

COLUMN EFFECTS IN THE GLC ANALYSIS  
OF DIELDRIN AND METHOXYCHLOR

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ABSTRACT

COLUMN EFFECTS IN THE GLC ANALYSIS  
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In this thesis different diatomite supports (Chromosorbs W, P, G and 750) and column tubing materials (glass, stainless steel, nickel, copper and aluminum) were evaluated for their suitability in the analysis of two typical chlorinated pesticides, dieldrin and methoxychlor. The adsorptive properties of the above supports and column tubings were evaluated at various column temperatures for different sample sizes.

Chromosorb W HP was found to be the best W support for dieldrin, while W NAW was the poorest. Chromosorbs W AW-DMCS and W HP were the least adsorptive supports towards methoxychlor. The 750 was the poorest. Chromosorb G NAW was the best G support for the analysis of both dieldrin and methoxychlor. All P supports were about the same for the analysis of dieldrin. The P supports catalyzed the decomposition of methoxychlor under all experimental conditions, and were not suitable for the analysis of this compound. The possibility of determining relative support adsorptivities by a comparison of the slopes of calibration curves was strongly evident,

The overall trends of the thermograms obtained with both dieldrin

and methoxychlor using the FID were, increases in peak area responses with column temperature, especially for methoxychlor. The physical properties of the coated supports were shown to change continuously from temperature to temperature and run to run because of liquid phase bleed and sample priming.

The overall trends of the thermograms for dieldrin and methoxychlor using the ECD were large decreases in peak area responses with increasing column temperatures, but the ECD behaviour was shown to be responsible for these effects.

Glass tubing was the least adsorptive column tubing. Comparatively, all metal tubings were poor, except for nickel, which was as good as glass for the analysis of methoxychlor.

v.

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To my loving wife, Argentelle, for her  
patience, understanding and support  
throughout this work.

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## 1.0 INTRODUCTION

### 1.1 PESTICIDES

World food production has not kept pace with the growth of population in this century, and half of the world's population today has an inadequate diet. Food supplies will have to be doubled in the next 30 years to achieve even a moderate increase in nutritional standards. One of the measures essential for achieving the massive expansion needed in food production is the increased use of pesticides and fertilizers (1).

Pests destroy up to one-third of the world's food crops during growth, harvesting and storage. In developing countries, crop losses are even higher. In Latin America, for example, they may reach 40% of everything produced. The large-scale use of agricultural chemicals is already one of the main factors in eliminating such losses.

It is not only food crops that need protection by pesticides. Without the use of insecticides, 50% of the cotton production would be destroyed by pests. The control of certain insect-borne diseases, like malaria, yellow fever and sleeping sickness, has only become possible with the use of modern insecticides (1).

Pesticides may be classified according to either their use (e.g. as insecticides, herbicides, fungicides, rodenticides) or their chemical type (organohalides, organophosphates, carbamates, organosulfurs, inorganics, anilines, ureas, phenols, amides, etc.). Compounds of the first three of these chemical types are probably the most important (2).

Approximately 90,000 formulations of about 900 chemical pesticide species were being produced, in amounts totaling more than 2 billion pounds annually, as of early 1972 (2).

Because of the widespread occurrence of pesticides in the environ-

ment, the availability of sensitive methods for the analysis of residues of these compounds is extremely important. These analytical methods allow research on the prevalence of pesticides in the environment (food, water, soil, air) and in man (tissue, blood, excreta), on genetic effects on humans, disposition of the chemical agents (metabolism, reaction, degradation), and removal of contaminants by physical and chemical means. Residue analysis is also important for surveillance and law enforcement and for investigations of accidental or intentional pesticide contamination (2).

## 1.2 CHLORINATED PESTICIDES

### 1.2.1. Methoxychlor

Although pesticides have been in use for many centuries, until the discovery of DDT in 1939, they were nearly all inorganic chemicals with the exception of petroleum oil sprays and some insecticides of plant origin (1). Modern organic pesticides in use today have been developed during the last 25-30 years. These modern materials are compounds which effectively control organisms that destroy or endanger man's food, health or environment (1).

Although DDT (dichlorodiphenyltrichloroethane) was synthesized by Zeidler in 1874, its insecticidal properties were discovered only in 1939. Its proper chemical name is 2,2-bis-(p-chlorophenyl)-1,1,1-trichloroethane (3, 4).

A considerable number of close relatives of DDT have insecticidal action and some have useful practical application as insecticides. One of these compounds, methoxychlor, or Bis-(p-methoxyphenyl)-1,1,1-trichloroethane, m.p. 89°C, is an especially useful compound as it does not become concentrated in animal fat (3, 4).

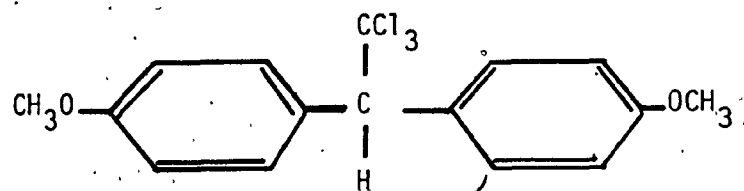


Figure 1

Methoxychlor

The toxicity of methoxychlor to insects is illustrated by an LD<sub>50</sub> to the fly (*Musca domestica*) of 3.4 mg/kg and to the mosquito larva of 0.067 ppm. Its insecticidal activity is related to the ease with which it is absorbed by the insect cuticle. Methoxychlor affects peripheral sensory organs to produce violent afferent impulses that result in hyperactivity and then convulsion of the insect. The paralysis and death that result are thought to occur from metabolic exhaustion or from production of a naturally occurring neurotoxin. Methoxychlor is relatively non-toxic to higher animals with an oral LD<sub>50</sub> of 6000 mg/kg to the rat. The use of methoxychlor upon crops intended for animals, or in forest areas, soils, etc., is favored because it is less persistent than DDT, and does not accumulate in animal tissues (3, 4).

### 1.2.2. Dieldrin

The cyclodiene insecticides are highly chlorinated cyclic hydrocarbons with endomethylene bridged structures, prepared by the Diels-Alder diene reaction. These materials arose from Hyman's discovery in 1945 that cyclopentadiene reacts with acetylene to give bicyclo-2,2,1-hepta-2,5-diene as a stable product previously supposed incapable of existence. The Diels-Alder reaction of this compound with hexachlorocyclopentadiene produces aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo, exo-5,8-dimethanonaphthalene). Reaction of aldrin

with peracetic acid or perbenzoic acid forms dieldrin, 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo,exo-5,8-dimethanonaphthalene, m.p. 176°C (3, 4).

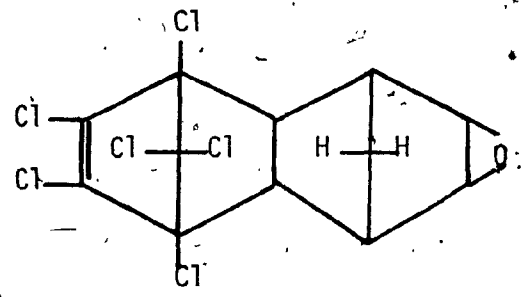


Figure 2 Dieldrin

As an example of the toxicity of dieldrin to insects and mammals, the LD<sub>50</sub> to the fly is 0.9 µg/g, to the mosquito larva 0.0078 ppm, and to the rat the oral LD<sub>50</sub> is 46 mg/Kg (3, 4). Dieldrin is readily absorbed by the insect cuticle. The symptoms of poisoning in insects are similar to those previously described for methoxychlor.

Dieldrin is used for the control of grasshoppers, insects of public health importance, and termites, and for mothproofing (3, 4).

### 1.3 DETECTION OF PESTICIDES

Residue analysis, particularly for chlorinated pesticides, was revolutionized by the application of gas-liquid chromatography. The rapid application of GLC as a technique, and in particular the development of selective methods of detection for halogenated compounds, has led to its world-wide use in residue analysis of chlorinated pesticides. Because of the sensitivity and selectivity that it can offer, GLC has become the preferred method for the whole group of compounds considered here.

#### 1.4. GAS LIQUID CHROMATOGRAPHY

Chromatography is a physical method of separation in which the components to be separated are distributed between two phases, one of the phases constituting a stationary bed of large surface area, the other being a fluid that percolates through or along the stationary bed (5).

Gas-liquid chromatography is a special form of the general chromatographic technique in which the moving phase is a gas and the stationary phase is a liquid supported on a solid. Separation of the components of mixtures is attained by differences in the distribution of each component between the liquid stationary phase and the moving phase. The liquid phase acts as a solvent for the sample components, and differences in solubility is the basis for their separation. The solid support should be an inert material and is used to hold the liquid phase in a thin film.

Its surface area should be as large as possible for maximum contact between the held liquid phase and gaseous phases (5, 6).

The sample to be analyzed is introduced into the moving gas stream, and is carried down the column containing the inert solid support coated with the liquid phase. The constituents of the sample distribute themselves between the two phases and because of differences in their solubilities, they are carried along the column at different rates, emerging at the end as distinct zones separated by pure carrier gas. The presence of the eluted solutes is measured quantitatively and/or qualitatively by a detector located at the exit end of the column. Usually, a recording potentiometer is used to draw a chromatogram which is a plot of detector response versus time or volume of carrier gas. This technique is suitable for the separation of materials which can be volatilized without decomposition, and can be used at temperatures

ranging from below room temperature up to 300°C, or above, depending on the thermal stability of the liquid phase (5, 6, 7).

A block diagram of a typical gas chromatograph is shown in Figure 3.

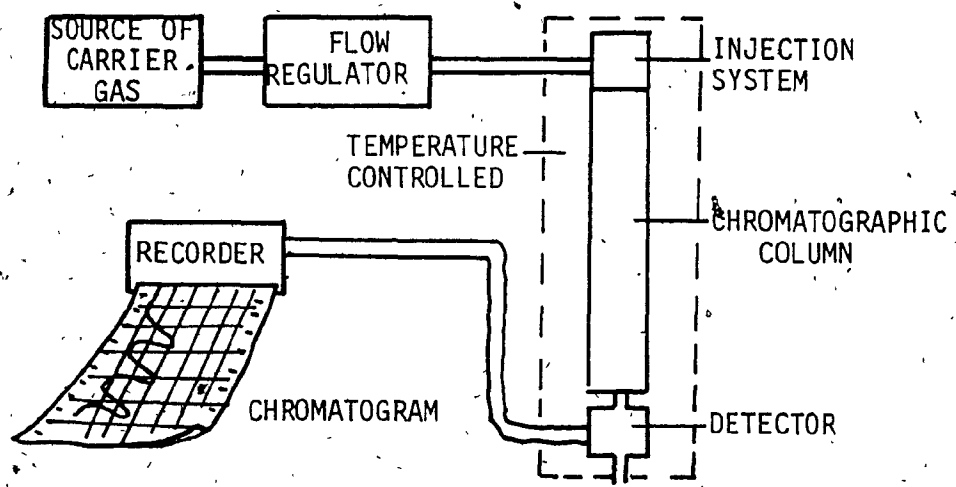


Figure 3 Diagram of a Simple Gas Chromatograph (7)

The source of the carrier gas is usually a cylinder of compressed gas. The flow is controlled by a series of pressure and flow regulators located before the injection system, which is itself located immediately ahead of the column. The injection area is equipped with a separate heating device which raises its temperature above that of the general oven or column temperature. This facilitates the rapid vaporization of the liquid sample, a prime requirement for efficient operation.

Before a sample is chromatographed, the column temperature and carrier gas flow rate are brought to the desired levels. The sample is injected into the injection system where it is instantaneously vaporized into the carrier gas stream and carried into the column. As soon as the solute molecules in the carrier gas come into contact

with the liquid phase, some portion of each component in the sample will dissolve in the liquid phase, depending on the amount of the latter that is present, and on the partition ratio of the solute between the gas phase and the liquid phase. The partitioning of each solute depends on the temperature of the column and the nature of the liquid phase. The molecules of components, which are highly soluble in the liquid phase will tend to dissolve more readily than those of less soluble components. Those molecules which are not dissolved are swept further down the column by the moving carrier gas. As new pure carrier gas passes through the original portion of the column, molecules dissolved in the liquid re-enter the gas phase in order to establish equilibrium. It is this constant movement in and out of the liquid and gas phases which is the fundamental mechanism of the gas chromatographic process. When a molecule is in the carrier gas, it is moving through the column at the same rate as the carrier gas, and therefore the time any molecule spends in the carrier gas is a constant. The components in a mixture will appear at the end of the column at a time proportional to the solubility of each component in the stationary phase. At the end of the column, a detector senses the presence of the eluted components and sends a signal to the recorder where the detector's response is plotted versus time (5, 7). The retention of the components of the sample depends on column temperature, type of liquid phase and amount, flow rate of the mobile phase, and column length (7).

Figure 4 shows a typical chromatogram which results from the pen tracing the output of the detector onto a moving chart (7).



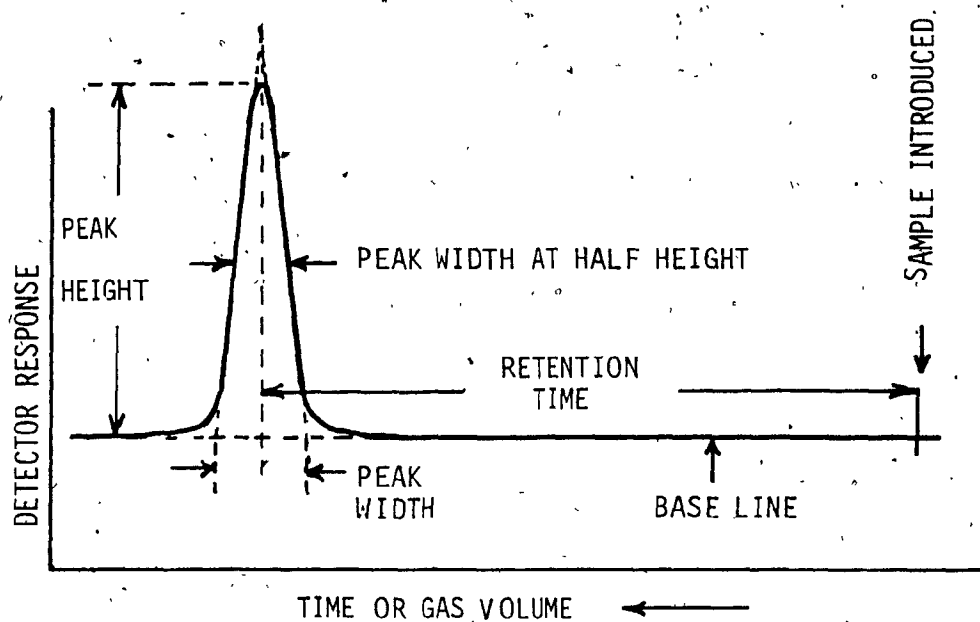


Figure 4

Typical Chromatogram

The abscissa is linear with time since the recorder chart moves at a constant rate. The ordinate is in millivolts. The base line is the response of the detector when no solute is present. When a solute passes through the detector, it is sensed and the change in response with concentration results in a peak. The peak base is the extrapolation of the base line under the peak. The area under the peak is the peak area. The peak height is the distance between the peak base and the peak maximum. The peak width is the distance along the peak base that is between the lines drawn tangent to the sides of the peak at the inflection points. The peak width at half height is the width of the peak at one half the peak height. The peak area or peak height is used for quantitative measurements. The time required for the solute to be eluted from the column after it has been injected is called the retention time,  $t_r$ . The retention time for the elution of a given solute is a qualitative property of that component (7).

### 1.5 QUANTITATIVE ANALYSIS

The size of a chromatographic peak is proportional to the amount of material contributing to that peak, and can be measured in a number of ways:

- (i) Peak height
- (ii) Triangulation
- (iii) Height times width at half-height
- (iv) Height times retention time
- (v) Planimetry
- (vi) Weight of cutout peak
- (vii) Electronic integrators and computers

Scott and Grant (8) determined the precision of three of the commonly used methods for the measurement of peak areas (peak height times peak width at half height, triangulation and planimetry). They concluded that the peak height times the width at half-height method was the most precise. Tests were also performed to investigate the sources of error in this method. Results showed that the error associated with measuring peak heights is greater than that for peak widths, but as the peak widths are generally much smaller than the heights, the errors contribute more or less equally to the error in the area measurement. The repeatability of peak-width measurements increased almost linearly with peak width, but the repeatability of peak-height measurements fell with increasing peak height. In general, the precision of peak height data should be lower than that for peak widths, since the heights depend on

the location of the base line. On sharp, narrow peaks, this lower precision has only a small effect on the accuracy of the peak width measurements as both sides of the peak are almost parallel. On later peaks, more flat and broad, the width at half-height becomes more dependent on the proper measure of peak height and this explains the decreasing precision of the peak width measurements. The accuracy of area measurement of a tall, narrow peak may be influenced more by the small error associated with the measurement of the peak width, than the larger error associated with the measurement of the larger peak height.

#### 1.6 COLUMN PERFORMANCE

The chromatographic process has been the subject of intensive theoretical work in order to elucidate the effect of various parameters on column performance. Gas chromatography has been compared to fractional distillation, as the behaviour of a chromatographic column is similar to a distillation column. A theoretical unit of measure of column performance, first used by Martin and Synge (1941) (9), and by James and Martin (1952) (10), has been assigned to the packed column, designated as the "height equivalent to a theoretical plate", usually abbreviated HETP. The column is visualized as a series of plates containing a gas and a liquid phase. The theoretical plate may be defined as the column space necessary for attainment of solute distribution equilibrium between the moving gas and the stationary liquid phases (11). The number of theoretical plates is a measure of peak broadening for a single component during its lifetime in the column. Thus, for a given column of constant length, the HETP represents the peak broadening as a function of retention time (12). The plate theory

(13), the van Deemter theory (14) and the more modern dynamic contributions by Giddings (15), all can be used to explain the performance and determine efficiencies of columns.

Factors such as column diameter and length, particle size of packing, the carrier gas, temperature of operation, etc., all have an effect on column efficiency. They have been well described by Horvath (16).

Another factor affecting column performance is sample size. The sample capacity is proportional to the amount of stationary phase in the column and thus approximately to the square of the column diameter. Column overloading will result in poor performance, tailing, and a shift in retention times. Also, non-linearity of the peak height-solute amount relationship must be considered (16).

## 1.7 THE SOLID SUPPORT

### 1.7.1 Support Requirements (17 - 19)

The function of the support material is to hold the stationary liquid phase in a finely dispersed form providing a high interfacial area in the column. The structure of the material contributes to the efficiency of the support, and the surface characteristics govern the degree to which the support enters into the separation.

A support material should fulfil the following requirements:

- (i) The surface area of the material should be high so that the liquid phase is spread out as a thin film.
- (ii) The structure should have the ability to hold the liquid phase in such a manner that the efficiency is high.
- (iii) The material should be mechanically strong to resist breakdown in handling.

- (iv) It must be capable of being packed into a uniform bed in a column.
- (v) It should possess chemical inertness and thermal stability and not adsorb sample components under the operating conditions.
- (vi) Its pore structure should be favorable for obtaining fast mass transfer in both phases.

No material is known at the present time which has all of these characteristics.

The support materials available are far from being inert and the choice and treatment of the solid support are probably as important as the liquid phase in the operation of a highly efficient column. The activity of the support frequently affects column behaviour and may completely dominate the retention behaviour of the column.

### 1.7.2 Peak Dissymmetry

Peak dissymmetry may take two forms. If the forward edge of the peak is distorted, this is called leading, and is caused by non-ideal solution effects. If the rear edge of the peak is elongated, this is called tailing, and is usually caused by the interaction of the sample and the support (20). Tailing may also be caused by the interaction of the sample and column tubing material, contamination of the injection port or the detector, and insufficient heat in the injection port (17).

#### 1.7.2.1 Leading or Fronting

Leading is caused by nonideal solution effects which occur, for example, when the solute and solvent have different functional groups. It may be controlled by using a more ideal solvent, or by raising the column temperature to make the solution more nearly ideal (20).

### 1.7.2.2 Tailing

Tailing is the most common column problem. A number of factors must be considered when discussing the problem of tailing.

- (i) The class of compounds and molecular weight.
- (ii) Sample size.
- (iii) Type of support surface.
- (iv) Nature of the liquid phase.
- (v) Percent liquid phase on the support.
- (vi) The column temperature.

Most classes of compounds, except for aliphatic hydrocarbons, show some tailing. Tailing increases with increasing ability of compounds to undergo hydrogen bonding. Compounds containing a hydroxyl group show the most tailing. Nitrogen compounds also show considerable tailing. Esters and ketones show less tailing, whereas ethers show little or no tailing.

### 1.7.3 Nature of Tailing

With the advent of more sensitive detectors, and greater sensitivity for small quantities of sample, the problem of support interaction has become severe and is a definite limitation of the chromatographic method. It has been shown that tailing increases with decreasing sample size (17). Giddings (21) suggested that tailing may be due to either an adsorption on sites on the support surface or that it originates from diffusion in the liquid phase.

In the first "active site" mechanism, tailing may originate when a sorption site exists which may hold molecules for a time equal to that necessary for one quarter of the zone to pass by. The tail part of the peak will increase as more solute molecules become attached to the active sites.

Tailing due to liquid diffusion may be caused by the way in which the liquid phase covers the support. If the liquid phase is held in long narrow pores, it will equilibrate slowly with the solute because of the large diffusion distances (17, 21).

Ottenstein (17) believes that the active site mechanism is by far the most probable for the majority of the tailing problems since modification of the surface usually results in reduced tailing.

It is known that tailing becomes more severe as the sample size is reduced and that the retention time of a compound changes with sample size. Scholz and Brandt (22) recognized that this was due to the adsorption by the support. If adsorption of the solute gives a nonlinear isotherm, different relative amounts of solute will be adsorbed depending on sample size. The difference in the fraction adsorbed would cause changes in retention time with sample size.

