Chromosorb W Supports Using High Concentrations of Pesticides.
Score and Rank of the Five Supports.

	<u>DISYSTON</u>			<u>PHORATE</u>			<u>MALATHION</u>			<u>SCORE</u>	<u>RANK</u>
	<u>MAX</u>	<u>150°</u>	<u>180°</u>	<u>MAX</u>	<u>150°</u>	<u>180°</u>	<u>MAX</u>	<u>150°</u>	<u>180°</u>		
HP	1	1	1	1	1	1	1	1	1	9	1
DMCS	5	5	5	5	5	5	4	3	2	39	5
NAW	4	3	2	4	3	2	5	5	5	33	4
AW	2	4	2	3	4	3	3	4	4	29	3
750	2	2	2	2	2	4	2	2	3	21	2

TABLE (17) : Classification of Chromosorb W Supports
Using Moderate Concentrations of Pesticides.
(Peak Area of 2nd Run at 150 deg C.)

	<u>HP</u>	<u>DMCS</u>	<u>NAW</u>	<u>AW</u>	<u>750</u>
DISYSTON 23.26 NG	990	280	440	300	250
RATIO	10	2.9	4.4	3.0	2.5
PHORATE 8.76 NG	620	240	150*	260	110
RATIO	10	3.9	2.4	4.2	1.8
MALATHION 11.86 NG	1400	300	**	390	**
RATIO	10	2.1	**	2.8	**

* 330 FOR RUN #1

** NO PEAKS.

TABLE (18) : Classification of Chromosorb W Supports
Using Moderate Concentrations of Pesticides.
(Peak Area of 2nd Run at 180 deg C.)

	<u>HP</u>	<u>DMCS</u>	<u>NAW</u>	<u>AW</u>	<u>750</u>
DISYSTON 23.26 NG	1000	420	760	420	290
RATIO	10	4.2	7.6	4.2	2.9
PHORATE 8.76 NG	810	470	210*	430	140
RATIO	10	5.8	2.6	5.3	1.7
MALATHION 11.86 NG	1630	570	**	570	**
RATIO	10	3.5	**	3.5	**

* 590 FOR RUN #1

** NO PEAKS

TABLE (19) : Classification of Chromosorb W Supports Using Moderate Concentrations of Pesticides.

(Peak Area of 2nd Run at Peak Maxima.)

	HP ^z	DMCS	NAW	AW	750
	<u>AREA/T°</u>	<u>AREA/T°</u>	<u>AREA/T°</u>	<u>AREA/T°</u>	<u>AREA/T°</u>
DISYSTON 23.26 NG	1170/160°	630/220°	760/180°	650/200° [#]	500/210°
RATIO	10	5.4	6.5	5.6	4.3
PHORATE 8.76 NG	920/170°	570/200°	270/200°*	560/190° [#]	220/230°
RATIO	10	6.2	2.9*	6.1	2.4
MALATHION 11.86 NG	1890/160°	910/200°	**	880/200°	240/230°
RATIO	10	4.8		4.7	1.3

* 580/170° FOR RUN #1

** NO PEAKS

SYMMETRICAL

TABLE (20) : Classification of Chromosorb W Supports
Using Moderate Concentrations of Pesticides.
Score and Rank of the Supports.

	<u>DISYSTON</u>			<u>PHORATE</u>			<u>MALATHION</u>			<u>SCORE</u>	<u>RANK</u>
	<u>MAX</u>	<u>150°</u>	<u>180°</u>	<u>MAX</u>	<u>150°</u>	<u>180°</u>	<u>MAX</u>	<u>150°</u>	<u>180°</u>		
HP	1	1	1	1	1	1	1	1	1	9	1
DMCS	4	4	3	2	3	2	2	3	2	25	3
NAW	2	2	2	4	4	4	5	4	4	31	4
AW	3	3	3	3	2	3	3	2	2	24	2
750	5	5	5	5	5	5	4	4	4	42	5

TABLE (21) : Classification of Chromosorb W Supports
Using Low Concentrations of Pesticides.

	<u>HP</u>	<u>DMCS</u>	<u>NAW</u>	<u>AW</u>	<u>750</u>
DISYSTON 13.76 PG	250*	70	62	60	31
RATIO	10	2.8	2.5	2.4	1.2
RANK	1	2	3	4	5
MALATHION 2.112 NG	1172*	186	277	151	73
RATIO	10	1.6	2.4	1.3	0.6
RANK	1	3	2	4	5

* SLIGHT TAILING

TABLE (23) : Summary of Score and Rank of Chromosorb W Supports at Three Sample Concentration.

	<u>LOW - ECD</u>		<u>MOD - ECD</u>		<u>HIGH - FID</u>	
	<u>SCORE</u>	<u>RANK</u>	<u>SCORE</u>	<u>RANK</u>	<u>SCORE</u>	<u>RANK</u>
HP	2	1	9	1	9	1
DMCS	5	2	25	3	39	5
NAW	5	2	31	4	33	4
AW	8	4	24	2	29	3
750	10	5	42	5	21	2

TABLE (24) : Classification of Chromosorb G Supports
for Moderate Concentrations of Pesticides.
(Peak Area of 2nd Run at 150 deg C.)

	<u>AW</u>	<u>DMCS</u>	<u>HP</u>	<u>NAW</u>
DISYSTON 23.26 NG	920	610*	850	650
RATIO	10.8	7.2	10	7.6
PHORATE 8.76 NG	540	370**	640	420
RATIO	8.4	5.8	10	6.6
MALATHION 11.86 NG	***	***	***	***
RATIO	***	***	***	***

* 1210 FOR RUN #1

** 620 FOR RUN #1

*** NO PEAKS

TABLE (25) : Classification of Chromosorb G Supports
for Moderate Concentrations of Pesticides.
(Peak Area of 2nd Run at 180 deg C.)

	<u>AW</u>	<u>DMCS</u>	<u>HP</u>	<u>NAW</u>
DISYSTON 23.26 NG	1330	1080*	1630	1080
RATIO	8.2	6.6	10	6.6
PHORATE 8.76 NG	940	760**	1290	710
RATIO	7.3	5.9	10	5.5
MALATHION 11.86 NG	∅	880***	880	∅
RATIO	∅	10.0	10	∅

* 1830 FOR RUN #1

** 1200 FOR RUN #1

*** 1890 FOR RUN #1

∅ NO PEAKS

TABLE (26) : Classification of Chromosorb G Supports for Moderate Concentrations of Pesticides.
(Peak Area of 2nd Run at Peak Maxima.)

	AW <u>AREA/T°</u>	DMCS <u>AREA/T°</u>	HP ₃ <u>AREA/T°</u>	NAW <u>AREA/T°</u>
DISYSTON 23.26 NG	1580/200°	1440/200°	1630/180°	1310/190°
RATIO	9.7	8.8	10	8.0
PHORATE 8.76 NG	1070/200°	1060/210°	1290/180°	850/190°
RATIO	8.3	8.2	10	6.6
MALATHION 11.86 NG	460/230°	1600/210°	1280/200°	*
RATIO	3.6	12.5	10	*
DISYSTON 23.26 NG RUN #1	1700/190°	1830/180°	1290/210°	1680/170°
RATIO	13.2	14.2	10	13.0

* NO PEAKS

TABLE (27) : Classification of Chromosorb G Supports for Moderate Concentrations of Pesticides.
Score and Rank of the Four Supports.

	<u>DISYSTON</u>			<u>PHORATE</u>			<u>MALATHION</u>			<u>SCORE</u>	<u>RANK</u>
	<u>MAX</u>	<u>150°</u>	<u>180°</u>	<u>MAX</u>	<u>150°</u>	<u>180°</u>	<u>MAX</u>	<u>150°</u>	<u>180°</u>		
HP	1	2	1	1	1	1	2	-	1	10	1
AW	2	1	2	2	2	2	3	-	3	17	2
DMCS	3	4	3	3	4	3	1	-	1	22	3
NAW	4	3	3	4	3	4	4	-	3	28	4

TABLE (28) : Classification of Chromosorb G Supports
for Low Concentrations of Pesticides.
(Peak Area at 180°C.)

	<u>AW</u>	<u>DMCS</u>	<u>HP</u>
DISYSTON 13.76 PG	72*	69*	47*
RATIO	15.3	14.7	10
RANK	1	2	3
MALATHION 2.112 NG	143**	149*	143**
RATIO	10	10.4	10
RANK	2	1	2
RANK AT MOD CONCN	2	3	1

* BROAD, TAILING

** BROAD, SYMMETRICAL

TABLE (29) : Classification of Chromosorb P Supports for
Moderate Concentrations of Pesticides.
(Peak Area of 2nd Run, at 150 and 180 deg C.)