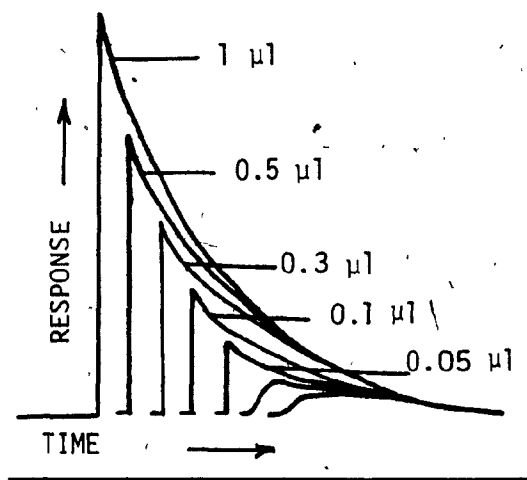


Figure 5

Changes in Retention Time with Sample Size (17)

Often a plot of either peak height or area of sample size passes through a point below the origin indicating loss of sample. Actually

the sample is only gradually eluted in very minute concentration from the column, below the sensitivity of the detector (17).

For a given adsorptive support surface, the retention time of the solute will decrease with increasing sample size until a point is reached where the retention time will hold constant with increasing sample size, and the peak height will then rise rapidly. At this point, there is enough sample introduced into the column to interact with the active sites. The amount of sample above this quantity will be seen as part of the peak causing the increase in peak height. If successive injections of the same sample are quickly made, the second sample will show greater peak height than the first because not all of the first sample has cleared the column. If the support surface is treated and modified by some technique, the number of active sites is reduced and the adsorptive character of the support is changed. The same solute sample size will show a larger peak on the treated support than on the untreated one because a smaller fraction of the solute is being adsorbed and subsequently slowly eluted from the treated support. The increase in peak height or area can be used as an indication of a change in the nature of the support surface.

Besides tailing, other solute interactions can occur, such as isomerization and dehydration, because of the support, the liquid phase, heat, contamination of the system, or the type of column tubing used. The reaction can occur quickly, and the entire solute converted at once, or, the reaction may go on as the solute moves through the column. In the former case the peak can be symmetric, whereas in the latter, two peaks may be seen, Figure 6, (17).



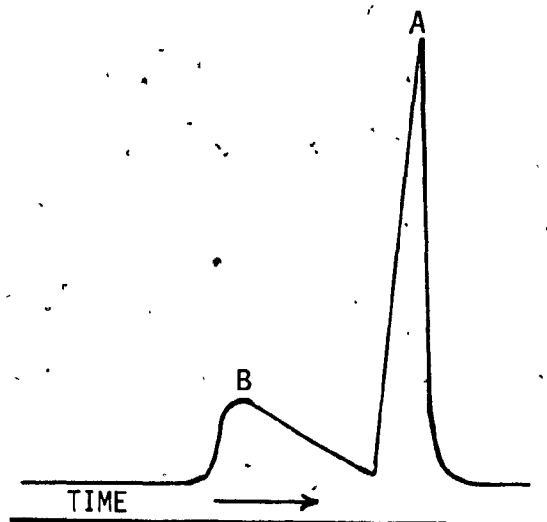


Figure 6      Chromatogram of Compound A Converting to Compound B  
During Passage Through Column (17)

Roman, Yates and Millar (23) observed peak tailing for some highly adsorptive columns, but many other such columns showed chromatograms without a marked alteration in peak symmetry. Under these circumstances, peak area rather than tailing is the best indicator of solid support adsorption. Similar chromatographic behaviour has been reported by Broteřl et al (24) whose work shows that over 85% of the pentafluoro-benzyl ether derivatives of pentazocine and detobemidone can be adsorbed without a significant change in peak shape.

#### 1.7.4: Diatomite Supports (17 - 19, 25)

The most commonly used supports are made from diatomite. James and Martin (10) used Celite 545, a filter aid, in their original work in gas liquid chromatography. Keulemans and Kwantes (26) reported the use of Sterchamol, a German diatomite firebrick, in 1955. In 1956, Dimbat et al (27) reported the use of Johns-Manville Sil-0-Cel C-22 brick as a support, also made from diatomite.

Two types of supports are made from diatomite. One is a pink material derived from brick, and the other is a white material obtained from filter aid. These two differ in physical properties as well as in performance as chromatographic supports.

The raw material for the supports is diatomite, also called diatomaceous earth, diatomaceous silica, or the German Kieselguhr. Diatomite is composed of skeletons of diatoms, single-celled algae, which accumulate in huge beds in various parts of the world. It is estimated that there are over 10,000 species of diatoms living in either fresh or salt water.

The basic structure of the many varieties is similar. The skeletons are made of hydrated microamorphous silica and some minor impurities, mainly metallic oxides. The skeleton consists of two half-cell walls, or valves joined together by a connecting band, or girdle, encircling and holding together the two halves. The skeleton as a whole, together with its physical markings, is regarded as the primary structure. The cell wall is perforated with many small round holes or pores about  $1 \mu$  in diameter. These pores are part of the primary structure. The electron microscope reveals that each pore has a fine structure, referred to as the secondary structure, in turn perforated with many small round holes called the tertiary structure. Due to the many levels of the pore structure in the cell wall, diatomite has a surface area of approximately  $20 \text{ m}^2/\text{g}$ .

#### 1.7.5 Preparation of Diatomite Supports (17 - 19, 25)

The filter aid or white material, also called Chromosorb W, is prepared by mixing diatomite with a small amount of flux, sodium carbonate, and calcining at temperatures above  $900^\circ\text{C}$ . During calcination,

the flux causes fusion of the finer particles forming coarser aggregates. A portion of the microamorphous silica is converted to crystalline form, cristobalite. The original light-gray diatomite becomes white because of the flux which is believed to convert the iron originally present as an oxide to a colorless complex, sodium iron silicate.

The pink material, also called Chromosorb P, is derived from Sil-O-Cel C-22 brick. The brick consists of diatomite which has been crushed, blended and pressed into brick, then calcined or burned above  $900^{\circ}\text{C}$  to permit its use as a high temperature insulator. During calcination the diatomite particles fuse, and a portion of the silica is converted to cristobalite. The mineral impurities form complex oxides or silicates. The iron oxide is thought to impart the characteristic pink color.

Another material available as a support is Chromosorb G, a flux calcined material designed to incorporate the relatively inert surface of Chromosorb W with the good handling characteristics of Chromosorb P. The Chromosorb G was designed for use in low-loaded columns with a top liquid phase loading of 5% (17, 28).

#### 1.7.6 Structure and Physical Properties of White and Pink Supports

(17 - 19, 25).

Chemical analysis shows the white and pink materials to be very similar. Table I is a typical analysis of the two. The higher  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  content of the white is due to the use of the flux in its preparation.

#### 1.7.6.1 Structure of Pink Particle

Each particle consists of a highly dense mass of diatomite fragments. A portion of the secondary diatomite structure remains. There is relatively little macropore space (space between the diatomite fragments) but there is considerable micropore space (space within the diatomite particle).

#### 1.7.6.2 Structure of White Particle

A white particle consists of diatomite fragments held together by sodium silicate glass. There is considerable macropore space within the particle. Much of the fine structure of diatomite has been destroyed and there is little micropore space.

#### 1.7.6.3 Physical Properties of Pink and White Supports

Baker, Lee and Wall (29) showed that the properties of the pink and white supports differed considerably with respect to surface area, pore distribution, pore volume, and packing density. Only the absolute or true densities are essentially the same. The majority of pores in the pink support are between 0.4 and 2 micron diameter with an average of about 1 micron. The white support has a wider pore size distribution with the average around 8 to 9 microns. No pores of less than 1 micron diameter are found.

Values of the typical physical properties of Chromosorbs W, P and G are compared in Table II. Much of the difference in the properties of the two materials stems from the differences in their preparation. The pink particle is a relatively dense mass of diatomite, and contains a small amount of internal void space consisting of small pores which produce a high surface area. Because of the compactness of the diatomite, and the fusion occurring during the calcination, the

TABLE I.                      TYPICAL CHEMICAL ANALYSIS OF DIATOMITE SUPPORTS (17)

	PINK		WHITE	
	<u>Non-Acid Washed Percent</u>	<u>Acid Washed Percent</u>	<u>Non-Acid Washed Percent</u>	<u>Acid Washed Percent</u>
SiO <sub>2</sub>	90.6	91.6	88.9	90.0
Al <sub>2</sub> O <sub>3</sub>	4.4	4.1	4.0	3.6
Fe <sub>2</sub> O <sub>3</sub>	1.6	1.4	1.6	1.4
TiO <sub>2</sub>	0.2	0.2	0.2	0.2
CaO	0.6	0.4	0.6	0.4
MgO	0.6	0.5	0.6	0.5
Na <sub>2</sub> O + K <sub>2</sub> O	1.0	0.9	3.6	3.2
Moisture	0.3	0.3	0.3	0.3

TABLE II                      TYPICAL PROPERTIES OF CHROMOSORB GRADES  
(DIATOMITE SERIES) (19)

PROPERTIES	CHROMOSORB		
	G	P	W
Color	Oyster white	Pink	White
Type	Flux-calcined	Calcined	Flux-calcined
Density, gm/cc			
(i) Loose weight	0.47	0.38	0.18
(ii) Packed	0.58	0.47	0.24
Surface area, m <sup>2</sup> /gm	0.5	4.0	1.0
Surface area, m <sup>2</sup> /cc	0.29	1.88	0.29
Maximum liquid phase			
loading	5%	30%	15%
pH	8.5	6.5	8.5
Handling characteristics	good	good	slightly friable

particle is relatively hard. The white particle consists of a mass of diatomite fragments lightly fused together in a very open structure giving it a large internal void space. Little of the very small pore character remains in the diatomite fragments. The open structure and the fact that the diatomite fragments are weakly fused together make the whole particle weak or friable. Differences in the structure of the two supports is reflected in the void space as the material lies in the column. A packed column of the uncoated white has approximately 90% void space; pink is approximately 80% void. If there was no internal void in the particle, the void space in the column would be approximately 67%.

#### 1.7.7 Differences in Behaviour of Chromosorbs P and W.

The difference in pore size was used to explain the variance in behaviour of Chromosorbs P and W. The pink support was seen as holding the liquid phase in small pores, and the white support in large pools. Since column efficiency is primarily controlled by the efficiency of mass transfer between liquid and gas phases, solute transit times in the larger liquid pools would be longer than in the smaller pools, and peak broadening would result (30).

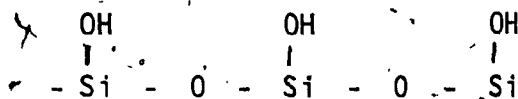
Harper and Hammond (31) examined the effects of porosity and pore size distribution, and found that the longitudinal diffusion term of the van Deemter equation decreased and the mass transfer term increased as support density and liquid load increased. The mass transfer term was also strongly affected by pore diameter and pore length. The ideal support was visualized as having a very open micro-structure containing short pores, of uniform diameter to hold the liquid.

The difference between the column performances of Chromosorb W and Chromosorb P was partially explained on the basis of a variation of molecular speeds due to pore size differences, and by multiple-path contributions to peak broadening. A further large contribution to total plate height was seen in the mass transfer term in the liquid phase which determines the magnitude of the third term in the van Deemter equation. The  $C_1$  term varies with the square of the liquid film thickness and therefore thick segments of a non-uniform coating will greatly increase plate heights. A thin uniform liquid film is thus the desired condition for keeping liquid mass transfer resistance small. This might be expected with materials which have a high surface-to-volume ratio, such as Chromosorb P, but would not be expected with wide pore supports of low surface area such as Chromosorb W (30).

Purnell (32) has observed that plate heights generally increase with increased liquid loading. This effect is not very pronounced, however, with the Chromosorb W support which has very broad pore distribution, and an average diameter of around 9  $\mu$ .

#### 1.7.8 Support Surface

Diatomite supports are siliceous materials with about 10% mineral impurities. The exact form of the mineral impurities is not known. It is well established that the surface of siliceous materials is covered with the silanol (Si-OH) and siloxane (-Si-O-Si-) groups, and can be represented as follows:



It is generally recognized that the pink calcined diatomite is consider-

ably more adsorptive than the white flux-calcined diatomite (17-19).

Perrett and Purnell (33) concluded from their studies that these supports are essentially low surface area silica gels. The two supports differ primarily in the extent of the surface rather than the nature of the surface. They reported the following values of silanol groups:

$4 \times 10^{19}$  groups/m<sup>2</sup> for pink

$2.5 \times 10^{19}$  groups/m<sup>2</sup> for white

The pink/white ratio is 1.6.

Scholz and Brandt (22) measured the number of active sites on the two supports, and reported a hydroxyl concentration per gram, ten times greater for pink than for white supports. If their values are corrected to equivalent areas of support, a pink/white ratio of 3 is obtained which is in the order of magnitude of that determined by Perrett and Purnell.

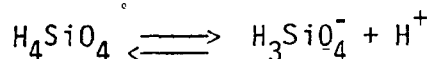
This difference in adsorptivity is related to differences in surface area, i.e. for the pink support, 1.87 m<sup>2</sup>/cc, and, for the white support, 0.24 m<sup>2</sup>/cc. The pink/white surface area ratio is approximately 8 (17, 18).

Blandenet and Robin (34) compared the performance of several pink and white diatomite supports in terms of adsorptive effects, and found that the adsorptive nature of the support is proportional to the surface area of the support. They concluded that the specific activity of the surface of each support is of the same order of magnitude, since they all have similar compositions.

The pink material is slightly acid (pH 6-7) and the white material



is slightly basic (pH 8-10). These differences in pH reflect the difference in the preparation where only the white material is calcined with a flux (17, 18). The acid nature of the pink support may arise from its silica-like surface. The silanol surface of amorphous silica is very weakly acidic. Roller and Ervin (35) gave the equilibrium constant for the reaction



as  $1.58 \times 10^{-10}$ , an acid strength comparable to phenol. Iler (36) suggested that this dissociation constant should be applicable to the silanol surface of a diatomaceous earth support as well.

#### 1.7.9 Nature of the Adsorption Sites (17 - 19)

As was described in Section 1.7.8, Perrett and Purnell (33) found that there may be two types of active sites on the support surface. Papa (37) also concluded that two types of sites exist, one of higher, and the other of lower activity. The higher activity site was found to cover 23 % of the surface.

The major types of active sites on the diatomite surface are the hydrogen bonding sites. Two types of hydrogen bonding sites exist, i.e. the silanol site, where the group is the proton donor in the hydrogen bonding, and the siloxane site, where the group acts as the proton acceptor. The acidic hydroxyl group is much more effective in forming a hydrogen bond than the silane oxygen. The extent of adsorption of the solute on the support depends on the strength of the hydrogen bond that the solute forms with the surface hydroxyl. Compounds such as water, alcohols and amines, which form strong hydrogen bonds show considerable tailing, while compounds such as ketones and esters which

hydrogen bond to a lesser degree, show less tailing.

Iler (36) showed that the surface silanol will complex with polar organic compounds containing electron-donor atoms. Hydrogen bonds between the electron-donor atoms and the silanol groups are probably involved.

Additional information suggests that a second type of active site which is acidic, and interacts with basic compounds, is present on the surface of supports. Knight (20) found that water deactivated the support surface towards alcohol solutes but not towards amine solutes. Similarly, amines deactivated the support towards other amines, but were inadequate to cause deactivation towards water.

Ottenstein (17) found that liquid phases having -OH groups were very effective in reducing tailing of alcohols, but were less effective for amines. A primary amine group in a liquid phase, however, was highly effective in deactivation for both amines and alcohols. This suggested that a liquid phase containing an -OH was effective in deactivating only one type of site, possibly the silanol, whereas the primary amine liquid phase could deactivate both the silanol site and the second active site, perhaps arising from mineral impurities. Basic solutes can undergo hydrogen bonding with the surface hydroxyl groups and can also interact strongly with acid sites.

The mineral impurities could also be the cause, in some cases, of dehydration or isomerization of the solute (17).

#### 1.7.10 Deactivation of the Support Surface

The elimination of adsorption on the support or its deactivation is carried out in a number of ways (17 - 19):

- (i) Saturation of the adsorption sites with a liquid phase.
- (ii) Removal of the sites by washing with acid.
- (iii) Priming of active sites with the sample.
- (iv) Removal of the sites by reaction of the silanol group.
- (v) Coating the support with a solid material.
- (vi) Adjusting the surface pH.

Only the first five will be discussed in detail. In this thesis no work was done on actually coating the support with a solid material, nor in varying the surface pH of supports.

#### 1.7.10.1 Saturation of Sites (17 - 19)

The active site on a support can be saturated or deactivated by means of polar materials. Scholz and Brandt (22), and Kusy (38), suggested that the deactivation is accomplished by hydrogen bonding. The deactivation may also be related to the liquid phase wetting of the surface. The greater the ability to wet the surface, the greater the deactivation. Because there is probably more than one type of active site on the support, a given liquid phase may be effective in deactivating one type and not the other. Since different solutes interact with the support to varying degrees, the satisfactory deactivation obtained because of liquid phase coating towards one type of solute, may be totally inadequate for another solute type. Other than support effects may also exist.

Saturation of the silanol groups can be accomplished by using a liquid phase having functional groups which can hydrogen bond with the silanol group of the support. The effectiveness of this deactivation depends on the extent to which the functional group of the liquid phase hydrogen bonds with the silanol group. Liquid phases containing

hydroxyl or primary amine groups are very effective. Functional groups such as carbonyl or ether linkage are also effective but not to the same degree. Non-polar liquid phases such as various hydrocarbons and silicone polymers lack functional groups which can effectively deactivate the active sites on the support. The trifluoropropyl silicones (QF-1, OV-210, SP-2401) are by far the poorest for deactivation purposes and consequently show much tailing. The dimethyl silicones (SP-2100, OV-101, OV-1, SE-30) are better, but are still quite poor. The methyl phenyl silicones (OV-3, 11, 17, 22, SE-52, SP-2250) are considerably better. The cyano silicones (OV-225, SP-2300, XE-60) are possibly a little better than the methyl silicones, but are less effective than the methyl phenyl silicones.

Not only is the type of liquid phase important, but also its amount. This is especially the case with a non-polar liquid phase. At low liquid phase loadings adsorption effects become more noticeable. This effect is seen to a greater degree with the pink supports than with the white, when relatively non-polar liquid phases are used. It seems that the non-polar liquid phase causes a certain amount of deactivation at high liquid loadings merely on the basis of thick coatings. This effect also applies to polar liquid phases, but to a lesser extent.

Scholz and Brandt (22) have shown that the minimum amount of liquid phase is a function of the support, liquid phase, solute, and temperature. In general, non-polar solutes show little adsorption on Chromosorb P and W columns down to about 0.25% liquid phase loadings, at which point van der Waal's forces on the solid support come into

play. Oxygen containing compounds are significantly adsorbed on a squalene-Chromosorb P column containing less than 8% squalene. The same oxygen containing compounds are little affected by the support down to 1% polyethylene glycol (PEG-400) coatings on Chromosorb P. The polar PEG-400 is able to cover the hydrogen bonding sites on Chromosorb P more effectively than is the non-polar squalene. Their results also showed that Chromosorb W is a less active support than Chromosorb P.

In low-liquid phase loading column operation, adsorption is accentuated because of column operation typically at temperatures well below the boiling points of solutes analyzed, and because of the small sample sizes that are used. Higher liquid loadings would be required to reduce adsorption, than the minimum values predicted by Scholz and Brandt who worked at temperatures near the boiling points of solutes. For example, while they determined that adsorption set in below 0.25% loadings on Chromosorb P, others found 3% silicone oil on C-22 firebrick (similar to Chromosorb P) to be the lowest acceptable liquid loading for the separation of a methyl-naphthalene mixture, at a temperature 150°C below the boiling point (39).

A solid support affects solute retention not only when the surface is incompletely covered, but also when a lightly loaded column with complete coverage is used. Keller and Stewart (40) have shown that solute molecules are able to diffuse through the liquid substrate, and be adsorbed on the support. Even on a 30% loaded column, the solute particle has time to diffuse to the solid support and be adsorbed there.

To readily observe the support interaction, however, loadings of

5% and lower should be used (19).

Support-solute interaction can also be seen as an increase in retention time of the peak with increasing adsorptive conditions. The retention volumes of certain solutes decrease proportionately less as the amount of liquid phase is decreased. This is due to the fact that support effects become more pronounced as the amount of liquid phase is decreased, giving slightly higher retention volumes than expected.

Scholz and Brandt (22) studied the change in the corrected retention volume per gram,  $V_{Rg}^0$ , of coated support with changes in % liquid phase, and reported support effects where there was a deviation from the expected linear relationship between  $V_{Rg}^0$  and liquid loading. Cremer and Huber (41) studied the solute-support interaction of Chromosorb P with varying amounts of PEG-400 by means of the adsorption isotherm derived from the peak shape. They reported a small interaction at 6% liquid loading and a still measurable interaction at 15% loading.

Tadmor (42) used  $^{36}\text{Cl}$  on the support and volatile chlorides as solutes to study solute-support interaction by means of isotopic exchange. He found that the exchange decreased with increasing amounts of liquid phase. Polar liquid phases were more effective in reducing the exchange than non-polar ones.

#### 1.7.10.2 Removal of Active Sites by Washing With Acid (17-19, 43)

It has been suggested that active sites caused by mineral impurities in the support can be removed by acid or base washing. Analysis of non-acid-washed and acid-washed supports shows some difference in mineral content. The mineral impurities that are removed appear to be at the support surface where solute interaction is detrimental. Com-

paring acid and base washing, acid washing is more effective than base washing in removing mineral impurities. A base washing does little to improve the surface that has already been effectively acid washed.

Smith and Radford (44) demonstrated that washing the support with base is not as effective as adding base to the support. In washing the support, some mineral impurities are removed from the support. However, it is difficult to wash away the last traces of base.

The significance of base washing may be primarily to make the support surface basic.

For many purposes, neither acid nor base washing is of great benefit. Acid washing may well worsen matters, possibly because of the difficulty of removal of the last traces of acid.

For example, Perrett and Purnell (33) found that the acid washed pink support is the most adsorptive support towards both benzene and acetone. On the other hand, Horning et al (45) showed conclusively that column performance is definitely improved by acid washing the support.

Zlatkis (46) showed that treatment of the support with aqua regia improved column efficiency, but careful examination of this work revealed that this treatment and subsequent washing with water removed much of the dust particles from the support and that this was responsible for the improved column efficiency.

Undoubtedly, acid washing is beneficial in certain cases, but possibly not in all cases.

#### 1.7.10.3 Priming of Active Sites With Solutes (17, 19)

Adsorptive effects of the support can be suppressed by repeatedly injecting large portions of the sample. When the peak height or peak

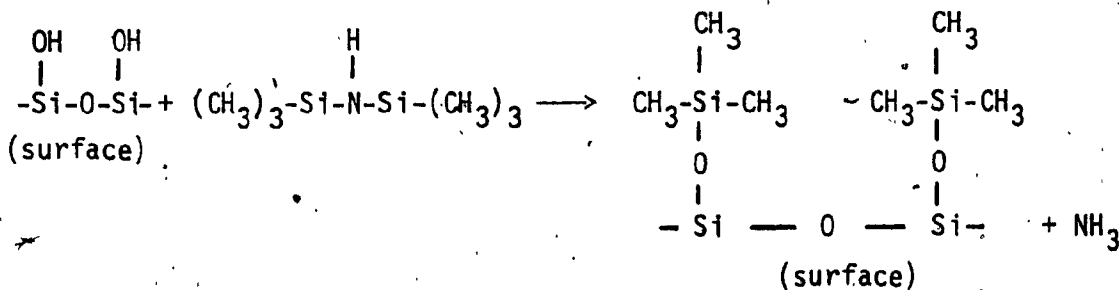
area stabilizes, the actual sample can be run. If carrier gas is subsequently allowed to flow through the column for a period of hours without it being used, and the sample is then injected again, the peak height or area will be decreased substantially. By repeated injections of the sample, a fairly large amount of sample is temporarily retained in the column. It serves to cover the active sites of the support. With time, the adsorbed sample is gradually lost from the column and it returns to its original state.

Gudzinowicz and Clark (47) injected a more concentrated solution of each component before the actual sample was introduced. After several hours they found it necessary to prime the column again with the more concentrated sample.

#### 1.7.10.4 Silanization of the Support Surface (17 - 19)

Modification of the support surface by reaction of the surface silanol group has become a very effective means of deactivation. Silanes have been the primary reactants although acetic acid has also been used. The treatment does not leave the surface totally inert, which suggests that the silanol groups are not completely removed, or that other sites are present besides the silanol groups (17 - 19).

Bohemen, et al (48) reported the use of hexamethyldisilazane (HMDS) to treat the surface of the pink support. The reaction proceeds as follows:

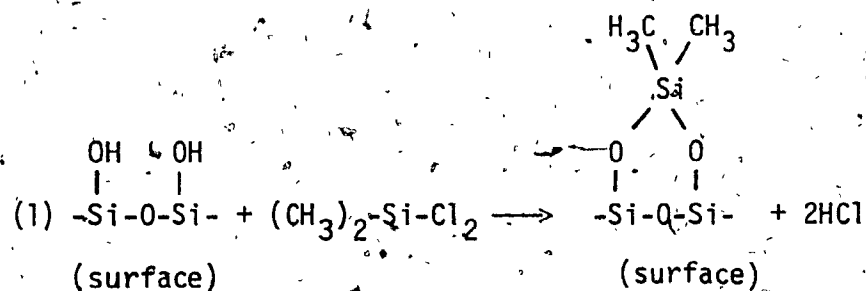




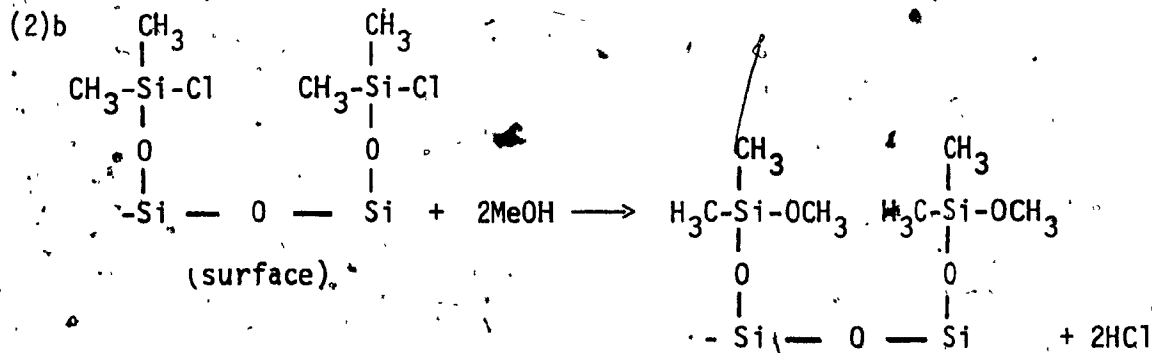
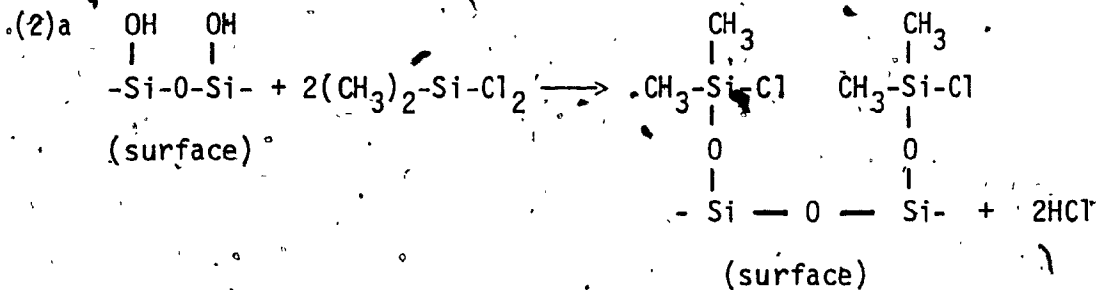
The surface silanol is converted to the trimethyl silyl ether and ammonia is given off (17, 18, 33):

Howard (49) treated the white support with dimethyldichlorosilane (DMCS).

Bohemien, Langer and Perrett (48) suggested that reaction proceeds in the following way:



or



The reaction may proceed either by mechanisms (1) or (2) or both could be involved.

The silanization is followed by a methanol wash in both cases to remove HCl, and also to convert the chlorosilyl ether to the methoxy derivative (17 - 19).

Perrett and Purnell (33) compared HMDS treated pink and white supports and found the white to be less adsorptive than the pink. In each case, the surface area of the support had been reduced by the treatment. They found that HMDS pink was comparable in adsorption to untreated white.

Sawyer and Barr (50) compared a number of support materials for the separation of a ketone mixture, and found the HMDS treated white support to be the most effective in terms of efficiency and adsorption.

Kirkland (51) compared the DMCS, HMDS and trimethylchlorosilane (TMCS) treatments on acid-washed white support, and found that the DMCS treated support gave the best peak symmetry.

Kabot et al (52) prepared HMDS and DMCS treated columns for steroid work, and obtained a greater degree of deactivation for the DMCS treated support.

Ottenstein (43) also compared different silane treatments of supports, and found that DMCS was the most effective, HMDS less so, and TMCS even less.

DMCS provides a more complete shielding of the support surface due to its greater degree of reactivity and its ability to penetrate the surface to a greater degree than HMDS (53). The DMCS treatment is now the preferred method of silanization (19).

Although acid washing alone is not very effective in reducing tailing, acid washing followed by silanization produces a support surface which is much more inert than a support which has only been silanized. Direct comparison of non-acid washed DMCS treated supports and acid washed DMCS treated supports shows the acid washed DMCS treated supports to be less adsorptive (19, 43).

The active sites that are removed by acid washing are few compared to the number of surface silanol groups present, and therefore, it is difficult to measure the reduction in adsorption caused by acid washing, considering the large number of silanol groups which remain. When the silanol group is converted to the silyl ether, however, it is very easy to see the difference between the non-acid washed and acid-washed supports. The use of acid-washed and silane treated supports has become very common. For most work it is recommended that the support used be both acid washed and silanized. Also, columns made with silanized supports appear to last longer than those made with non-silanized supports. The surface silanol groups appear to react with the stationary liquid phases causing them to deteriorate more rapidly than is the case in their absence (19).

#### 1.7.10.5 Coating Support Surfaces with Solid Materials

Ormerod and Scott (54) coated the pink support with silver, and using Apiezon grease as the liquid phase, they obtained symmetrical peaks for alcohols. On the same support without silver, the alcohols tailed badly. They also tried gold, but, only the silver provided a uniform coating. They found, however, that the silvered support reacted with sulfur compounds and amines.

Coating of diatomite supports with polymers such as Teflon 6 has

also been tried. Successful separation of strongly polar substances was obtained (18).

#### 1.7.10.6 Other Methods of Support Treatment

Blandenet and Robin (55) tried to improve the qualities of the siliceous supports with respect to the analysis of polar solutes by modifying the texture of these materials by thermal treatment. Celite heated at  $1350^{\circ}\text{C}$ , Chromosorb P at  $1450^{\circ}\text{C}$  and Chromosorb W at  $1300^{\circ}\text{C}$  for 6 hours allowed the determination of much smaller quantities of specific solutes, than was possible before heat treatment, adsorption being strongly diminished. This improvement was brought about by the decrease of the surface of the support in the constant volume within the chromatographic column. This improvement occurred in proportion to the temperature of heating, but was found to be limited by the thermal breaking down of the pore volume of the solid, and even by its tendency to soften.

Although thermal treatment has the advantage of simplicity, and produces better results for the analysis of small quantities of polar substances than is obtained by treatment with HMDS, it does so at the expense of lowering the efficiency of the column.

Wickramanayake and Aue (56) attempted to improve regular supports by changing the iron (and other elements) on the surface from an oxide to a reduced state by treating the supports (Chromosorbs W and P) with hydrogen at  $700^{\circ}\text{C}$ . They reasoned that by using a reduced support, they could counteract degradation of both stationary liquid phases and solutes attributable to the unwanted presence of oxidizing agents. Also, reducing the support surface could change its adsorptive and catalytic properties, and alter the solid-liquid interface region by rearranging the

orientation of liquid phase molecules with respect to the surface.

The treatment resulted in larger, sharper and more symmetrical peaks, and also in reduced bleed rates of the liquid phases used. Reduction in bleed appeared to correlate roughly with the phases' susceptibility to oxidation.

#### 1.7.11 Non-Wetting of Silane Treated Supports

Ottenstein (17) mentioned that highly polar liquid phases, those containing a high concentration of hydroxyl groups, do not wet the surface of the silane-treated supports, and therefore, yield columns with poor efficiency and resolution. This problem does not arise with less polar liquid phases. Van den Heuvel et al (57) also found a comparable situation of non-wetting with a polyester liquid phase. Withers (58) observed strong adsorption with a silanized support, when working with free acids,  $C_2 - C_5$ . When a non-silanized support was used, the problem was eliminated.

Using 10% SP-1000 on Chromosorb W, acid washed and DMCS treated, Ottenstein (59) found that a silanized support strongly adsorbed acetic acid and propionic acid. He suggested that the non-polar nature of the silanized supports makes it difficult for the liquid phase to completely cover the surface, leaving exposed some active sites. When a diatomite support is silanized, its surface becomes hydrophobic. With improper wetting of the surface, some active sites remain exposed causing adsorption.

Jönsson, Mathiasson and Suprynowicz (60) reported that silanized supports have intermediate adsorption, and wettability properties. They also stated that the extent of wetting is dependent on the procedure of acid washing the initial support. They argued that siloxane layers

formed by silanization are such low-energy surfaces that they are poorly wetted by most liquids used as stationary phases, even by n-hydrocarbons, which have the lowest surface tensions of any stationary liquids used. The wetting properties of a solid are governed by the critical surface tension,  $\gamma_c$ , of the solid. For silanized supports Serpinet (61) has estimated  $\gamma_c$  to be 22 dynes/cm, which is lower than the surface tensions of most liquids.

There is clearly a conflict here, between the aims of getting a surface which is as inert as possible, and a surface which is still well wetted by the stationary phase (60).

## 1.8 THE LIQUID PHASE

### 1.8.1 Requirements of the Liquid Phase

The essential requirements which a liquid must possess in order to be used as a stationary phase are listed below (62):

- (i) It should be selective for the components in the mixture for which it is to be used.
- (ii) It must be liquid under the conditions of column operation.
- (iii) The amount of liquid phase which is volatilized either through vapour pressure or through decomposition should not exceed an acceptable level.
- (iv) The liquid phase should be stable under the conditions of operation.
- (v) It should not react with the solutes to be separated.

### 1.8.2 Liquid Phase Distribution on the Support

While it was not the purpose of this thesis to study effects of liquid phases, it was considered worthwhile, at this point, to discuss their interactions with support surfaces for two reasons. They can act

to deactivate support surfaces, as has already been mentioned. Also, how they interact with support surfaces may well be indicative of how sample solutes may behave when exposed to non-liquid phase coated regions of the supports.

Baker et al (29) showed that as liquid phase was added to a support, it selectively filled the finest available pores, and that the observed loss in pore volume was equal to the volume of liquid phase added. This indicated that most of the liquid phase was located in the finest available pore structure, with only a thin film of liquid phase over the remainder of the surface.

Since there is a difference in the pore distribution of the white and pink supports, the liquid phase is held in relatively small pores in the pink support, and in relatively large pores in the white support (17, 18).

Martin (63) showed that the surface area of the column packings prepared from the pink and white supports differed considerably as the amount of liquid phase was varied on each support. The surface area of the pink support dropped from  $3.9 \text{ m}^2/\text{g}$  with no liquid phase, to  $2.5 \text{ m}^2/\text{g}$  at 3% liquid phase. With the white support, the surface area dropped from  $0.8 \text{ m}^2/\text{g}$  with no liquid phase, to  $0.5 \text{ m}^2/\text{g}$  at 3% liquid phase.

Saha and Giddings (64) studied pore-size distribution in more detail to correlate the structure of the support with the liquid phase diffusion term,  $C_1$ . The white supports gave reasonable agreement between experimental and calculated values for the  $C_1$  term but a considerable difference was found for Chromosorb P and G supports. The  $C_1$  value for Chromosorbs P and G showed strong dependence on particle size. There was a certain amount of variation in pore distribution from

batch to batch. Their values for pore distribution differed from those of Baker et al (29), who reported that for pink supports, the highest number of pores is in the range of  $0.5 \mu$  whereas for the white supports the value is about  $4\mu$ .

According to Giddings (65), any liquid added to a porous, wettable solid is subject to both adsorption and capillary forces. The intermolecular attraction of solid and liquid leads to adsorption in monolayers and multilayers. The liquid-liquid intermolecular attraction, responsible for surface tension, leads to capillary condensation in pores. If the liquid is not flooding the support, the adsorption and capillary forces compete with one another for liquid. As liquid phase is added, the entire surface is coated with a monolayer and higher layers. For the pink support a monolayer is formed with about the first 0.2% of liquid phase. After the surface forces have been satisfied, liquid begins to condense in the various pores, with condensation occurring in the smallest pores first. When large amounts of liquid are added, the large cavities, and interstitial network, become partially or totally filled.

A typical packed column contains more capillary liquid than adsorbed liquid, and the former contributes essentially to the entire plate height term. With a liquid loading of 15%, 2 to 4% is adsorbed liquid, and about 12%, capillary liquid. If the pores of a support range from 1 to  $10 \mu$  the thickness of the adsorbed liquid layer in equilibrium with these pores will be about 50 to  $100 \text{ \AA}$  (65).

Liquid film thicknesses greater than about 33 angstroms show uniform properties of the bulk liquid. If such films are less than 33 angstroms



in thickness, the underlying surface of the support alters the liquid to affect its partitioning properties. Surface forces are known to cause changes in the dielectric constants (and therefore the solubility) of liquids adsorbed on silica gels and porous glass (30).

Keller and Stewart (40) suggested that up to 0.5% liquid phase, only a portion of the support surface is covered, and consequently bare support is present.

The maximum level of stationary phase that can be used with column efficiency still being high is given below for various supports:

Pink	15%
White	10%
Chromosorb G	3%

These values are very general, and vary from one liquid phase to another. The variation may be related to the viscosity of the stationary phase (19).

Other factors that influence liquid phase distribution are gravitational and gas flow forces. Gravitational forces cause an excess accumulation of liquid in the lowest segments of tubing containing column packing. Gas flow forces liquid towards the downstream end of the tube. In addition, evaporation of liquid into the gas stream in the early part of the column will lead to a liquid deficiency there (65).

### 1.8.3 Column Lifetime

The upper temperature limit of a liquid being used as a stationary phase is closely related to the column lifetime. At moderate temperatures, where there is almost no loss of liquid phase, the column should last indefinitely. At a high enough column temperature, liquid phase is lost at an appreciable rate due to either volatilization or decomposition.

Columns operated in this condition will have a finite period of usefulness (66).

An early criterion for liquid phases was that the specific retention volumes should not vary by more than 2% over a three-month period of continual use at a given temperature. It has also been recommended that the optimum maximum column temperature is that at which no more than 50% of the liquid phase is lost in 1000 hours of use at a flow-rate of 15 ml/min. (66 - 68).

The temperature at which a 2% change in the specific retention volume occurs is generally close to the temperature at which 50% of the liquid phase is lost in 1000 hours, and these limits correspond to a volatility of  $1.1 \times 10^{-3}$  g of liquid phase per liter of carrier gas, or a vapour pressure of between 0.05 and 0.10 mm Hg (66, 68). A reasonable upper temperature limit, therefore, is that temperature at which  $1 \times 10^{-3}$  g of liquid phase is present in one liter of carrier gas (66).

The upper temperature limit of polymers which do not have boiling points, is limited by their decomposition temperatures.

In actual practice, the maximum useful temperature limit of a liquid phase is also determined by the sensitivity of the detector (66, 68, 69). Attempts have been made to define the limit of liquid phase loss on the basis of detector behaviour. The maximum allowable operating temperature was defined as that where the base line showed a maximum deflection of 0.5% of full scale at maximum sensitivity (66, 67).

#### 1.8.4 Decomposition of Stationary Phases

This discussion is included to illustrate how column changes can occur during gas chromatographic analysis, and to show that in some

instances, every run on a particular column may change its properties and thereby lead to non-reproducibility of results from run to run.

All stationary phases appear to be volatile to some extent, and many decompose rather readily (68). Keppler, Dijkstra and Schols (70) found that polythenes, halogenated ethylene polymer, silicones, and Apiezon M grease were lost at the rate of 3 - 8 mg/hr. at 210 - 250°C, and 15 ml/min. carrier flowrate.

Dijkstra (71) measured a loss of 50 mg of material in the first eight hours from a column holding 3 g of silicone (temperature not indicated). Kwantes (72) observed such a loss above 180°C.

Other workers found that silicone oil was continually lost to a stream of nitrogen at 260°C, during 200 hours of use, with the rate of loss decreasing with time (67).

Dal Nogare and Safranski (73) chromatographed a silicone oil which gave 16 peaks attributed to homologs and volatile degradation products. Hawkes (74) operated a column containing Apiezon L vacuum grease for the equivalent of two months at 290 - 295°C with no noticeable change in peak areas. A darkening of the stationary phase did not impair efficiency. No attention was paid to peak position.

Taylor and Dunlop (75) found that calibration factors for peak areas and heights did not differ significantly for old and new columns whereas there was a difference in peak positions.

Guild, Bingham and Aul (76) reported a loss of immobile phase when the temperature of a column, containing 30% w/w Apiezon L grease on C-22 firebrick, was increased. Repeated heating of the column gradually reduced this loss. They suggested that frequent heating of the column near or above the recommended temperature limit would eventually reduce the

amount of immobile phase and seriously alter resolution and retention volumes.

Tuey (77) found no relation between the change in retention properties, and the loss or chemical change of a silicone stationary phase. He found a change in retention times and efficiency with no observable change in the partitioner, while Hawkes (74) reported changes in the immobile phase with none in chromatographic behaviour.

Knight (78) remarked that most of the loss comes from the first part of the column. Moderate losses will reduce retention times but the relative retention times will be unchanged.

Dinonylphthalate was found to escape from a column at a rate of 0.017 mg per liter of carrier gas at 50°C, and 5.0 mg per liter at 181°C, from a 10% immobile phase Celite column with carrier gas run at 8 ml/min. (67, 68).

Polyesters showed considerable thermal degradation between 180°C and 220°C. Degradation and bleeding were reduced, the conditioning period shortened, a more uniform distribution of the liquid obtained, and a greater reproducibility experienced between packings using the same ester, if the acid washed Celite support was first coated with a silicone before application of the polyester. The instability of polyesters was blamed on the presence of acid impurities on the support (67).

The bleeding from columns containing 20% silicone gum rubber, or diisodecyl phthalate, supported on 60/80 mesh Chromosorb, at temperatures where bleeding was significant, was studied, and attributed to some chemical reaction or degradation. A similar observation was made with polypropylene (67).

Keller, Bate, Costa and Forman (67) found that for tricresylphos-

phate and dinonyl phthalate columns, liquid phase loss occurred only from the first part of the column. The carrier gas was rapidly saturated with partitioner in the first portion of the column, and further evaporation did not occur. For a polyethylene glycol column, they found that during the initial conditioning process, and low temperature separations, easily volatilized materials were driven off. At higher temperatures, another group of "volatiles" was removed. Each partitioning liquid in combination with its support is an individual problem since a variety of changes can occur.

The maximum temperature of polymeric liquid phases is limited by their decomposition. Small temperature fluctuations in the column can cause large changes in the decomposition rate giving an unsteady baseline. With ionization detectors, changes in the carrier gas flow rate will also result in base line changes because of the increase or decrease in the amount of decomposed material which enters the detector (66).

There are several types and causes of decomposition of the liquid phases at elevated temperatures (66). Impurities in the carrier gas such as oxygen will cause changes in liquid phases. Five ppm of oxygen is enough to darken polymeric hydrocarbons at elevated temperatures. Silicones will oxidize in the presence of oxygen and water at elevated temperatures. Non-volatile impurities in the liquid phase (such as hydrogen ions and catalysts used in making the polymer or compound) may cause catalytic decomposition. Some liquid phases are catalytically decomposed by acidic and basic sites on diatomite supports on which they are coated. Deactivation of the support by silylation, or the use of modifiers to saturate these sites may be effective in reducing or elimi-

nating decomposition: In some cases the liquid phase is catalytically decomposed by its own degradation products. This decomposition is highest at the exit end of the column, and when slower carrier gas flow rates are used.