	150°			180°		
	<u>AW</u>	<u>NAW</u>	<u>DMCS</u>	<u>AW</u>	<u>NAW</u>	<u>DMCS</u>
DISYSTON 23.26 NG	3090	410*	650	2520	1540	1090
RATIO	10	1.3	2.1	10	6.1	4.3
RANK	1	3	2	1	2	3
PHORATE 8.76 NG	1020	250	220	1120	440	290
RATIO	10	2.5	2.2	10	3.9	2.6
RANK	1	2	3	1	2	3

* 1320 FOR RUN #1

TABLE (30) : Classification of Chromosorb P Supports
for Moderate Concentrations of Pesticides,
(Peak Area of 2nd Run at Peak Maxima.)

	<u>AW</u> <u>AREA/°T</u>	<u>NAW</u> <u>AREA/°T</u>	<u>DMCS</u> <u>AREA/°T</u>
DISYSTON 23.26 NG	3340/160°	1540/180°	1310/210°
RATIO	10	4.6	3.9
RANK	1	2	3
PHORATE 8.76 NG	1130/160°	440/180°	310/190°
RATIO	10	3.9	2.7
RANK	1	2	3

APPENDIX (V)

Thermograms for Six Consecutive Runs Done
On a Column Containing CW-AW Support Using
the Electron Capture Detector.