The degradation products in the gas stream increase in concentration as the carrier gas proceeds through the column, and may cause the greatest reaction to occur near the outlet end. This type of decomposition must be initiated by one of the other modes of column degradation. If contaminants in the carrier gas are responsible for the change in the liquid phase, careful purification of the gas will help to retain the original identity of the stationary phase (67). If the reaction is one of thermal condensation, catalyzed by non-volatile impurities in the partitioner, or by the support, carrier purification will not solve the problem, and the reaction will proceed throughout the life of the column to a greater or lesser extent. One may attempt purification of the partitioner, and deactivation or masking of the support (67).

Both chemical changes and evaporation produce a redistribution of the liquid phase on the support which is generally most marked at the inlet end of the column where the entering gas is free of contaminants. As the hot carrier gas enters the column from the flash heater, it becomes saturated with vapour from the liquid phase. This saturation is probably hastened since the carrier gas has been heated in the flash heater to temperatures above the column temperature. In the extreme case, all of the liquid phase is removed from the inlet end of the column and the uncoated support will adsorb polar solutes, giving rise to artifact or ghost peaks when later samples are introduced (66, 67).

The distribution of liquid phase may show a gradual change as one proceeds along the length of the column, or it may be discontinuous. The discontinuity may be a sudden change from a low loaded section to one of higher loading, or there may be a sudden change in the retention process, e.g. a change from "adsorption" to "solution". Such a discontinuity is most likely to result from evaporation of the liquid phase from the support at the inlet end of the column. Small losses in the early sections of the column, however, should not appreciably affect chromatographic behaviour. Redistribution of liquid phase and bleeding effects may change continually during the use of a column (67).

A liquid phase which is bleeding due to volatility of the liquid should have two properties which will distinguish it from a bleeding liquid phase which is decomposing. If the liquid phase is volatilizing, the amount of bleeding material per minute should increase with the flow rate for a fixed length of column, while if it is due to decomposition, the amount of bleeding should remain constant. Also, if the column is long enough so that the gas phase is saturated, a further increase in length will not result in an increase in the bleeding level. A decomposing liquid phase should result in an increased bleeding level when the column length is increased (66, 67). Bleeding with liquid phases containing impurities whose volatilities are greater than the volatility of the liquid phase, as in the case of polymers containing low molecular weight homologs, causes different problems. The impurities distill off the front part of the column first. As bleeding proceeds they are removed progressively down the length of the column (66).

### 1.8.5 The Use of Silicone Polymers as Stationary Phases in GC

Siloxane materials are the most widely used liquid stationary phases in gas chromatography today (79). Their normally high thermal and chemical stability along with low bleed characteristics, and the possibility of introducing suitable functional groups into their structures to modify their retention properties, have resulted in a large number of applications (79, 80). The organofunctional groups currently commercially available are methyl, phenyl, cyanoalkyl, fluoroalkyl and chlorophenyl. This offers a range of polarities from the essentially non-polar methyl, to the very polar cyanoalkyl (80).

Most silicone polymers are produced by polymerizing a cyclosiloxane in the presence of a small amount of hexamethyldisiloxane as chain stopper. A basic catalyst is employed at moderate temperatures which must be removed or neutralized to prevent depolymerization under conditions where the volatile cyclosiloxanes could be continuously removed, as in a GC column. The polymerization proceeds by the cleavage and reforming of siloxane bonds. In many commercial silicones, the catalyst is simply neutralized with an acidic additive such as one of the triarylphosphites, or carbon dioxide. This method is not as effective as water washing, or the use of a catalyst, which may be removed by thermal decomposition or volatilization, such as tetramethylammonium hydroxide (80). Silicone liquid phases should be coated on a neutral solid support. Strong protonic acids, and some Lewis acids, catalyze the cleavage of siloxane bonds.

The incomplete removal of the relatively volatile lower molecular weight fractions of the polymer will result in excessive column bleed of



commercial silicones. In higher molecular weight polymers, this fraction may be removed by thorough column conditioning without significantly altering the column loading.

The silicones are quite inert, chemically, but solutes which are strongly acidic or basic should be avoided. Electrophiles, such as chlorine, may cause cleavage of silicon-carbon bonds (80).

Phenyl silicones covering a wide range of phenyl contents and molecular weights are currently available. This range of phenyl contents is achieved by co-polymerizations involving the cyclic monomers which are methylphenylcyclotrisiloxanes, octaphenylcyclotetrasiloxane, and octamethylcyclotetrasiloxane, using base catalysts.

The OV phenyl silicones (Ohio Valley) and SP-2250 (Supelco) are manufactured by a process which leaves no residual catalyst, and involves a good devolatilization. OV-17, used in this thesis, is a methylphenyl, (50% phenyl), silicone polymer (80).

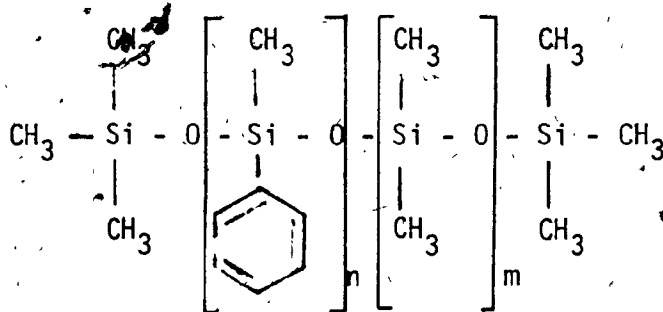


Figure 7      Structure of OV-17 Liquid Phase

Williams (81) showed that in atmospheric nitrogen, thermal degradation of silicone polymers is not a problem. The phenyl silicones have thermal stabilities somewhat higher than the methyl silicones. Since

thermal degradation involves depolymerization to produce volatile cyclosiloxanes, the effect of the depolymerization is to reduce column loading rather than alter the chemistry of the polymer. In the presence of oxygen at temperatures near 250°C, the silicon-carbon bond is ruptured, leading to crosslinking and gelling of the polymer (80, 82). In fact, oxidative changes begin to occur at temperatures above 175°C, even when using carrier gas containing as little as 0.1% oxygen (68). Similar oxidative changes have been observed for other polymer phases. For example, Dijkstra (71) attributed the oxidation of Apiezon greases, and polythenes to oxygen in the carrier gas.

#### 1.8.6 Conditioning of Liquid Phase Coated Supports

Conditioning refers to the heating of a column at some optimum temperature for a number of hours or days, with inert carrier gas flowing through it, before it is put into use. The thermodynamic activity of the coated liquid, that is, the surface energy and the vapour pressure, depends on the geometry of each cavity and the liquid in it. If the liquid phase has been coated so that the activities of the liquid in the pores are not all equal, then a potential for a microscopic redistribution will exist and such a redistribution will continue until the activity of the liquid is the same all over the support. This can occur in two ways. The liquid may physically flow from one cavity to another (from areas of high energy to areas of lower energy), or immobile phase may evaporate from one cavity, and condense in another. These processes are accelerated by increasing the conditioning temperature. Liquid may also redistribute at the contact points between particles where there is a very small radius of curvature of the liquid film. This can only occur after the column is packed (65 - 67).

In addition to the redistribution of the liquid phase, lower boiling impurities or lower homologs, if the liquid phase is a polymer, will be removed from the column during conditioning. In addition to removal of volatile components (which limit the maximum allowable operational temperature) some combination of polymer molecules may occur, thus improving the stability of the packing. These conditioning processes may take as long as several days or a week before maximum stability is attained (66).

Preheating in the presence of air, either at atmospheric or reduced pressure, is undesirable. Even in the presence of small amounts of oxygen, the liquid phase may undergo changes to something new, undesired and unknown. Some changes will occur with all liquid phases during conditioning, but it is best to minimize them and to keep them as reproducible as possible (66).

#### 1.9 COLUMN TUBING MATERIALS

The materials most commonly used for column tubing are pyrex glass, copper, aluminum, stainless steel, nickel and Teflon.

Glass columns are considered to be the most inert for most applications, and allow inspection of the state of the packing both during the preparation of the column, and subsequently after use. The greatest disadvantage to the use of glass columns is that they are fragile. Glass columns are often difficult to connect into the chromatographic system, they lack flexibility, and must be formed with precision in order to fit a specific instrument (83).

Stainless steel is more easily handled and is quite satisfactory for many analytical applications. For example, for the analysis of fatty acid esters, and many hydrocarbons, stainless steel is perfectly

adequate. On the other hand, glass gives fewer problems for analysis of acidic barbiturates, amines, free acids and other highly polar compounds.

Copper and aluminum are no longer used to the extent they once were. Both of these two column materials form oxides which act as adsorbents or even as catalysts, and cause decomposition. Also, since these tubings are so soft, the column can easily be deformed with the support particles being subjected to unnecessary stresses and breakage (83). There has been a report however, where less tailing was observed for water and alcohols analyzed with a copper column packed with 10% Carbowax 20 M on 40/60 Chromosorb T than with a stainless steel column filled with the same packing. Plastic tubing is seldom used because of temperature limitations, and because oxygen and atmospheric vapours can diffuse through the walls of the column into the packing even against the normal column pressures (83).

Fenimore, Whitford, Davis and Zlatkis (84) have found that nickel tubing may be substituted for glass for use with samples of biological interest. Comparisons of separations of mixtures of steroids, narcotic alkaloids, phenothiazines and amphetamines on stainless steel, glass and nickel packed columns showed little or no observable sample decomposition on glass or nickel compared to complete loss of certain compounds on stainless steel. Other classes of compounds which were chromatographed on nickel columns were barbiturates, cannabinoids, catecholamines and catecholamine metabolites. Without exception, nickel and glass columns yielded comparable chromatograms. These same workers also observed that the performance of packed nickel columns may be improved by silylation.

Beckman and Bevenue (85, 86) studied the effect of column tubing composition on the recovery of chlorinated hydrocarbons by gas chromatography. They found increasing recovery of the insecticides injected into columns of copper, stainless steel, aluminum and quartz respectively. An all-glass or all-quartz system, including the sample injector area, seemed to be preferable.

It has also been shown that Pyrex glass is as effective as quartz for the analysis of many chlorinated insecticides (87). Arnold and Fales (88) compared copper, aluminum and stainless steel columns with each other and with respect to siliconized glass as a standard. They found that a glass column is slightly superior to aluminum or stainless steel. However, they felt that the observed differences appeared to be within the limits of variation due to extraneous factors such as packing technique, and degree of pre-conditioning. With copper, basic substances, like codeine and phenazocine, were nearly completely adsorbed and the cholesterol peak was greatly diminished. Subsequent injections caused the partial appearance of the above mentioned compounds. Apparently many adsorption sites were saturated in the first injection, but the expected peak heights were not obtained. This suggests that some of the adsorption sites were partially saturable while others continuously adsorbed or decomposed the compounds. The fact that basic substances were so greatly affected suggests the presence of acidic sites or complexing salts.

Teflon tubing also caused considerable tailing on peaks arising from both polar and nonpolar compounds according to results of Arnold and Fales (88). Groth and Doyle (89) found that the use of copper or aluminum sampling loops resulted in significant errors in the analysis of

CO<sub>2</sub> at low concentrations. Little error was associated with the use of stainless steel under the same conditions.

Ottenstein and Bartley (59) found that metal columns (stainless steel and aluminum) strongly adsorbed free acids (C<sub>2</sub> - C<sub>5</sub>). Adsorption was also observed with a stainless steel inlet. Each injection gave different results. With repeated injections, the peaks gradually sharpened and the shoulders on the peaks diminished. If the column was subsequently allowed to go unused for a short period of time, the next injection showed the same adsorption pattern as the first injection. They also observed that metal at the inlet of the column appeared to be more detrimental than metal at the exit, probably because of the much higher temperature of the inlet. Stainless steel tubing was also found to be destructive in a study of barbiturates. Metal tubing was unsatisfactory for polyols and vanillins.

Another factor to be considered in the choice of column tubing material is column efficiency. Glass produces higher efficiency columns than stainless steel which in turn is better than aluminum, according to Supina (83). Copper produces the least efficient columns. The difference between the three metals may be due to the difference in hardness of the tubing, and possible damping of the vibration used to compact the packing while filling the column. The reason why glass gives higher efficiencies than stainless steel is not clear. Perhaps it can be more efficiently packed, merely by being able to see the packing (83).

Another fact that should be mentioned about metal columns is the many grades of aluminum and stainless steel tubing on the market, which vary in composition. A "shiny" finished stainless steel tubing was compared with a "dull" finished tubing using the pesticide endrin

(90). The result was a multippeak phenomena with the dull column, but a single symmetric peak with the shiny column. The shiny tubing contained ten times more titanium than the dull tubing. The quality of the inside surface can also vary from batch to batch from the same manufacturer (19).

#### 1.10 EXTRANEOUS ADSORPTION LOSSES

The glass wool used to plug column ends can also cause adsorption. Glass wool has a surface area of approximately  $1 \text{ m}^2/\text{g}$ . This high surface area can be a source of adsorption since glass wool, like glass tubing, has surface silanol groups. Generally the glass wool is silanized to reduce adsorption, but, with acidic compounds even silanization is not adequate, and phosphoric acid treatment of the wool is necessary. The fact that the injection port is usually warmer than the column makes the glass wool in the injection area especially liable to be harmful (19, 91).

Carbonaceous matter can accumulate in the injection port over a period of time. This material can be either from decomposition of the sample, or a residue of non-volatile material in the sample. These carbonized deposits in the injection block can bring about adsorption and decomposition of many compounds, such as the pesticides DDT, dieldrin and endrin (59, 87).

It is becoming normal practice in analyzing thermally unstable compounds such as pesticides, to dispense with an injection block, and to inject directly on the column in order to avoid decomposition at this point (87).

#### 1.11 SOLUTE ADSORPTION AT THE GAS-LIQUID INTERFACE (92)

It has been proposed that adsorption of the solute can occur on

the surface of the liquid phase as well as on the surface of the support. This effect is most pronounced when

- (1) the liquid phase is highly polar, and a poor solvent for the solute analyzed;
- (2) the surface area of the support is high;
- (3) the liquid loading is low;
- (4) the temperature is low.

Adsorption of nonpolar molecules on polar liquid surfaces is not an uncommon phenomenon, and leads to an excess concentration of solute on the surface. Furthermore, the polarity of the liquid phase largely determines whether the solute will adsorb preferentially on the liquid surface, or, on the solid support. Adsorption on the liquid should be more important with polar phases, especially for nonpolar solutes, while adsorption on the solid should be more important with nonpolar phases, especially for polar solutes.

Two classes of adsorption can be seen at the gas-liquid interface:

1. One type is characterized by large solute activity coefficients (the bulk liquid phase is a poor solvent).  
Here, the less polar the solute is with respect to the liquid phase, and the less soluble it is in the bulk liquid, the larger the surface excess concentration of solute.
2. The second type is characterized by relatively low solute activity coefficients, significant solute solubility in the bulk liquid, and a solute and liquid phase molecule of comparable high polarity. Here, the solute molecules are preferentially adsorbed because of strong dipole-dipole interactions or hydrogen bonding between the



solute and the liquid surface.

It has also been pointed out that a more complicated mechanism probably exists than that of simple liquid phase or solid support adsorption.

#### 1.12 COMMERCIALY AVAILABLE MODIFIED AND NON-MODIFIED GC SUPPORTS

The supports which are commercially prepared from filteraids fall into two major categories. One group is prepared from Celite filteraids, and includes Chromosorb W, Supelcoport, Varaport 30 and Diatoport S (which has been discontinued). Another group is prepared from Celatom brand filteraid, and these supports include Gas Chrom and Anakrom. Celatom is a fresh water diatomite mined in Nevada, while Celite is a salt water diatom from California. It has been reported that supports prepared from Celatom tend to be slightly less adsorptive than those prepared from Celite, while the ones prepared from Celite are capable of producing columns of slightly higher efficiency than those prepared from Celatom.

Most of the firebrick type supports sold in the United States, such as Chromosorb P and Gas Chrom R, are manufactured from the Johns-Manville C-22 firebrick. A European brand diatomite firebrick, Sterchamol, is also used, but supports derived from this brick have an appreciably higher surface area, and consequently, result in more peak tailing of polar compounds than supports derived from the C-22 brick. Most supports in use are silane treated and/or acid washed. The variations in techniques by the different manufacturers account for greater differences in the brands of supports than do the differences in the source of raw materials (93).

Johns-Manville produces Chromosorbs G, P and W. These are available

in both untreated and in treated forms, as well as in a choice of various mesh ranges (94, 95).

All of the Chromosorb supports in the untreated form are referred to as non-acid washed (NAW). Therefore, untreated Chromosorbs G, P and W are labelled Chromosorb G NAW, Chromosorb P NAW and Chromosorb W NAW respectively. Chromosorb grades G, P and W are also available with the acid washed treatment (AW) and with the combined acid washed and dimethyl-dichlorosilane (AW-DMCS) treatment.

High performance (HP) grades of Chromosorbs G and W have been developed for use with steroids, bile acids, alkaloids, and for other analyses of pharmaceuticals, medical and toxicological compounds. Chromosorb HP, according to Johns-Manville, is a high quality, carefully acid washed, and DMCS treated, flux-calcined diatomite. It has superior inertness and column efficiency, no catalytic surface activity, and requires a short column conditioning time (95). High performance Chromosorbs G and W are labelled as Chromosorb G-HP and Chromosorb W-HP.

Chromosorb 750 is a very inert support, non-friable, free flowing and highly efficient designed specifically for biomedical and pesticide analysis. It is prepared from high purity diatomite with exhaustive acid-washing and effective silane treatment. It has a surface area between 0.5 and 1.0 m<sup>2</sup>/g and a loose weight density between 0.32 and 0.35 g/cm<sup>3</sup>. According to the manufacturer, Chromosorb 750 has a high degree of chemical inertness, hard particles, provides uniform distribution of the liquid film on the particle surface, minimum adsorption for polar compounds, minimum decomposition of sensitive samples, and short column conditioning time (96). Table III lists some of the more widely used supports and shows brand name equivalents (93).

TABLE III

DIATOMITE SUPPORTS - BRAND NAME EQUIVALENTS (93)

(These are grouped by type but not necessarily by equivalent quality.)

	MFR	NONACID WASHED	ACID WASHED	ACID WASHED DMCS TREATED	OTHER TREATMENT	DESIGNATED
Gelite	1	Chromosorb W NAW	Chromosorb W AW	Chromosorb W AW-DMCS	HMDS	Chromosorb W HMDS
	1			Chromosorb W HP		
	2			SUPELCOPORT		
	3	Gas Chrom CI	Gas Chrom CLA	Gas Chrom CLZ	Acid + Base	Gas Chrom CLP
	4 5			Diataport S Varaport 30		
Celatom	2		SUPELCON-AW	SUPELCON AW-DMCS	Acid, Base & DMCS	Gas Chrom Q
	3	Gas Chrom S	Gas Chrom A	Gas Chrom Z		
	6	Anakrom U	Anakrom A	Anakrom ABS	Acid, Base & DMCS	Anakrom ABS Anakrom Q Anakrom SD
C-22 Firebrick	1	Chromosorb P NAW	Chromosorb P AW	Chromosorb P AW-DMCS	HMDS	Chromosorb P HMDS
	3	Gas Chrom R	Gas Chrom RA	Gas Chrom RZ		

1 Johns-Manville  
2 Supelco, Inc.

3 Applied Science  
4 Hewlett-Packard

5 Varian  
6 Analabs

The results of tests conducted at the Johns-Manville Research Center showed the following order of decreasing activity of their chromatographic supports (94-96).

For Chromosorbs W, P and G, the order of adsorptivity was:

NAW > AW > AW-DMCS > HP

Chromosorb 750 was claimed to be the most inert support for biomedical and pesticide analysis.

Chromosorb G is described as less adsorptive than Chromosorb W and other flux calcined or white diatomite supports. The most adsorptive supports are the Chromosorb P's.

#### 1.13 SOME COMPARISONS AND EVALUATIONS OF COMMERCIALY AVAILABLE

##### SOLID SUPPORTS

Comparisons of supports have been made by many workers using different types of compounds. Conclusions have varied significantly. Some examples follow.

In a study of commercially available solid supports produced from diatomaceous earths, Bevenue, Ogata and Beckman (97) found that, in 1968, the methods used for the preparation of solid supports had not improved to a point to assure reproducible results with different batches of the same type of support. There is evidence to suggest that the same is true today. Characteristics such as surface area, number of active sites, or other physical properties, may be responsible for the variations between different batches of the same support.

Smith, Oathout and Cook (98) evaluated the relative degree of inertness of various competitive gas chromatographic supports towards the very sensitive trimethyl-silylated amino acid derivatives. While

this was principally a measure of residual surface silanol groups, it was felt that the results obtained could also prove to be a good general index of the residual activity of the various supports. The results of Smith et al's tests are given below. All the high performance (H.P.) supports tested were practically equivalent. The high performance Chromosorb W-HP was less adsorptive than the "home-made" DMCS treated support, which was less adsorptive than the corresponding HMDS treated support. The acid washed, unsilanized supports were significantly less adsorptive than the non-acid washed supports from which they were made. Perhaps this reflected the removal of "fines" and other impurities from the untreated commercial supports. The "home-made" DMCS treated supports were significantly less adsorptive than the commercial regular grade supports. All silanized supports were significantly less adsorptive than the unsilanized supports. Chromosorb P, a relatively high surface area support, was more adsorptive than the untreated white supports despite its DMCS treatment.

Roman, Yates and Millar (23) evaluated solid supports for the gas chromatographic analysis of esterified estrogens. They observed that in some columns quantitation became difficult because the area of the peak increased during repeated injections. They suggested that this increase in area was due to a combination of:

- 1) Silylation of silanol groups on the support with the excess reagent in the sample, and
- 2) A temporary deactivation of the active sites on the support due to priming by the estrogens from the previous injections.

They blamed the poor chromatographic performance of some of the com-

mercial supports on particle attrition during the shipping and handling of the material and on improper silanization of the diatomite. The presence of excessive "fines" in the support can adversely affect the chromatographic performance of a column by causing peak broadening. In addition, if the "fines" result from particle attrition after the support has been silanized, active sites could be generated that would give rise to adsorption. Their results indicated that depending on the cause of the poor chromatographic performance, the supports could be improved, deactivated either by re-sieving to remove fine particles or, by re-sieving and resilanization.

Blandenet and Robin (34) studied the chromatographic behaviour of several commercially available siliceous supports with respect to the analysis of polar compounds. They obtained the following decreasing order of effectiveness: Celite, Gas Chrom; Chromosorb W; Porovina; C-22; G.C. Super Support; Chromosorb P; Rysorb Blk; and Sterchamol.

Krupcik, Tesarik, Liska, Nemeč and Duchesne (99) studied the effect of the support on the gas chromatographic separation of fatty acid methyl esters. The following supports were found unsuitable when coated with 10% Apiezon L: Porovina, Rysorb Blk, Chezasorb II, Kieselguhr, Celite 545, Celite Hyflo and Chromosorb P, since partial or complete adsorption occurred. The highest responses were obtained on Chromaton N AW-HMDS, followed by Chromosorb W and silanized Gas Chrom P.

Filonenko, Tertykh, Pavlov, Guka and Korol (53) compared the adsorptive properties, towards polar solutes, of the following supports coated with squalene: Chromaton N AW, Chromaton N AW-DMCS, Chromaton N AW-HMDS, Chromaton N Super, Chromosorb G AW-DMCS, Chromaton N AW

treated with  $D_4^*$ -DMCS-TMCS (2:1:1) and Chromaton N AW treated with PMS -500.\*

They found a marked decrease in the relative retention of n-propanol on Chromaton N AW after silanization, which supports the theory of the elimination of hydroxyl groups from the support surface. However, the elimination of hydroxyl groups from the support surface was insufficient for an ideal support to be obtained.

No improvement was obtained for supports treated with PMS-500. Chromaton N Super and Chromaton N AW treated with  $D_4$ -DMCS-TMCS (2:1:1) were found to be the most inert for polar solutes. Chromaton N AW-DMCS was more inert than Chromaton N AW-HMDS. Little difference was obtained between Chromaton N AW and the HMDS-silanized support. Both Chromosorb G and Chromaton N AW showed similar sorption properties with respect to polar solutes.

For the analysis of methyl ethyl ketone, Chromaton N Super and Chromaton N AW treated with  $D_4$ -DMCS-TMCS (2:1:1) were again the best with the latter slightly better.

The above examples serve to illustrate the variety of commercial supports that are in use and their pre-treatments.

#### 1.14 GAS CHROMATOGRAPHIC DETECTORS.

Gas chromatographic detectors are a vital part of any gas chromatograph since they are responsible for detecting and measuring the sub-

\* $D_4$  = octamethylcyclotetrasiloxane

\*PMS-500 = polymethylsiloxane

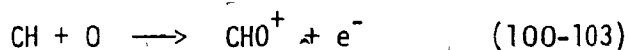
stances eluted from the column.

It was not the purpose of this thesis to study detectors, but it was felt that a short discussion of the operation of the detectors used, would prove useful in explaining some of the results obtained.

#### 1.14.1 The Flame Ionization Detector

The flame ionization detector (FID) has become the most commonly used detector in gas chromatography. This mass sensitive detector possesses many favourable features such as high sensitivity, large linear range and ease of operation. It responds to almost all organic compounds (100).

The operation of the FID is based on the fact that in a pure hydrogen-air flame, radicals such as H, O, OH, O<sub>2</sub>H and excited versions of the same are formed, but there is no detectable ionization. The electrical conductivity of a hydrogen flame burning in an air atmosphere is low. Appreciable ionization takes place when organic compounds are introduced into the hydrogen-air flame. The mechanism by which ions are produced in the flame is uncertain. It is thought to be due to the radical reaction



The ions are collected by applying a D.C. voltage to the parallel electrodes placed above the nozzle. The applied voltage must be high enough for efficient collection of ions and varies with the design of the electrodes and the gap between them (100, 102). The Shimadzu FID uses 300 V (102). The ion current is amplified by an electrometer and the resulting signal is then recorded to give a chromatogram (100, 102).

Only about 1 ppm of the organic compounds that enter the flame



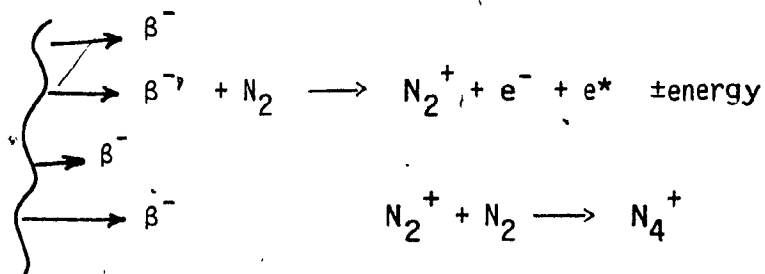
are ionized, but the number of ions produced is proportional to the total quantity of the compounds burnt in the flame, as long as the quantity of the compound vapour produced is less than 1% of the total flame gas volume (102).

Although the FID is relatively insensitive to variations in operating conditions, it has been shown that for each column flow rate there are optimum hydrogen and air flow rates for a given detector. Optimum flow rates for commercial detectors are usually given by the manufacturer (103, 104).

#### 1.14.2 The Electron Capture Detector (ECD)

The electron capture detector is the most sensitive of all gas chromatographic detectors for electron affinitive compounds. It is one of the family of ionization detectors which uses  $\beta$ -particle radiation to impart a charge to otherwise neutral gas molecules. Typically, Ni-63, is sealed in a small detector cell. When carrier gas is flowing through the detector cell, a current is produced because of secondary electrons formed from inelastic collisions between  $\beta$  electrons emitted from the radioisotope, and carrier gas molecules, e.g. nitrogen (105, 106).

The reactions occurring are as follows (107):



In the case of ionization of an inert gas like nitrogen, only electrons are present as far as negative particles are concerned.

The probability of the recombination of these electrons with positive ions is low because of their very different velocities. The velocity of an electron is about  $10^4$  times greater than that of positive ions (108).

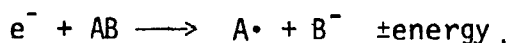
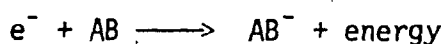
The average energy of the primary  $\beta$ -electrons is about 67 KeV compared to that of the thermalized secondary electrons, 0.01 eV (106). Although ionization of nitrogen gas by high energy radiation produces electrons ( $e^*$ ) with a mean kinetic energy greater than that of the neutral gas molecules, the excess energy decays by inelastic and elastic collisions with other molecules. In fact, thermalization of electrons occurring from high energy  $\beta^-$  particles is necessary in order to allow the electron capturing process, while minimizing solute ionization (107).

When a potential difference is applied to a pair of electrodes placed across the cell, an ion current flows between the electrodes. The potential is adjusted to a value sufficient to collect all of the electrons liberated from the gas by the ionizing radiation.

If an electron affinitive compound, i.e. one which has a strong ability to absorb electrons, enters the detector cell, it absorbs electrons, and becomes a negatively charged particle (negative ion) (107). The velocity of these anions is much lower than that of the free electrons, and the probability of recombination between negative and positive ions is, therefore,  $10^5 - 10^8$  times higher than that between electrons and positive ions. Thus, the ion current in the cell decreases when an electron affinitive compound enters the cell. This decrease in the ion current is proportional to the concentration of

the electron affinitive compound for low concentration ranges of the compound (106, 108).

The basic reactions of electron absorption are:(105, 106, 107)



The solute molecule may attach an electron to form either a negative molecular ion, or a neutral radical and a negative ion.

In the first reaction where a molecular ion is formed, the energy of electron capture is liberated either as radiation, or shared with other molecules on subsequent collisions. With this type of reaction the probability of electron absorption decreases with an increase in temperature or electron energy (105, 107). In the second type of reaction, the molecule dissociates after electron absorption to give a free radical and an atomic or molecular negative ion. In this reaction, the energy required to dissociate the molecule is often greater than that released by the formation of the negative ion. An increase in temperature, or of electron energy may increase the probability of electron absorption.

Thus, the probability of the electron affinitive molecules absorbing electrons depends to a large extent on the energy of the free electrons. It is greatly influenced by the potential of the electrons, and the temperature of the detector cell (105, 107).

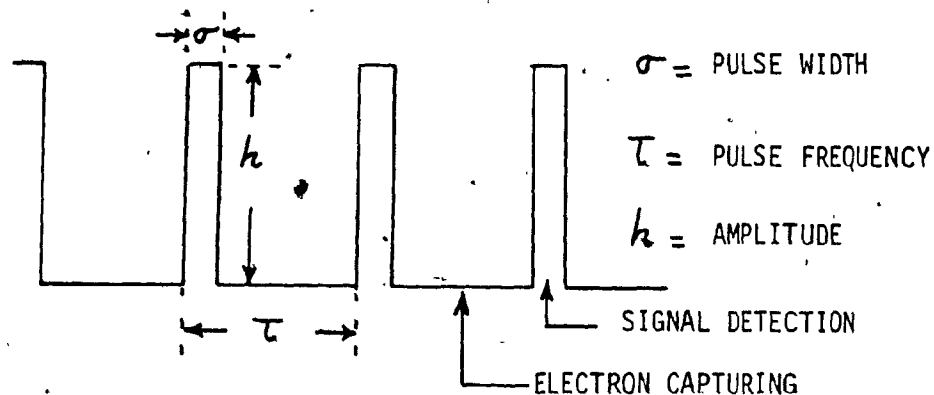
The theory of electron absorption is very similar to Beer's Law for light absorption. The number of electrons reaching the anode per second,  $N$ , in the presence of electron affinitive compounds of con-

centration,  $C$ , in the carrier gas is

$$N = N_0 \exp(-KCX)$$

where  $N_0$  is the number of electrons reaching the anode per second in the pure carrier gas,  $K$  is the electron absorption coefficient and  $X$  is a proportionality constant (105, 109).

Recent model electron capture detectors, as for example, that in the Shimadzu GC-6AM, use a pulsed voltage as shown below to overcome the effect of contact potentials (contamination of the radioactive source and/or the surface of the electrodes from some eluted component) and space charges (accumulation of positive ions near the cathode).



The pulse voltage used for ECD, generally, has a pulse width range of 1 - 10  $\mu$ sec., a frequency of 1 - 100 KHz, and an amplitude of 40 - 50 v. The pulse conditions that give the highest sensitivity differ with the structure of the ECD cell and the electrodes (110).

The probability of electron capture by different types of molecules covers a range of  $10^6$ , and depends on the presence of electrophores in the molecules. In addition to the type of electrophore, the number of bonds and electrophores, and the structure of the molecular fragment also affect the detection sensitivity.

There seems to be no simple method for the accurate prediction of response for any particular compound. In the case of halogen compounds, the detection sensitivity increases from fluorine to iodine. In addition, the response is not proportional to the number of halogen atoms in the molecule, but it increases rapidly with an increasing number of atoms.

The detector is sensitive not only to the compounds containing halogens, phosphorus, sulphur, lead, and oxygen, but also to the more complex hydrocarbons such as cyclooctatetraene, azulene and most polycyclic aromatic hydrocarbons. In addition, some inorganic compounds, including carbon disulfide, ozone, the oxides of nitrogen and probably many others, are electron absorbers (105, 107 - 109).

The response of the ECD is largely reduced by contaminants such as water and oxygen in the carrier gas, or by various substances originating from the different parts of the chromatograph, such as the supports, the liquid phases, septums, plastic fittings, and deposits of pyrogenated materials in the injection port (111, 112).

Erroneous results may be obtained if the peak of interest is superimposed on other peaks, or over a large background which effectively decreases the amount of electrons available for interaction with sample solutes. This can result in non-linear behaviour by the detector (113).

Novak, Ruzickova, Wicar and Janak (114) found that the response due to the background in the column effluent resulting, for example, from a bleeding stationary phase may not only shift the concentration range of the solute closer to, or even beyond the upper limit of the overall range of linearity of detector response, but may also cause a definite decrease of the net response even when the detector is

operated well within the linear range.

Stationary phase bleeding can occur either because of its volatility, or because of its decomposition. The rate of bleeding increases exponentially with temperature. With conventional detectors, bleeding results in base line drift, instability and noise. Baseline drift may be compensated by a dual column arrangement (111). Baseline instability and noise result in a decrease of the performance of conventional detectors only at bleeding rates great enough to adversely affect column performance. The bleeding rate must be kept moderate in order to prolong the lifetime of the column and to prevent the overloading of conventional detectors. Precise quantitative analysis can be performed even in the presence of appreciable bleeding as long as the peak area response remains proportional to the amount of solute in the sample. (111).

With the electron capture detector, however, even a small bleeding rate can result in a very large decrease of the base current and consequently, in a dramatic loss of sensitivity, provided that the liquid phase vapour, or pyrolysis products have a large electronic affinity. The depletion of the thermal electrons lowers the probability of reaction between electrons and the solute molecules. Devaux and Guiochon (111) found that the behaviour and usefulness of most liquid phases was very different when they were used with the electron capture detector, or the flame ionization detector. The non-polar phases (e.g. SE-30, Apiezon L, Squalane) gave small current reductions in the ECD, most probably because the bleeding vapours have a low coefficient of electron absorption. Polar phases (e.g. di-n-decylphthalate and tris-2,4-xylenylphosphate) were found to have a much greater

effect on reducing ECD sensitivity. The vapours of polar phases, or their decomposition products, are much more likely to have a high electron affinity than those of non-polar phases.

In most cases, when working with an electron capture detector, the use of a stationary liquid phase must be restricted to temperatures much lower than is the case with the FID.

Liquid phase bleed, however, is not the only cause of changes in the base current. Trace contaminant vapours in the carrier gas can also alter the level of the standing current. Ions such as  $[(H_2O)_n H^+]$  and  $[(H_2O)_n O_2^-]$  can result when oxygen and water vapour are present in the nitrogen carrier gas and will affect the ECD sensitivity. Although water alone does not change the electron level appreciably, in combination with oxygen, a significant decrease does occur (113).

The electron absorbing, and potentially damaging role of oxygen is recognized. It can be present in ppm amounts in the carrier gas, or it can be introduced by back diffusion through small leaks all along its flow path. It can even back-diffuse through the exit line or through holes in the EC detector itself (113).

The main disadvantages of the ECD are its susceptibility to contamination, its small linear range, and the unpredictability of its response. When analyzing unknown mixtures it is impossible to decide whether an unknown peak represents a small amount of a compound of high electron affinity or a large amount of a compound of low electron affinity (109).

#### 1.15 SUPPORTS FOR THE ANALYSIS OF CHLORINATED PESTICIDES

Numerous review articles (2, 87, 115, 116) and books (117, 118)

have appeared in the literature on the analysis of chlorinated pesticides. A tremendous amount of work has been done in developing and improving extraction and clean-up procedures, in developing more inert supports, in investigating the effectiveness of various liquid phases, in improving the level of detection through improvements in column technology and detectors, and in quantitative and qualitative analysis of many pesticides. However, the ideal support for the gas chromatographic analysis of chlorinated pesticides has not yet been developed.

Furthermore, little work has been done in examining and comparing the existing supports as to their suitability in the analysis of chlorinated pesticides.

The most widely used supports for pesticide analysis are of the diatomaceous type previously discussed. There is no "best" support for the analysis of chlorinated pesticides. Bonelli et al (119) have used Chromosorb W (DMCS-treated) with some degree of success for chlorinated pesticides. It was observed that Chromosorb W resolved methyl parathion and ethyl parathion, but not paraoxon. Replacing Chromosorb W with Chromosorb G, all three of the organophosphorus compounds were resolved.

The FDA laboratories have recommended the use of Anachrom ABS (an acid-base-washed, siliconized, support)(90). Thompson (120) recommended the use of Chromosorb W HP for the analysis of a large number of chlorinated pesticides. Suzuki, Yamato and Watanabe (121) used Chamelite CS (an acid-washed, DMCS-treated, Celite 545 support) in their investigation of the resolution of organochlorine insecticides on mixed phase column systems.



Schafer, Peeler, Gardner and Campbell (122) used either Gas-Chrom Q or Anakrom ABS for the assay of organochlorine pesticides in drinking water. Thompson, Mann and Apodaca (123) used Chromosorb W HP or Gas-Chrom Q as supports in their determination of relative retention ratios for 95 organochlorine and organophosphorus pesticides. Taylor (124) designed a column for the gas chromatographic analysis of chlorinated hydrocarbon pesticides in which he used Gas Chrom Q as the support.

Setiawan (125) carried out studies similar to those undertaken in this thesis, using the chlorinated pesticides, lindane and aldrin. It was found that peak area responses for lindane and aldrin, on Chromosorb W, P and G supports, generally decreased with an increase in the column temperature. This decrease was attributed to a reaction of the pesticides with the liquid phase, probably catalyzed by the support material. The decreasing thermogram patterns showed that the anticipated decreasing adsorption with increase in column temperature was more than compensated for by increasing reactivity of lindane and aldrin. It was also stated that at a high enough column temperature, the same peak area responses would be obtained for all W supports, all G supports and all P supports, regardless of the pre-treatment to which each support had been subjected.

The most advantageous results based on peak area response data were obtained with the Chromosorb W supports and the poorest with the Chromosorbs P. The best single support for analysis of chlorinated pesticides, such as lindane and aldrin, was Chromosorb W AW with Chromosorb 750 being a close second. Within each family of supports the behaviour of the acid-washed products was surprisingly good and

led to the conclusion that acid washing is the most effective means of deactivation of diatomite supports for the analysis of lindane/aldrin types of pesticides. Poor responses for lindane and aldrin were obtained on silanized W and G supports, including the high performance products (HP). For Chromosorb 750, the one exception, the manufacturing process must have given a product with surface properties very different from those of the other silanized supports.

The differences in response were accentuated for the higher concentrations of samples tested. This was attributed to loss of small samples on each support in priming of the supports. In the case of the Chromosorb P supports, the silanized product gave better lindane/aldrin responses than the acid washed, and non-acid washed products. This was attributed to the much greater surface area, and larger number of active sites on pink supports compared to white supports. Priming with lindane and aldrin to reduce surface activity and lead to greater responses was effective only in the case of Chromosorb G NAW.

A significant correlation was also found between peak area responses of lindane and aldrin, and slopes of their peak area responses versus concentration curves on the corresponding columns. A greater slope was observed for both lindane and aldrin curves on those columns upon which the greatest absolute responses were obtained for these compounds. Accordingly, slope data may be used effectively as another criteria for estimation of relative adsorptivities of supports towards compounds like lindane and aldrin.

## 1.16 PURPOSE OF THESIS

In the work carried out for this thesis an attempt has been made:

- (i) to evaluate different diatomite supports for their suitability in the analysis of two chlorinated pesticides (dieldrin and methoxychlor);
- (ii) to study the temperature dependence of the adsorptive properties of diatomite supports;
- (iii) to determine the adsorptive properties of column tubing materials (glass, stainless steel, nickel, copper and aluminum);
- (iv) to investigate the effect of column temperature on the responses of dieldrin and methoxychlor, with the flame ionization detector, FID, and the electron capture detector, ECD, using different diatomite supports and column tubing materials;
- (v) to determine the effects of column priming, liquid phase bleed, and other experimental parameters on the responses of dieldrin and methoxychlor;
- (vi) to determine, whether or not dieldrin and methoxychlor would behave in the same fashion as has been previously found for lindane and aldrin

## 2.0 EXPERIMENTAL

### 2.1 INSTRUMENTATION

Three different gas chromatographs were used for the completion of this project. The preliminary work was performed using a Microtek GC 2000-R Gas Chromatograph equipped with dual columns, a Thermal

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Conductivity Detector (TCD) and a differential Flame Ionization Detector (FID).

The majority of the FID work was carried out employing a Shimadzu GC-6AM Gas Chromatograph having dual columns and a differential Flame Ionization Detector. All the ECD experiments were conducted utilizing a second Shimadzu GC-6AM instrument equipped with a single column and an Electron Capture Detector.

The carrier gas used for the FID and the ECD work on the Shimadzu instruments was extra pure nitrogen. For the preliminary FID work on the Microtek, regular grade nitrogen was employed.

Air and hydrogen gases needed for the FID, on both the Microtek and the Shimadzu, were regular grade, and passed through gas-dry filter traps before use. Additional hydrocarbon traps were installed only on the Microtek instrument.

All cylinder gases were produced by Union Carbide, and shipped in standard steel cylinders.

The flowrate of the carrier gas, typically 20 ml/min., was measured at room temperature at the column outlet, with a soap bubble flowmeter. The flowrates of the hydrogen gas and the air for the Shimadzu FID unit were adjusted to the optimum levels recommended in the manual for the Shimadzu Gas Chromatograph. The flowrates used with the Microtek Gas Chromatograph were 295 ml/min. hydrogen and 330 ml/min. air.

Sample injections were performed with a 10  $\mu$ l Hamilton microsyringe. The microsyringe was rinsed with solvent before and after each injection. The injection technique consisted of the following procedure. One microliter of solvent was drawn into the syringe,

followed by three  $\mu$ l of air, followed by sample. The sample volume was adjusted to the required amount by forcing out any excess sample. An additional two  $\mu$ l of air were drawn into the syringe. The exact required volume of sample, lying between two air pockets, was injected into the injection port of the instrument.

## 2.2 MATERIALS

All materials required for the building of columns, and the standard chlorinated pesticide samples, were purchased from a commercial source, Chromatographic Specialties Ltd., unless otherwise specified. The pesticides used were Dieldrin (100%) and Methoxychlor (99%), where the percentage values in brackets indicate the purity of the pesticides, and were packaged by Polyscience Corp. The solvent used to prepare standard solutions was pesticide grade hexane, purchased from Fisher Scientific Co.

The liquid phase used was OV-17.

The chromatographic supports, tested, 80/100 mesh, are listed below:

Chromosorb W NAW

Chromosorb W AW

Chromosorb W AW-DMCS

Chromosorb W HP

Chromosorb G NAW

Chromosorb G AW

Chromosorb G AW-DMCS

Chromosorb G HP

Chromosorb P NAW

Chromosorb P AW

Chromosorb P AW-DMCS

Chromosorb 750

The various column tubing materials used were as follows:

Stainless steel

Nickel

Copper

Aluminum

Glass

### 2.3 SAMPLE PREPARATION

The following sample solutions in hexane were prepared in 100 ml volumetric flasks, and stored in a refrigerator, in 15 ml Hypo-vials, sealed with Teflon<sup>R</sup> discs until used.