IDENTIFICATION OF THERMOGRAMS

x ----> Phorate (8.8 ng) thermograms

Y ----> Disyston (23.3 ng) thermograms

Z ----> Malathion (11.9 ng) thermograms

IDENTIFICATION OF RUNS

Curve 1 ----> Run 1

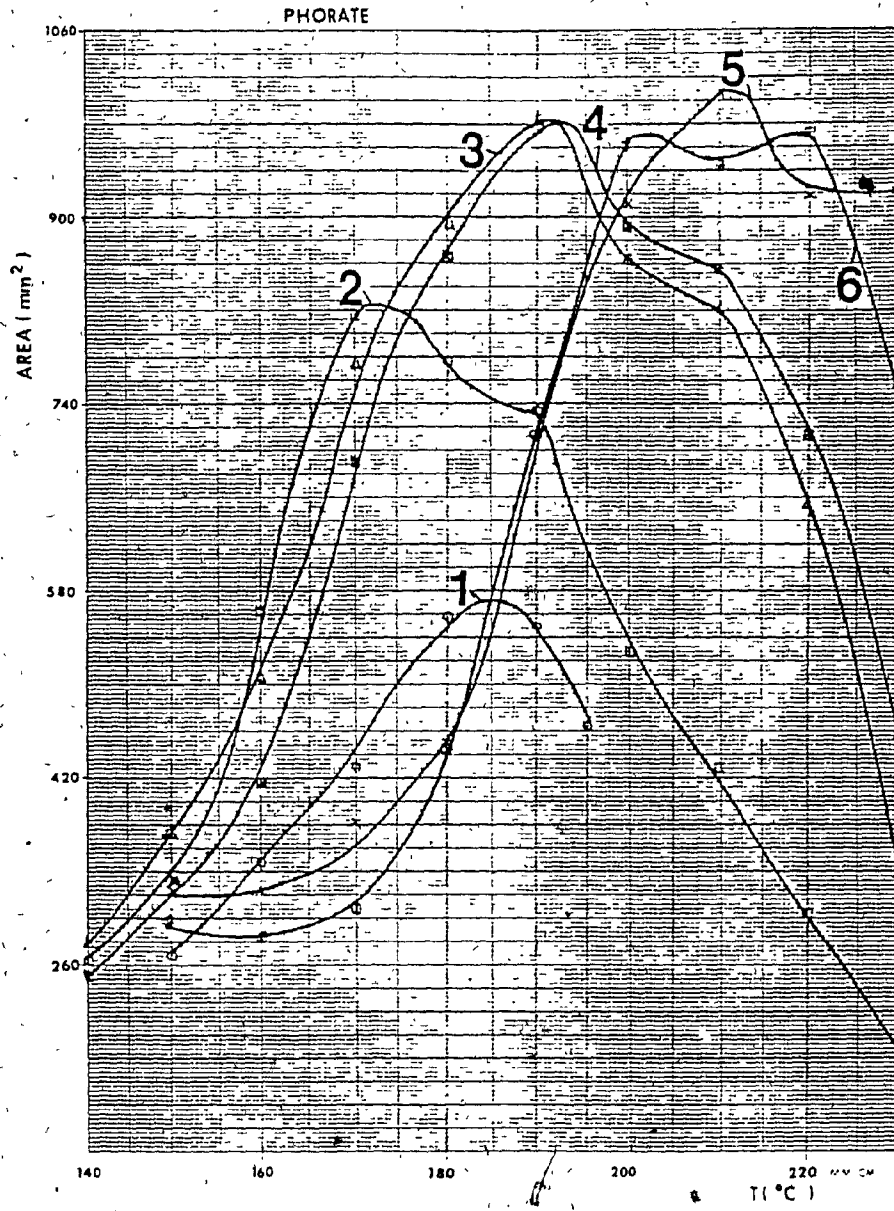