(i) Dieldrin: 5.00  $\mu\text{g}/\mu\text{l}$ , 10.00  $\mu\text{g}/\mu\text{l}$  and 5.00 ng/  $\mu\text{l}$ .

(ii) Methoxychlor: 5.00  $\mu\text{g}/\mu\text{l}$ , 10.00  $\mu\text{g}/\mu\text{l}$  and 5.00 ng/ $\mu\text{l}$ .

Additional samples prepared in 10 ml volumetric flasks, and stored in 15 ml Hypo-vials under refrigeration are listed below:

(i) Dieldrin ( $\mu\text{g}/\mu\text{l}$ ) 0.5; 1.0; 1.5; 2.0; 2.5

(ii) Methoxychlor ( $\mu\text{g}/\mu\text{l}$ ) 0.5; 1.0; 1.5; 2.0; 2.5

All sample solutions were prepared by weight.


### 2.4 COLUMN PREPARATION

#### 2.4.1 Coating of the Support

→ Solid supports were coated with the liquid phase using the solution evaporation method. The required amounts of support and liquid phase, were each weighed into separate 100 ml beakers. Hexane was added to dissolve the liquid phase and the support was slowly poured into the resulting solution. The solvent was evaporated from the packing under a stream of dry nitrogen, at room temperature, with

constant swirling of the mixture to ensure a uniform coating with a minimum breakage of the support particles. After the solvent was expected to have been evaporated, the packing was spread out on a glass plate, and allowed to dry overnight. Typically, to prepare a 3.5% w/w OV-17 on support packing, 0.17 g and 5 g of each, respectively, weighed to the nearest tenth of a milligram, were required. Proportions were varied as necessary to prepare 7 and 14% w/w OV-17 on support columns.

#### 2.4.2 Packing the Column

All metal columns were packed straight and bent into a "U" to fit the Shimadzu oven or shaped into the following form "  " to fit the Microtek oven.

Silanized glass wool was placed in one end of the metal column and a packing funnel was attached to the other end. The packing was poured into the funnel in small amounts while the column was lightly tapped. Packing was added until the column was full. Then a silanized glass wool plug was inserted to hold the packing in place.

Glass columns were obtained pre-coiled by the glass blower into the required shape. The inner surface was silanized with DMCS, washed with methanol, and dried by passing dry nitrogen through the tubing. A silanized glass wool plug was inserted into one end of the column, and this end was attached to a vacuum. A funnel was connected to the other end, the vacuum was turned on, and the packing was added very slowly with slight tapping of the column. When the column tubing was full, a silanized glass wool plug was inserted.

All columns were conditioned overnight at a temperature of 280°C while passing nitrogen through at a rate of about 40 ml/min.

## 2.5. PRELIMINARY EXPERIMENTS

A considerable amount of preliminary experimentation was carried out to establish suitable conditions for the analysis of methoxychlor. Tables IV and V list the various operating conditions used.

## 2.6 ADSORPTIVE STUDIES OF SOLID SUPPORTS

The adsorptive properties of the solid supports listed in Section 2.2 were studied using the pesticides, dieldrin and methoxychlor. The columns prepared for this study are listed in Table VI. All the columns were packed in stainless steel tubing 2" x 1/8" o.d. (0.020" wall thickness), and the liquid phase was 3.5% w/w OV-17.

Two types of studies were performed: temperature studies, and concentration studies.

Tables VII to XII list the exact experimental conditions that were used in each study.

## 2.7 ADSORPTIVE STUDIES OF VARIOUS COLUMN TUBING MATERIALS

The adsorptive properties of various column tubing materials (stainless steel, glass, aluminum, nickel and copper) were studied using the Shimadzu GC-6AM Gas Chromatograph with FID, and dieldrin and methoxychlor as test samples.

The columns prepared for this study were all 2 feet x 1/8" o.d. (except the glass column, which had an i.d. of 3 mm), packed with Chromosorb W AW-DMCS, 80/100 mesh, coated with 3.5% w/w OV-17. All columns (Al, Cu, Ni and glass) were newly prepared. The stainless steel column, s.s., used was column C, previously employed in the study of the adsorptive properties of the solid supports. The internal diameter of the various tubing materials varied and as a re-



sult the amount of packing material in each column differed.

Table XIII lists the columns used except for Column C (stainless steel).

Two types of studies were carried out, temperature studies and concentration studies. Tables XIV to XVI list the experimental conditions used in the various studies.

TABLE IV OPERATING CONDITIONS FOR THE PRELIMINARY EXPERIMENTS  
USING THE MICROTEK GC 2000 R GAS CHROMATOGRAPH.

## ANALYTICAL COLUMNS:

- (i) 2' x 1/8"o.d. nickel tubing; 3.5% w/w OV-17  
 on Chromosorb W HP, 80/100 mesh.
- (ii) 2' x 1/8"o.d. nickel tubing, 3.5% w/w OV-17  
 on Chromosorb W NAW, 80/100 mesh.
- (iii) 2' x 1/8"o.d. stainless steel tubing, 3.5%  
 w/w OV-17 on Chromosorb W HP, 80/100 mesh.
- (iv) 2' x 1/8"o.d. stainless steel tubing, 3.5%  
 w/w QF-1 on Chromosorb W HP, 80/100 mesh
- (v) C, L (TABLE VI)

DETECTOR: FID

INPUT ATTENUATION:  $10^2$ 

OUTPUT ATTENUATION: 32

TEMPERATURE: Detector: 266  
 Injection Port: 242  
 Column: 200, 210, 220, 230, 240, 250,  
 260, 270, 280

FLOW RATES: Air: 330 ml/min.  
 Hydrogen: 295 ml/min.  
 Nitrogen: 20 ml/min.

SAMPLE SOLUTION: Methoxychlor 10  $\mu\text{g}/\mu\text{l}$ .VOLUME INJECTED: 5  $\mu\text{l}$ .

TABLE V

OPERATING CONDITIONS FOR THE PRELIMINARY  
EXPERIMENTS WITH THE SHIMADZU GAS CHROMATOGRAPH

## ANALYTICAL COLUMNS:

(i) 1 1/2' x 1/8" o.d. stainless steel tubing,  
 7% w/w OV-17 on Chromosorb W NAW, 80/100  
 mesh.

(ii) 1' x 1/8" o.d. stainless steel tubing,  
 14% w/w OV-17 on Chromosorb W NAW, 80/100  
 mesh.

DETECTOR: FID

SENSITIVITY:  $10^3$

RANGE: 256

## TEMPERATURE:

Detector: 300

Injection Port: 300

Column: 230

## FLOW RATES:

Air: 0.79 l/min.

Hydrogen: 26 ml/min.

Nitrogen: 20 ml/min.

SAMPLE SOLUTION: Methoxychlor 10  $\mu\text{g}/\mu\text{l}$ .

VOLUME INJECTED: 2  $\mu\text{l}$ .

TABLE VI

COLUMNS PREPARED WITH STAINLESS STEEL TUBING  
AND THE VARIOUS GC SUPPORTS STUDIED, COATED  
WITH 3.5% W/W OV-17 STATIONARY PHASE

COLUMN	TYPE OF SUPPORT, 80/100 MESH
A	Chromosorb W NAW
B	Chromosorb W AW
C	Chromosorb W AW DMCS
D	Chromosorb W HP
E	Chromosorb G NAW
F	Chromosorb G AW
G	Chromosorb G AW DMCS
H	Chromosorb G HP
I	Chromosorb P NAW
J	Chromosorb P AW
K	Chromosorb P AW DMCS
L	Chromosorb 750

TABLE VII      OPERATING CONDITIONS FOR THE ADSORPTIVE STUDIES  
OF SOLID SUPPORTS USING DIELDRIN, CONCENTRATION  
RUNS

ANALYTICAL COLUMNS:	A TO L
DETECTOR:	Shimadzu FID
SENSITIVITY:	$10^3$
RANGE:	128 - low concentrations 1024 - high concentrations
TEMPERATURE:	
Detector	260
Injection Port	260
Column	230
FLOW RATES:	
Air:	0.79 l/min.
Hydrogen:	26 ml/min.
Nitrogen:	20 ml/min.

	<u>LOW CONCENTRATIONS</u>	<u>HIGH CONCENTRATIONS</u>
Sample Soln.	0.5, 1.0, 1.5 2.0 and 2.5 $\mu\text{g}/\mu\text{l}$	10 $\mu\text{g}/\mu\text{l}$
Volume Injected	2 $\mu\text{l}$	1, 2, 3, 4, and 5 $\mu\text{l}$ .

TABLE VIII. OPERATING CONDITIONS FOR THE ADSORPTIVE STUDIES OF  
SOLID SUPPORTS USING METHOXYCHLOR, CONCENTRATION  
RUNS

ANALYTICAL COLUMNS: A to L  
DETECTOR: Shimadzu FID  
SENSITIVITY:  $10^3$   
RANGE: 32 - low concentrations  
512 - high concentrations  
TEMPERATURE:  
Detector: 300  
Injection Port: 300  
Column: 240  
FLOW RATES:  
Air 0.79 l/min.  
Hydrogen 26 ml/min.  
Nitrogen 20 ml/min.

	<u>LOW CONCENTRATIONS</u>	<u>HIGH CONCENTRATIONS</u>
Sample Solutions	0.5, 1.0, 1.5, 2.0 and 2.5 $\mu\text{g}/\mu\text{l}$	10 $\mu\text{g}/\mu\text{l}$
Volume Injected	2 $\mu\text{l}$	1, 2, 3, 4 and 5 $\mu\text{l}$

TABLE IX      OPERATING CONDITIONS FOR THE TEMPERATURE RUNS  
WITH DIELDRIN

DETECTOR:                      Shimadzu FID  
 SENSITIVITY:                   $10^3$   
 RANGE:                            256  
 TEMPERATURE:  
     Detector:                    260  
     Injection Port:              260

ANALYTICAL COLUMNSCOLUMN TEMPERATURES

A to D	160, 170, 180, 190
I to L	200, 210, 220, 230 240, 250
E to H	170, 180, 190, 200 210, 220, 230, 240 250, 260, 270

FLOW RATES:

Air:                                0.79 l/min.  
 Hydrogen:                        26 ml/min.  
 Nitrogen:                        20 ml/min.  
 SAMPLE SOLUTION:              5  $\mu$ g/ $\mu$ l  
 VOLUME INJECTED:               2  $\mu$ l.

TABLE X                      OPERATING CONDITIONS FOR THE TEMPERATURE RUNS  
WITH METHOXYCHLOR

ANALYTICAL COLUMNS:	A to L
DETECTOR:	Shimadzu FID
SENSITIVITY:	$10^3$
RANGE:	256
TEMPERATURE:	
Detector:	300
Injection Port:	300
Column:	200, 210, 220 230, 240, 250 260, 270, 280 290
FLOW RATES:	
Air:	0.79 l/min.
Hydrogen:	26 ml/min.
Nitrogen:	20 ml/min.
SAMPLE SOLUTION:	5 $\mu\text{g}/\mu\text{l}$
VOLUME INJECTED:	2 $\mu\text{l}$



TABLE -XI      OPERATING CONDITIONS FOR THE TEMPERATURE RUNS  
WITH HIGH CONCENTRATIONS OF DIELDRIN AND METHOXYCHLOR

ANALYTICAL COLUMN:	C	
DETECTOR:	SHIMADZU FID	
SENSITIVITY:	10 <sup>2</sup>	
RANGE:	128	
<u>TEMPERATURE OF</u>	<u>DIELDRIN</u>	<u>METHOXYCHLOR</u>
Injection Port	260	300
Detector	260	300
Column	160, 170, 180	200, 210, 220
	190, 200, 210	230, 240, 250
	220, 230, 240	260, 270, 280
	250, 260	
FLOW RATES:		
Air:	0.79 l/min.	
Hydrogen:	26 ml/min.	
Nitrogen:	20 ml/min.	
SAMPLE SOLUTIONS:	10 µg/µl	
VOLUME INJECTED:	5 µl	

TABLE XII      OPERATING CONDITIONS FOR THE TEMPERATURE RUNS  
WITH VERY LOW CONCENTRATIONS OF DIELDRIN AND  
METHOXYCHLOR

ANALYTICAL COLUMNS:      A, D, E, H and K

DETECTOR:                      Shimadzu ECD

PULSE:                              20

SENSITIVITY:                      100

RANGE:                              32 - Dieldrin  
    16 - Methoxychlor

TEMPERATURE:

    Detector                      300

    Injection Port:              300

    Column:

METHOXYCHLOR

200, 210, 220

230, 240, 250

260, 270, 280

290.

DIELDRIN

160, 170, 180

190, 200, 210,

220, 230, 240,

250, 260, 270

FLOW RATE OF NITROGEN:      20 ml/min.

SAMPLE SOLUTIONS:              5 ng/  $\mu$ l

VOLUME INJECTED:                2  $\mu$ l

TABLE XIII      COLUMNS PREPARED WITH 3.5% w/w OV-17 ON CHROMOSORB  
W AW-DACS AND VARIOUS COLUMN TUBING MATERIALS

COLUMN	COLUMN TUBING MATERIAL
M	Nickel
N	Copper
O	Aluminum
P	Glass

TABLE XIV      OPERATING CONDITIONS FOR THE ADSORPTIVE STUDIES  
OF COLUMN TUBING MATERIALS USING DIELDRIN,  
CONCENTRATION RUNS.

ANALYTICAL COLUMNS:      C, M, N, O and P.  
DETECTOR:                      Shimadzu FID  
SENSITIVITY:                     $10^3$   
RANGE:                            128 - low concentrations  
                                      512 - high concentrations  
TEMPERATURE:  
    Detector:                    260  
    Injection Port:            260  
    Column:                      230  
FLOW RATES:  
    Air:                            0.79 l/min.  
    Hydrogen                    26 ml/min.  
    Nitrogen:                    20 ml/min.

	<u>LOW CONCENTRATIONS</u>	<u>HIGH CONCENTRATIONS</u>
Sample Solutions:	0.5, 1.0, 1.5, 2.0, and 2.5 $\mu\text{g}/\mu\text{l}$	10 $\mu\text{g}/\mu\text{l}$
Volume Injected:	2 $\mu\text{l}$	1, 2, 3, 4 and 5 $\mu\text{l}$

TABLE XV                      OPERATING CONDITIONS FOR THE ADSORPTIVE STUDIES  
OF COLUMN TUBING MATERIALS USING METHOXYCHLOR.  
CONCENTRATION RUNS.

ANALYTICAL COLUMNS:    C, M, N, O and P  
DETECTOR:                    Shimadzu FID  
SENSITIVITY:                 $10^3$   
RANGE:                        64 - low concentrations  
                                  512 - high concentrations

## TEMPERATURES:

Detector:                    300  
Injection Port:              300  
Column:                      240

## FLOW RATES:

Air:                          0.79 l/min.  
Hydrogen:                    26 ml/min.  
Nitrogen:                    20 ml/min.

LOW CONCENTRATIONS

Sample  
Solutions: 0.5, 1.0, 1.5<sup>8</sup>  
                  2.0 and 2.5  $\mu\text{g}/\mu\text{l}$

HIGH CONCENTRATIONS

Volume  
Injected: 2  $\mu\text{l}$                       1, 2, 3, 4 and 5  $\mu\text{g}/\mu\text{l}$

TABLE XVI

OPERATING CONDITIONS FOR THE ADSORPTIVE STUDIES  
OF COLUMN TUBING MATERIALS, TEMPERATURE RUNS  
WITH DIELDRIN AND METHOXYCHLOR

ANALYTICAL COLUMNS: C, M, N, O and P.  
 DETECTOR: Shimadzu FID  
 SENSITIVITY:  $10^3$   
 RANGE: 256

<u>TEMPERATURE OF</u>	<u>DIELDRIN</u>	<u>METHOXYCHLOR</u>
Injection Port:	260	300
Detector:	260	300
Column:	160, 170, 180 190, 200, 210 220, 230, 240	200, 210, 220 230, 240, 250 260, 270, 280 290

## FLOW RATES:

Air: 0.79 l/min.

Hydrogen: 26 ml/min

Nitrogen: 20 ml/min.

SAMPLE SOLUTIONS: .5  $\mu$ g/ $\mu$ lVOLUME INJECTED: 2  $\mu$ l

### 3.0 OBSERVATIONS AND DISCUSSIONS

#### 3.1 PRELIMINARY EXPERIMENTS

A considerable amount of preliminary work had to be carried out to establish satisfactory gas chromatographic conditions for the analysis of methoxychlor, before a systematic investigation of support and temperature effects could be carried out.

The first tests were carried out with two columns, both 2 ft. x 1/8 p.d., nickel tubing, one packed with Chromosorb W HP, 80/100 mesh, coated with 3.5% w/w OV-17, and the other with Chromosorb W NAW, 80/100 mesh, coated with 3.5% w/w OV-17. The sample size used was 50  $\mu$ g of methoxychlor. It was expected that the chromatograms on both columns would consist of a single peak for methoxychlor. The actual results obtained are shown in Figures 8 and 9. In both cases, four peaks were obtained. It was assumed that the extraneous peaks may have been due to any or all of the following:

- (i) Impurities in the sample of methoxychlor used.
- (ii) Thermal decomposition of methoxychlor.
- (iii) Reaction of the compound with the stationary phase, column tubing, or support material, leading to reaction products.

To test the first assumption, two different grades of methoxychlor were tried. One was labelled as 99% pure, the other was technical grade. On the W HP column, both gave very similar results - the same four peaks. Also, using a sample of methoxychlor recrystallized twice from hexane, no change was observed in the relative area of the four peaks. If the extra peaks were caused by impurities, there

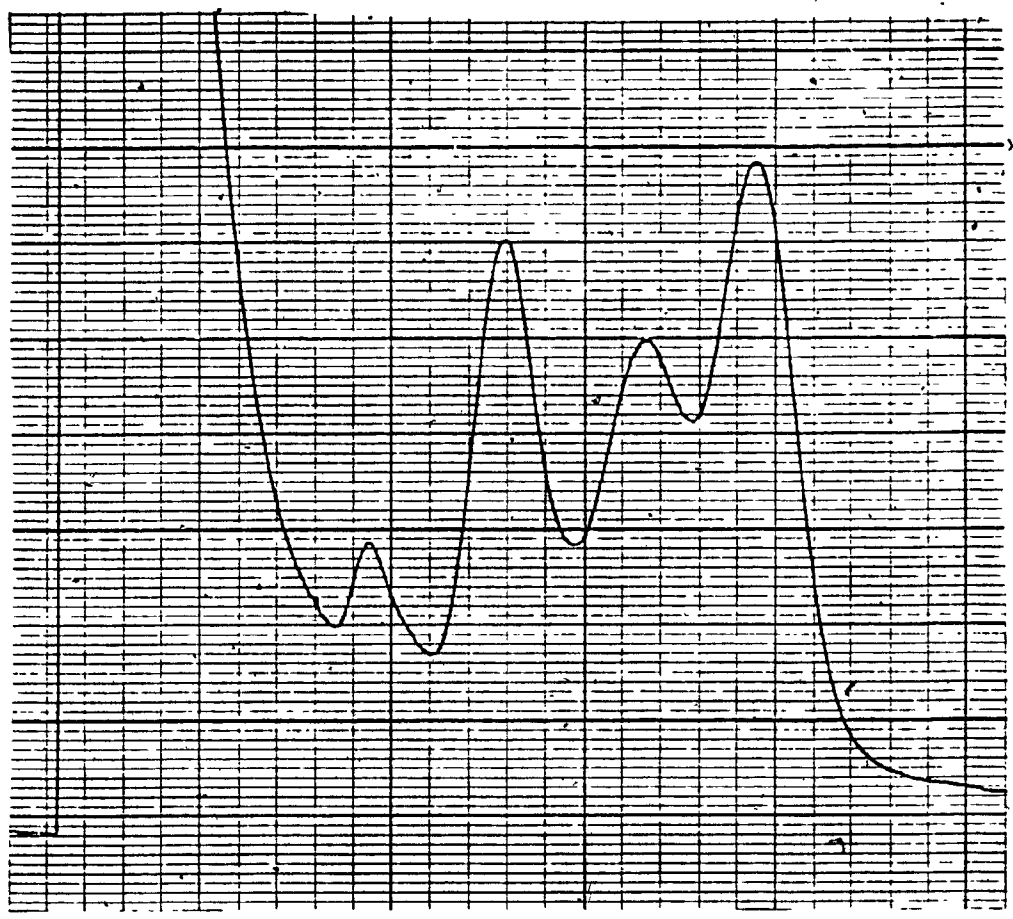


Figure 8 Analysis of Methoxychlor, 50  $\mu$ g, on 3.5% w/w OV-17  
Coated on Chromosorb W HP at 220°C; Before Priming.



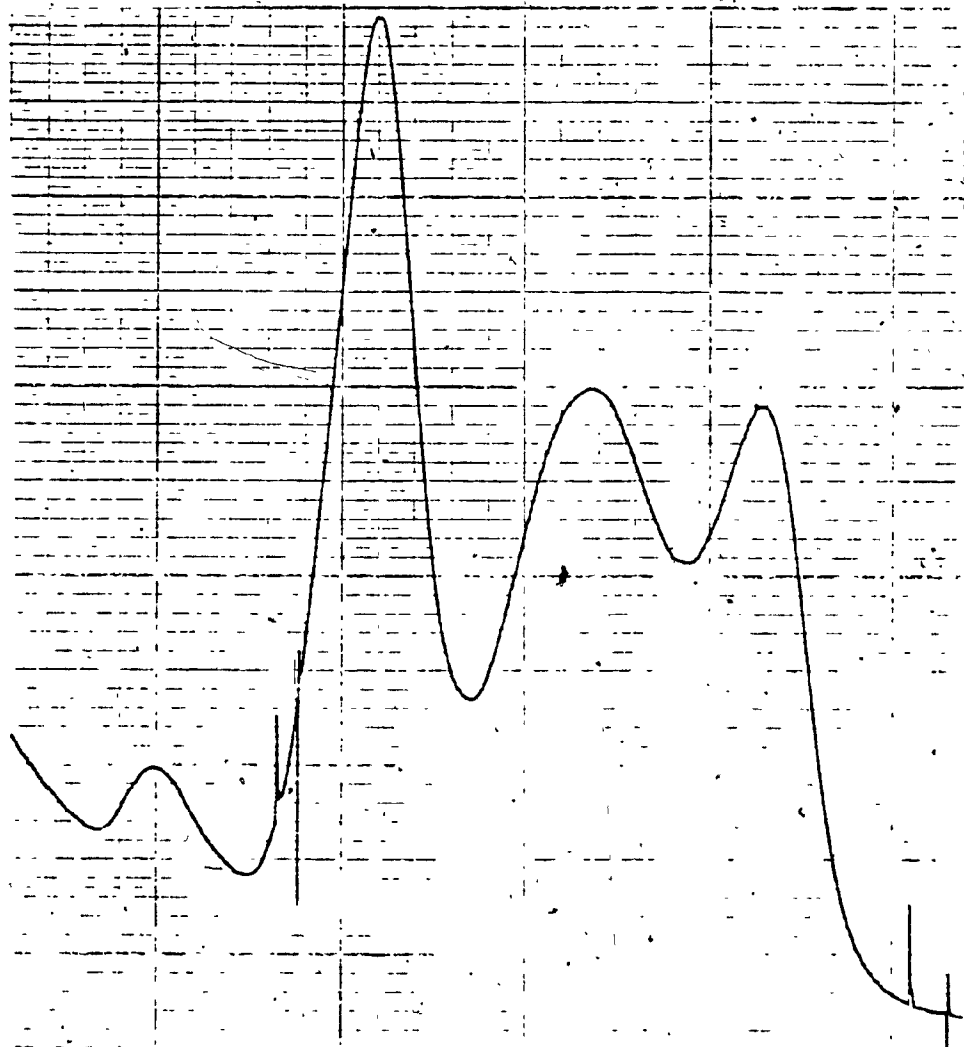


Figure. 9 Analysis of Methoxychlor, 50  $\mu$ g, on 3.5% w/w OV-17  
Coated on Chromosorb W NAW at 220°C; Before Priming.

should have been a difference in the relative area of the four peaks from one sample to another and after recrystallization.

To determine whether decomposition of methoxychlor occurred in the injection port, the injection port temperature was lowered in stages, from 242°C to 160°C, while maintaining column temperature constant at 210°C. No meaningful change was observed in the four peaks obtained. At the lower injection port temperatures, the third and fourth peaks seemed to overlap while the first two peaks became smaller. At an injection port temperature of 160°C, only one broad peak was obtained. It was likely that too low an injection port temperature resulted in the sample being introduced at a very slow rate into the column, and that this caused incomplete resolution of the peaks. This injection port test, therefore proved very little as to the origin of the extra peaks.

The next tests were carried out with different column tubing material and liquid phase. Using a stainless steel column packed with Chromosorb W HP coated with 3.5% w/w OV-17, no change was obtained in the number of peaks nor in their relative areas, for the methoxychlor sample. However, on a stainless steel column packed with Chromosorb W HP, 80/100 mesh, coated with 3.5% w/w QF-1, a decrease was observed in the areas of the first three peaks in relation to the area of the fourth peak, Figure 10.

Liquid phase QF-1 is more polar than OV-17, and may have caused some deactivation of the active sites on Chromosorb W HP support, and this could have been responsible for the decrease in the areas of the first three peaks. On this limited basis, the first three peaks

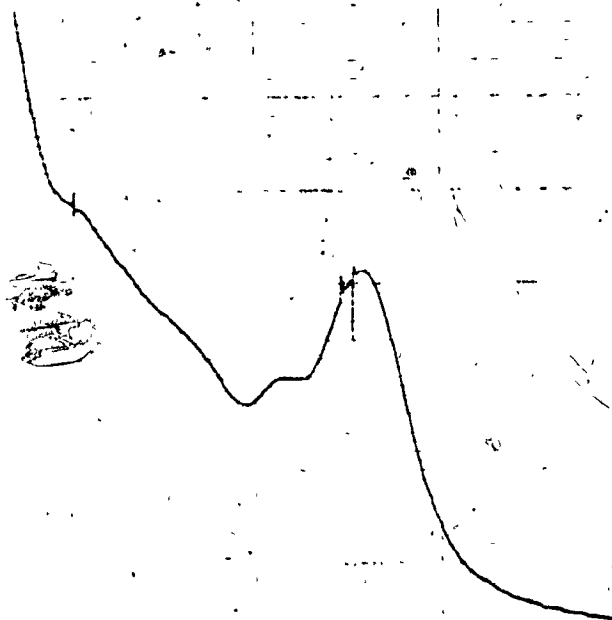


Figure 10. Analysis of Methoxychlor, 50  $\mu$ g, on 3.5% w/w QF-1 Coated  
on Chromosorb W HP at 200°C

were concluded to be degradation products of methoxychlor produced by thermal or catalytic decomposition of the compound on the solid support.

Further tests on the W HP and W NAW columns, using the FID, showed that the relative areas of the four peaks obtained changed with repeated injections of 50  $\mu$ g of methoxychlor, Figures 11 and 12, respectively. Repeated injections resulted in the covering of some of the active sites on the support, and greatly reduced the decomposition of methoxychlor. Column priming seemed to be an effective method of solid support deactivation in terms of reducing degradation of methoxychlor.

Preliminary tests on columns C and L, containing OV-17 coated Chromosorbs W AW-DMCS and 750, respectively, also showed some degradation of methoxychlor. Priming effects did reduce decomposition of the pesticide on Chromosorb W AW-DMCS, Figures 13(a) and (b), but not on Chromosorb 750, Figures 14(a) and (b).

Increasing the amount of liquid phase from 3.5% w/w on Chromosorb W NAW to 7% and to 14% resulted in a reduction in the decomposition of methoxychlor with higher liquid phase loadings, Figures 15 and 16. This was attributed to the fact that increased liquid phase loadings resulted in thicker coatings on the solid support, and produced a more efficient covering of the active sites. Even at a loading of 14% w/w OV-17 on Chromosorb W-NAW, however, there was still evidence of some degradation, Figure 16. The compound probably diffused through the layer of liquid phase and reacted with the active sites on the surface of the support.

While it looked as if GC conditions could be evolved for the analysis of methoxychlor, there were still problems to be solved. Tests

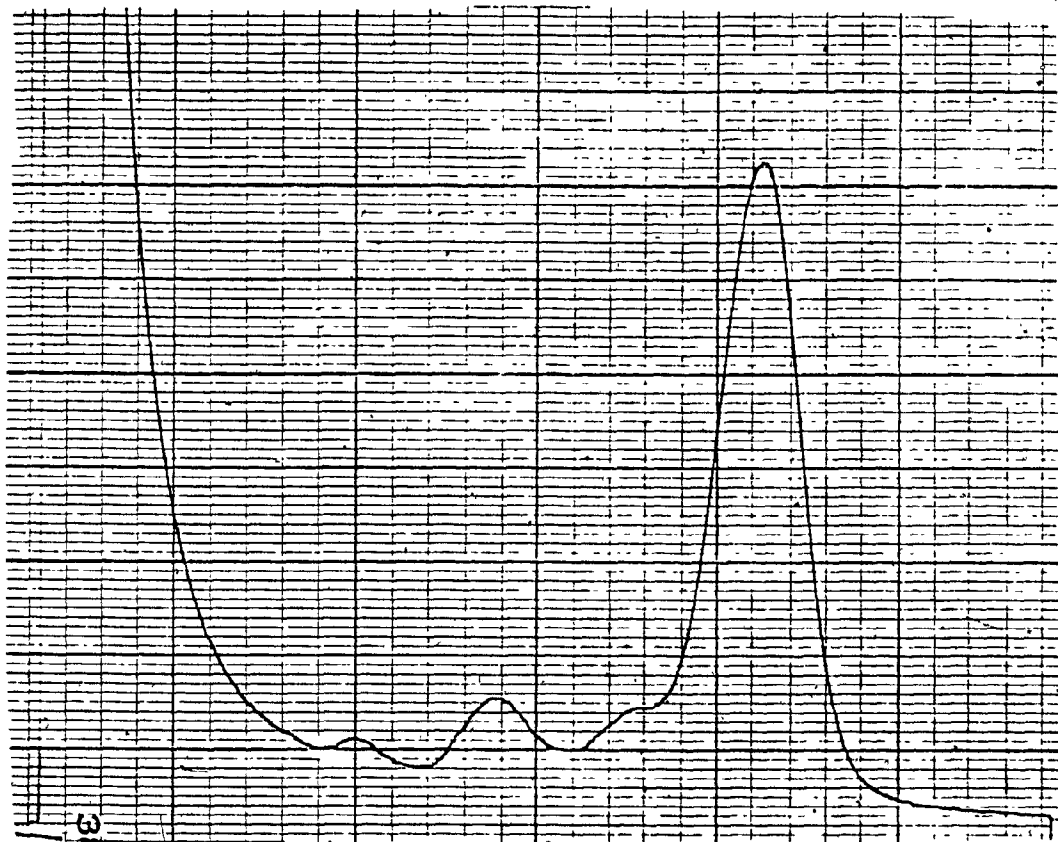


Figure 11 Analysis of Methoxychlor, 50  $\mu$ g, on 3.5% w/w OV-17  
Coated on Chromosorb W HP at 220°C; After Priming.

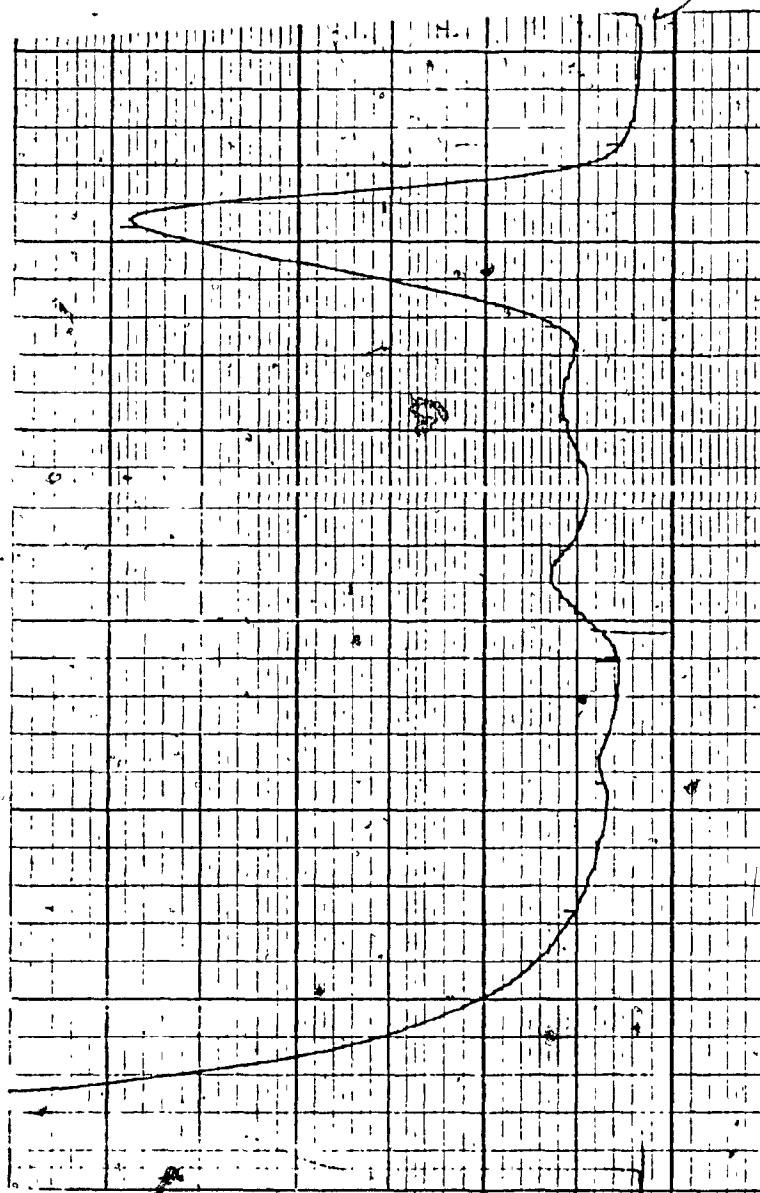


Figure 12 Analysis of Methoxychlor, 50  $\mu$ g, on 3.5% w/w OV-17 Coated on Chromosorb W NAW at 220°C; After Priming.

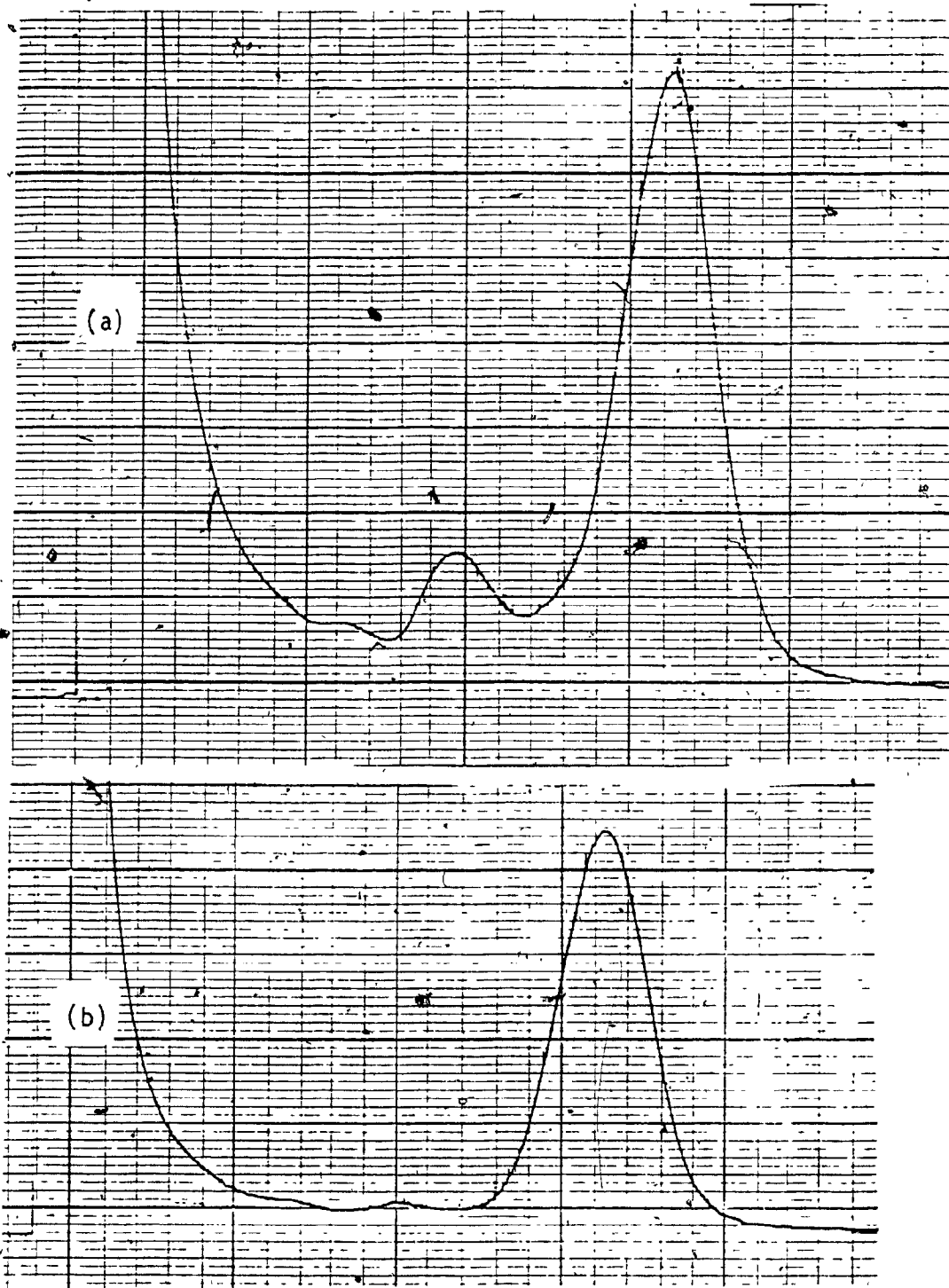


Figure 13 Analysis of Methoxychlor, 50  $\mu$ g, on 3.5% w/w OV-17  
Coated on Chromosorb W AW-DMCS at 220°C ; (a) Before  
Priming (Range 16), (b) After Priming (Range 32).

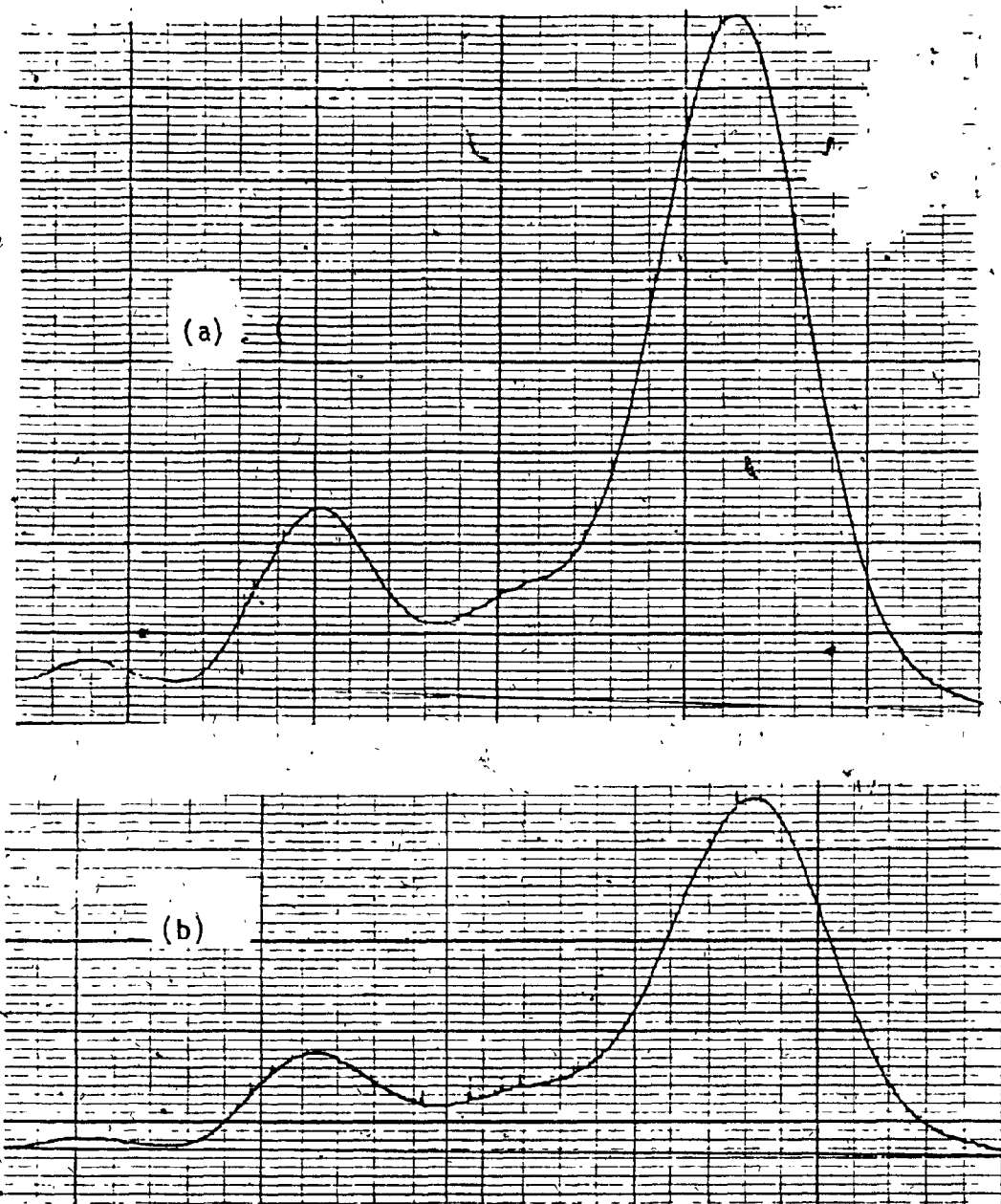


Figure 14 Analysis of Methoxychlor, 50  $\mu$ g, on 3.5% w/w OV-17  
Coated on Chromosorb 750 at 220°C; (a) Before Priming  
(Range 16), (b) After Priming (Range 32).



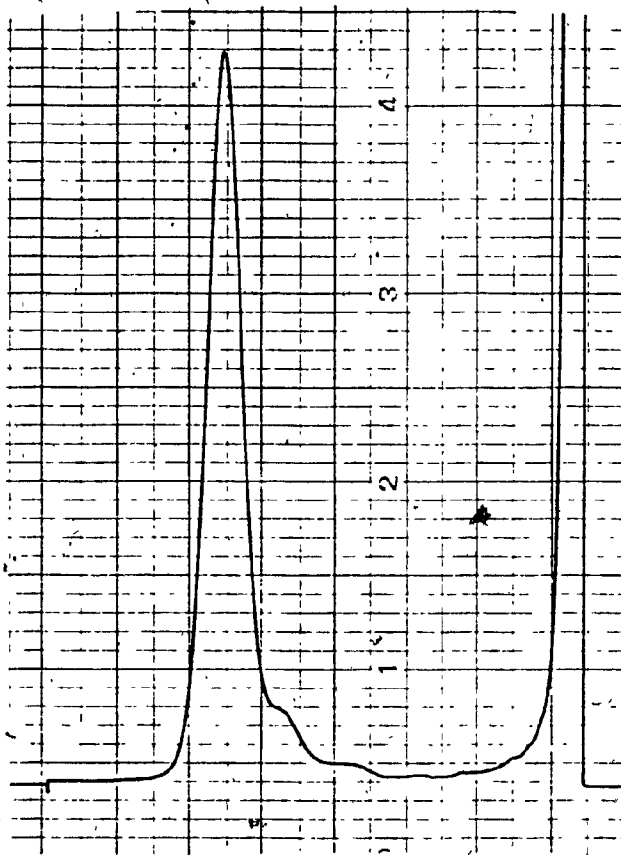


Figure 15 Analysis of  
Methoxychlor, 10- $\mu$ g, on  
7% w/w OV-17 Coated on  
Chromosorb W NAW at 230°C.