Curve 2 ----> Run 2

Curve 3 ----> Run 3

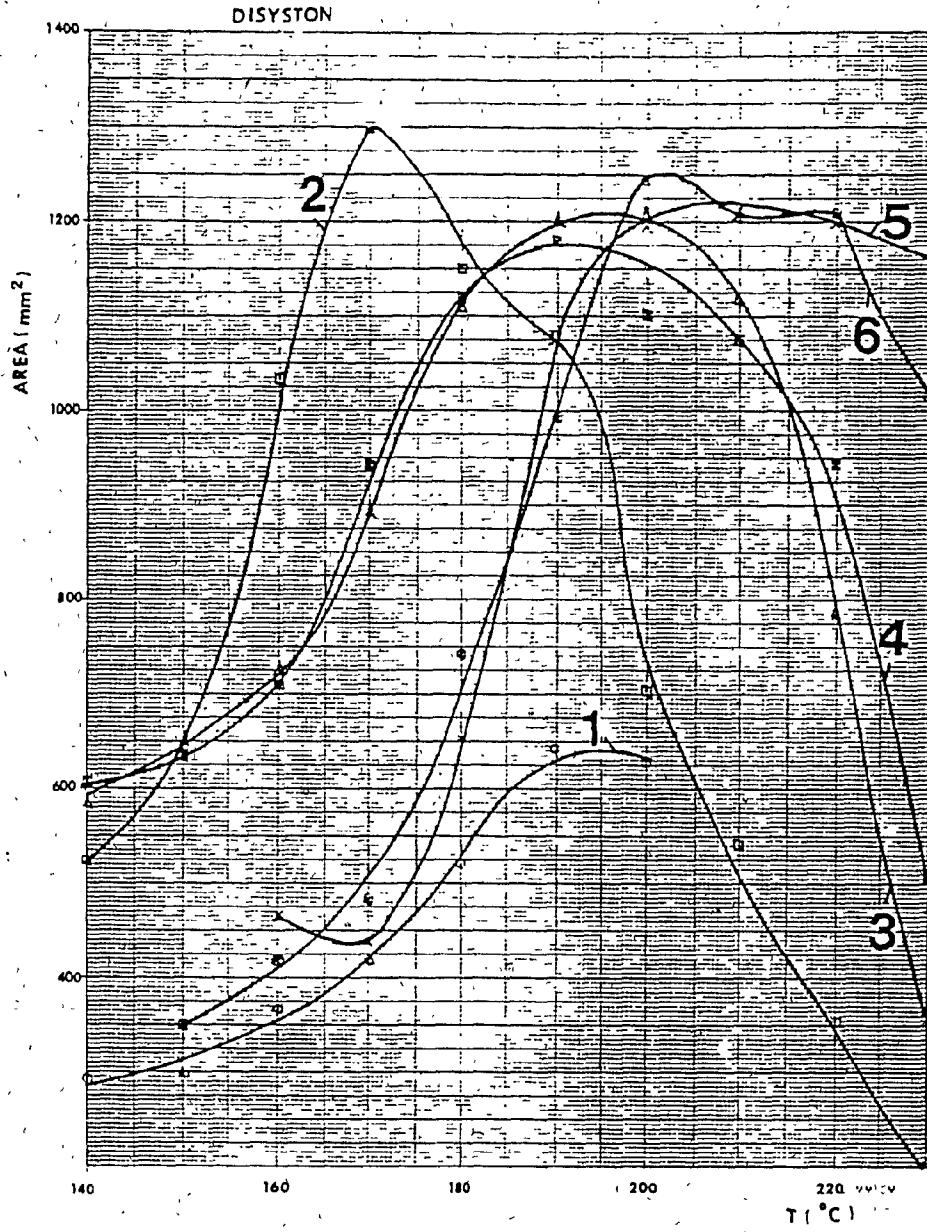
Curve 4 ----> Run 4

Curve 5 ----> Run 5

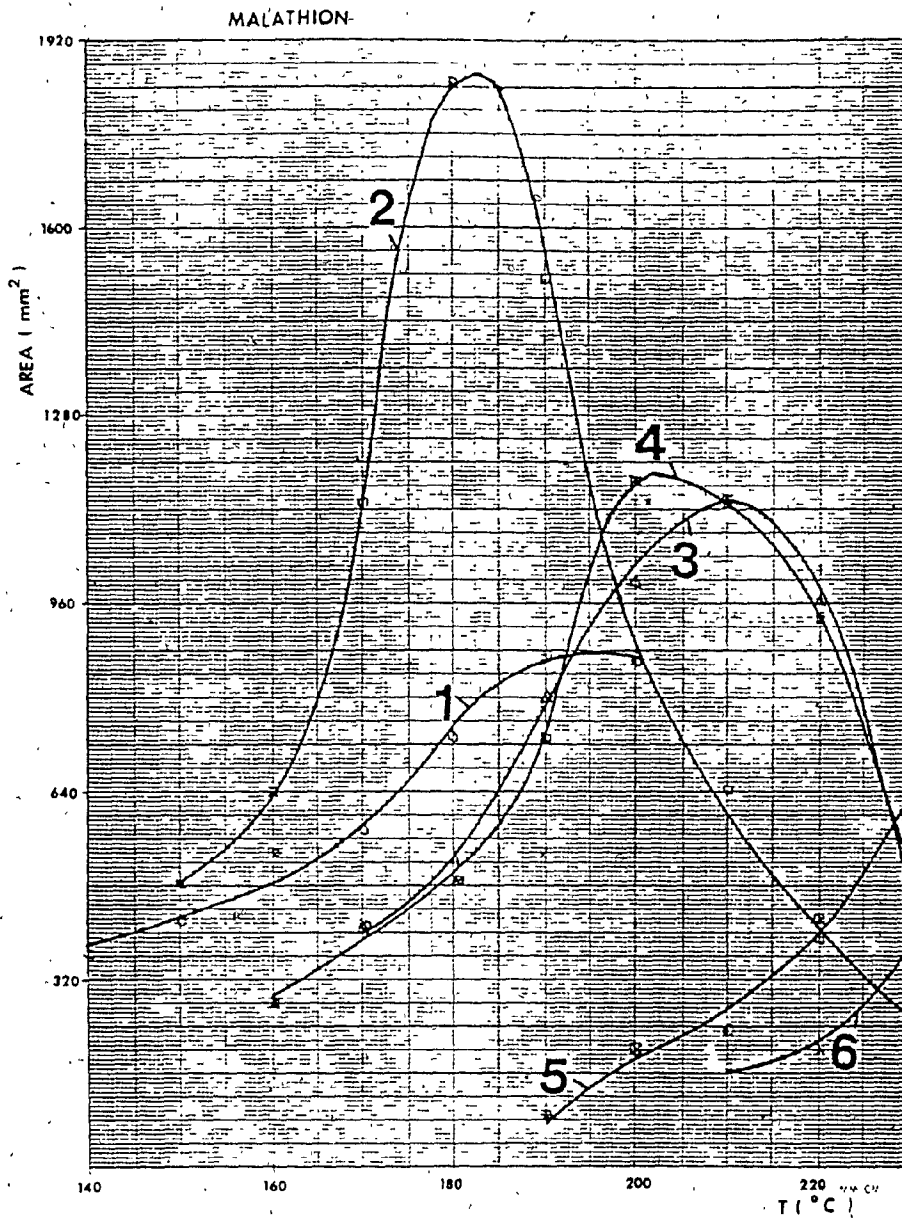
Curve 6 ----> Run 6



X



Y



Z