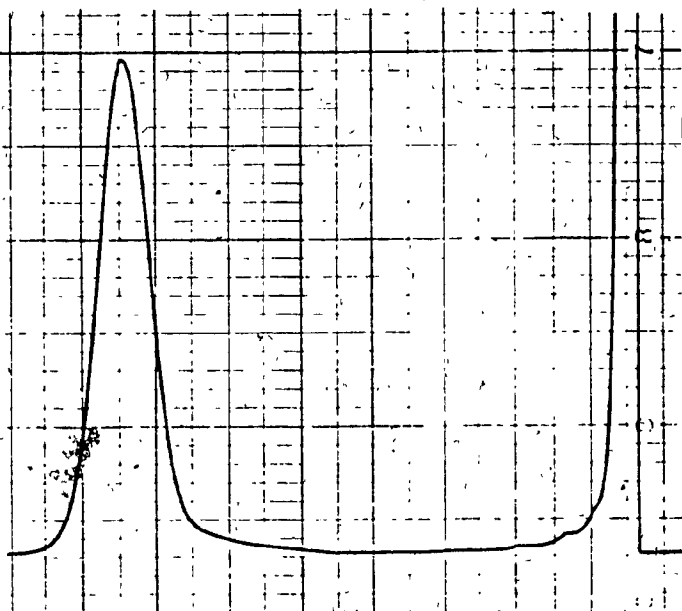


Figure 16 Analysis of  
Methoxychlor, 10  $\mu$ g, on  
14% w/w OV-17 Coated on  
Chromosorb W NAW at  
230°C.

using methoxychlor were therefore postponed until all the experiments described in this thesis, using dieldrin and the FID were completed.

No decomposition of dieldrin occurred on any of the Chromosorb W, P, G and 750 supports studied. When dieldrin tests were completed, and work was resumed with methoxychlor on the same columns, there was hardly any evidence of degradation. A single symmetrical peak was obtained in every case. Only the W NAW column gave some sign of a small amount of decomposition taking place, Figure 17. It appeared as if priming with dieldrin had deactivated supports to the extent that they could now be used without problem to analyze 10  $\mu$ g quantities of methoxychlor. However, as will be seen in Section 3.6, p. 156, the ECD series of tests revealed that decomposition had not been completely eliminated, when using small amounts of sample, i.e. 10 ng. This was a thousand times smaller than the amount injected into the columns for the FID tests, i.e. 10  $\mu$ g. The larger amount of sample used on the columns in the FID work prevented the detection of any traces of decomposition which may still have occurred.

After these findings, all work subsequently carried out with methoxychlor, and reported in the bulk of this thesis, was carried out on columns which had previously been used for dieldrin studies.

### 3.2 GUIDELINES

As mentioned in Section 1.7.3, p. 13, peak area can be used as a measure of the adsorptive properties of chromatographic supports in cases where peak tailing may be very small or undetectable. In fact, peak area may be a better method since tailing may follow from other effects as well as adsorption. Hence, the comparison of the adsorptive properties of the solid supports investigated in this thesis, was based

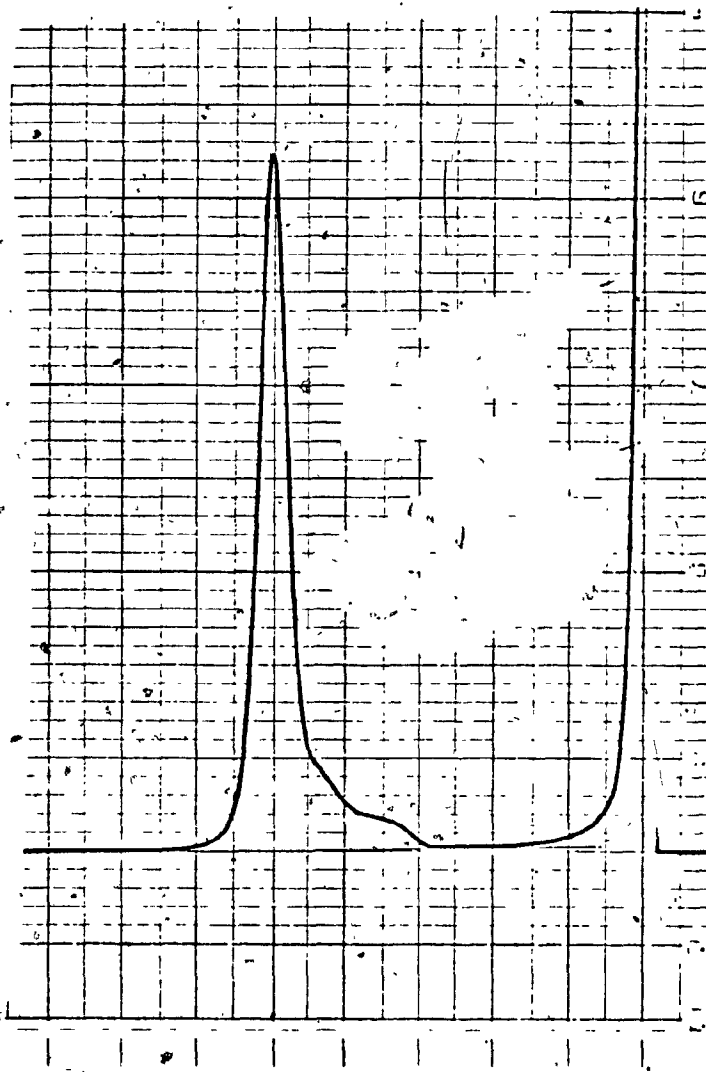


Figure 17 Analysis of Methoxychlor, 10.  $\mu$ g,  
on 3.5% w/w OV-17 Coated on  
Chromosorb W NAW at 230°C.

on peak area responses at different column temperatures for equal amounts of pesticide injected, and on peak area responses for different sample sizes injected at a constant column temperature.

The largest response was expected to be obtained from the least adsorptive column and the smallest response from the most adsorptive column.

The results reported should not be used to make comparisons between different families of supports, i.e. Chromosorb W's with G's or P's. Due to differences in physical properties of these supports, they are not deactivated to the same extent when coated with the same loading of stationary liquid phase and when used on an equal volume basis, as was the case in this study.

The various chromatographic supports differ from each other considerably in bulk density. As a result, the total quantity of liquid phase in columns of equal volume will vary from one type of solid support to another. A 3.5% w/w loading of OV-17 liquid phase on Chromosorbs W, P, G and 750 results in columns of equal dimensions having the following volume concentrations of liquid phase compared to the column packed with Chromosorb W:

Chromosorb P - 6% v/v

Chromosorb G - 8.8% v/v

Chromosorb 750 - 6% v/v

The greater the amount of liquid phase in a column, the poorer its efficiency. Another factor to be considered is surface area. The difference in surface area of the solid supports result in differences in the distribution and thickness of the stationary phase layer formed on these supports. As a consequence, the degree of deactivation of the

support surfaces resulting from the liquid phase coating will vary from one type of support to another.

Chromosorb P, due to its small pores and large surface area (Section 1.7.6, p. 18) receives less deactivation from the liquid phase than either Chromosorbs W or G. Chromosorb 750 has a surface area between 0.5 and 1.0 m<sup>2</sup>/g, close to that of Chromosorbs W and G, and as a result, the deactivation produced by the liquid phase is of the order of that received by Chromosorbs W and G, for the same w/w concentration of liquid phase. The overall deactivation of the solid supports, then, resulting from a given percent w/w loading of liquid phase, should follow the order

$$P < 750 < G < W$$

It was not the purpose of this thesis to compare W to P to G supports. Had this been necessary, then all packings would have been prepared to contain the same thickness of stationary phase coating on the solid support surfaces.

### 3.3 THERMOGRAMS OBTAINED ON THE VARIOUS CHROMOSORB W, P AND G SUPPORTS USING THE FID, AND DIELDRIN AND METHOXYCHLOR AS TEST SAMPLES

The adsorptive properties of various Chromosorb W, P and G supports were studied using the flame ionization detector, and the pesticides, dieldrin and methoxychlor as test samples. The columns used for this study were columns A to L, listed in Table VI, p. 83. The column temperature range covered in the case of dieldrin was 160 to 240°C for the W supports, and 170 to 250°C for the G and P supports. The column temperature range used in the case of methoxychlor was 200 to 280°C for all the supports. Duplicate thermograms were obtained for each pesticide on all the supports tested.

Each temperature run consisted of making multiple injections (3 to 5) of the pesticide, starting at the lowest column temperature and then at higher temperatures, in 10° intervals. At each column temperature, the peak area of each peak eluted was calculated, and the average peak area determined. Plots of average peak area responses versus column temperatures were made of both first and second runs, for each pesticide, and each support studied. Figures 18 to 29, Appendix C, are the thermograms obtained with dieldrin and Figures 30 to 38, Appendix D, consist of the thermograms obtained with methoxychlor.

#### 3.3.1 Preliminary Observations

It was observed that peak area responses for both dieldrin and methoxychlor often varied from sample injection to injection, for a set of injections made at each column temperature. For example, peak area responses sometimes increased with repeated injections of the sample, then suddenly decreased to values close to that originally obtained, only to follow the same increasing pattern with further sample injections. Another trend noticed, was an increase in peak area to some maximum value, and then a gradual decrease in peak area with repeated injections of the sample. Still another trend sometimes observed was a fairly constant peak area with repeated injections of the sample, and then a change to another constant value for peak area with more repeated injections of the sample. The responses obtained within a set of injections also varied with no discernible pattern in some cases. Thus, the variations in peak areas observed were very irregular. These variations in the responses obtained, within a set of injections, were attributed to sample priming effects.

It has already been explained (Section 1.7.10.3, p. 30 ), that a part of a sample injected into a column may be retained in the column, and result in some support deactivation. The deactivation results from the covering of some of the active sites with the sample. Hence, it can be argued that whenever an increasing trend in response was observed, it was the result of priming, i.e. covering and deactivation of active sites on support surfaces by the samples previously injected. The observed decreases in response had to be the result of the formation of fresh active sites, equivalent to a depriming of the support surface. The mechanism for this process is not known, but may be related to the behaviour of the liquid phase on the support, as influenced by the presence of sample solutes. What is clear is that the nature of the column was changing from one injection of sample to the next.

### 3.3.2 Thermograms Obtained for Dieldrin and Methoxychlor

The thermograms obtained for dieldrin are shown in Figures 18 to 29, Appendix C. From these it can be seen that:

- (i) all thermograms consisted of curves with numerous maxima and minima;
- (ii) the thermograms obtained from the various supports differed from each other as to the number and position of the many maxima, and the size of responses at each column temperature;
- (iii) the overall trends of the thermograms were a small increase in peak area responses with increasing column temperatures, with few exceptions;
- (iv) on any single support, the thermogram obtained from the second run differed from that obtained from the first run

in terms of the number, and position of the many maxima, but the general trend was similar in both cases.

Furthermore, no general conclusions could be reached as to which run produced the higher responses.

At certain temperatures some supports produced higher responses during the second runs while at other temperatures higher responses were obtained during the first runs. For example, in the case of Chromosorb W AW-DMCS (Figure 20), the support was less adsorptive during the first run at column temperatures of 160<sup>o</sup>, and 180<sup>o</sup> to 200<sup>o</sup>C, while at temperatures of 170<sup>o</sup>, and 210<sup>o</sup> to 240<sup>o</sup>C, the support was less adsorptive for the second run. The only clear cases where higher responses were obtained during the second run, which was what had been expected, were those involving Chromosorbs P AW (Figure 28) and W, NAW (Figure 18), but even for the latter there was an exception at 210<sup>o</sup>C. Chromosorb G AW (Figure 24) is an example where higher responses were obtained during the first run at all temperatures, with the exception of 180<sup>o</sup>C.

The thermograms obtained for methoxychlor are given in Figures 30 to 38, (Appendix D) from which the following general observations were made. Results were similar to those observed for dieldrin in that:

- (i) All thermograms contained many maxima and minima.
- (ii) The thermograms obtained from the various supports differed as to the number and position of the many maxima, and as to size of response at the various column temperatures.
- (iii) Although the general trends of the thermograms obtained from the first and second runs on the same supports were similar, the thermograms were not identical due to changes in the number and position of the many maxima from run to run.



- (iv) In all cases, the peak area responses of methoxychlor increased with an increase in the column temperature. This increase, however, was quite dramatic compared to what was observed for dieldrin. The response for methoxychlor, on most supports, approximately doubled in going from a column temperature of 200°C to 290°C.
- (v) The rise in response with an increase in the column temperature was initially very rapid (from a column temperature of 200° to about 250° or 260°C), and then levelled off to a more or less constant value above 260° or 270°C.
- (vi) It was not certain whether the priming effect of the first run decreased the adsorptivity of the supports, because the responses of the second runs were not always greater than those of the first runs. As in the case of dieldrin, some supports showed generally greater responses in the first runs, e.g. on Chromosorb G AW (Figure 36). Other supports showed generally greater responses for the second run, e.g. on Chromosorbs W NAW, W HP, G-AW-DMCS and G HP (Figures 30, 33, 37 and 38 respectively).

On Chromosorbs W AW, W AW-DMCS, 750 and G NAW, at some temperatures, higher responses were obtained in the first runs, and at other temperatures higher responses were obtained in the second runs (Figures 31, 32, 34 and 35 respectively).

### 3.3.3 Discussion of Thermograms Obtained for Dieldrin and Methoxychlor

The numerous maxima/minima which occurred on all the thermograms, for both pesticides, can be attributed to sample priming and liquid phase

bleed effects.

At the start of the temperature run, repeated injections of the sample may have resulted in the adsorption of a fairly large amount of sample by the active sites on the surface of the support resulting in some support deactivation (priming). The magnitude of responses obtained depended on the quantity of sample adsorbed.

During a column temperature change, and the period required for equilibration, no sample injections were made, and the adsorbed sample may have been partially or completely removed by vaporization into the carrier gas passing over it, in which case, the column would have returned to its original state. Further injections at the new temperature would have resulted in adsorption of sample again. If adsorption of the sample happened to be of the same proportion as it was during the previous column temperature, then responses similar to those previously acquired, would again have been obtained. If more adsorption of sample occurred at the new column temperature, then responses slightly lower than those previously acquired would have been obtained.

If, during the column temperature change very little adsorbed sample had been removed by the carrier gas, the column would have remained slightly less adsorptive than during the first injections, since some portion of the active sites on the support would have still been covered. Further injections at the new column temperature would then have resulted in a decrease in the amount of sample adsorbed, and hence an increase in peak area responses.

The increases or decreases in the responses obtained at each column temperature, thus depended on the amount of sample priming which occurred throughout sample injections at the previous column temperatures, and on

the amount of adsorbed sample lost when the column temperatures were increased and the columns equilibrated.

Each temperature increase represented a possibility where partial or complete loss of adsorbed sample could have occurred. Often the thermograms obtained showed a steady increase in response with a number of increases in the column temperature, following which a sudden decrease in response was observed for the subsequent higher one or two temperatures, followed by a sharp increase again at some still higher column temperature (e.g. second runs on W AW-DMCS and G AW-DMCS supports, Figures 20 and 25, respectively).

The increases can be explained by support priming effects as before. The sudden decrease in response was most likely the result of liquid phase bleeding, because of increased temperature, resulting in new active sites being exposed on the support surface. These newly exposed sites then would have adsorbed subsequently injected samples leading to a lower response than was observed at prior, lower temperatures.

The column would regain its less adsorptive character once enough sample had been adsorbed to prime the majority of the new active sites. Later work with the electron capture detector confirmed that bleeding of the liquid phase did occur during running of the thermograms. Furthermore, the bleeding liquid phase may well have carried with it some already adsorbed sample, and further increased the adsorptive properties of the supports.

For methoxychlor thermograms (Figures 30 to 38, Appendix D) the increase in response with column temperature must be due to decreasing adsorptivity of the support active sites (as is normal with increase in temperature) as well as sample priming effects.

The levelling off in response at column temperatures of about 260°C and above, may mean that at these temperatures, any decrease in adsorption because of these factors, was balanced out by an increase in adsorption because of exposure of new active sites due to liquid phase bleeding. Another possibility was that most of the active sites on the supports had become saturated with sample, and no further decreases in adsorption were possible. The decline in responses at high column temperatures, for example, dieldrin on G NAW and methoxychlor on W AW-DMCS (Figures 23 and 32) could not have been due to saturation of the active sites. It is more likely that the bleeding liquid phase exposed a great many new active sites, thereby greatly increasing adsorption. The higher the column temperature, the more bleeding that occurred, the more active sites that could be uncovered.

The priming effects of the first runs should have resulted in decreased adsorption throughout the second runs for all supports tested. Samples adsorbed during the first run should have deactivated the supports by saturating the active sites. This prediction, of course, ignores the effects of liquid phase bleed at the high column temperatures during the first runs. Higher responses were obtained for a few supports, as was discussed previously, but for most supports, the responses were variable because of the apparent effects of priming and liquid phase bleeding.

The fact that on the majority of supports, no real improvement in response was observed during the second run was an indication that support deactivation from sample priming was a temporary effect, at best. Much of the priming was probably lost by the end of the first run higher temperature tests. Any sample left adsorbed after the first run was completed may subsequently have been removed from the column by the car-

rier gas which flowed through the column during the shut-down period of the Gas Chromatograph between runs or during the warm-up period just before the start of the second run.

Chromosorb G AW, towards dieldrin, and Chromosorbs W AW-DMCS and G AW towards methoxychlor, were cases where, overall, the supports were more adsorptive during the second run. Furthermore, Chromosorb P AW-DMCS (for dieldrin) and Chromosorb W AW (for methoxychlor) showed higher adsorption at the start, low temperature end, of the second run. If during the first runs there was a certain amount of liquid phase bleed at the high column temperatures exposing new active sites, and if sample priming was inadequate in deactivating the active sites exposed (especially if the retained sample was lost from the column before the start of the second run) then, the support would have become more adsorptive during the second run.

If, however, the liquid phase bleed was low during the first run, and the number of new active sites exposed relatively few, then sample priming may have been capable of deactivating the new active sites, and leaving this support in its original state or even somewhat deactivating it. This was probably what occurred for Chromosorbs P AW-DMCS and W AW. From the comparative appearance of the thermograms, quite clearly, there must have been big differences in the amount of stationary phase bleeding that occurred from support to support (column to column).

The fact that Chromosorb G AW was more adsorptive during the second run towards both pesticides indicated that this was a poor batch of support, or that it had not been successfully coated with liquid phase to begin with. If during its preparation, the acid washing had not been

done properly, and deposits of acid had remained on the support, decomposition of the silicone liquid phase could have occurred at the high column temperatures (see Section 1.8.4, p. 41 ). Acid washed supports have been reported to be very poor for the analysis of dieldrin and methoxychlor for precisely this reason (see Section 1.7.10.2 p. 29 ).

Chromosorb W AW-DMCS showed a very drastic increase in adsorption during the second run with methoxychlor, but not with dieldrin. The much higher column temperatures used with methoxychlor at the end of the first run may have caused large amounts of bleed of the liquid phase from this support. If the deactivation treatments used in the preparation of this support were done improperly, such that free acid or chloro-groups were left on the support, then liquid phase decomposition may have taken place. In addition, it is known that it is difficult to coat silanized diatomite surfaces with polar, stationary liquid phases, and OV-17 is relatively polar (see Sections 1.7.11 and 1.8.5, pp. 36 and 47).

### 3.3.4 Comparison of the Thermograms Obtained for Dieldrin with Those Obtained for Methoxychlor

The thermograms obtained on Chromosorbs W, P and G using dieldrin as the test sample showed, overall, small increases in response with increases in the column temperature. On the other hand, the thermograms obtained on the same columns using methoxychlor as the test sample showed very drastic increases in peak area with increases in the column temperature.

The following points were considered in accounting for the above differences:

- (i) Different solutes can interact with the same support to varying degrees.

- (ii) Different temperature ranges were used for each pesticide.
- (iii) All coated supports were first tested with dieldrin, and then with methoxychlor.

An indication that different solute-support interactions were taking place for each pesticide was the completely symmetrical peaks obtained for methoxychlor compared to the slightly tailing peaks obtained for dieldrin. This tailing was an indication that dieldrin was being more strongly adsorbed by the solid support in the temperature range studied. Although no tailing was observed with methoxychlor when analyzed on supports primed by dieldrin, this compound underwent decomposition on freshly coated and conditioned Chromosorb support columns and extraneous peaks were obtained. Such decomposition was reduced with repeated injections of methoxychlor, and disappeared after the columns had been used with dieldrin, (see Section 3.1, p. 94, for a detailed discussion). Dieldrin obviously primed the columns by covering the active sites responsible for the degradation of methoxychlor. The large increases in response for methoxychlor with the increase in column temperature were attributable, therefore, to the ease with which the very few remaining active site-methoxychlor interactions were overcome with increasing column temperature, and priming by methoxychlor itself. As more and more sample accumulated on the supports from the injections at each new column temperature, the supports became less and less adsorptive and hence, the large increases observed in response with the column temperature.

On the other hand, the interactions between dieldrin and the newly prepared coated supports were stronger (more adsorption) as was indicated by the tailing of the peaks. Sample priming during dieldrin tests was

incapable of greatly reducing this adsorption. This lack of pre-priming before testing with dieldrin resulted in the small increases observed in response for dieldrin with increase in the column temperature.

The generally flattening out of methoxychlor responses at very high column temperatures was likely the result of exposure of fresh active sites on the support surfaces due to onslaught of liquid phase bleeding (see Section 1.8.4, p. 41).

### 3.3.5 Thermograms Obtained Using High Concentrations of Dieldrin and Methoxychlor - FID

Figures 39 and 40 consist of thermograms obtained on column C using 50  $\mu$ g dieldrin and methoxychlor, respectively. A comparison of these thermograms with those obtained previously on the same column, but using only 10  $\mu$ g dieldrin, or methoxychlor (Figures 20 and 32 respectively), showed that sample size had an effect on the thermogram patterns, and hence on column behaviour. The larger amount of sample injected was probably more effective in covering the active sites initially present, and those subsequently exposed by liquid phase bleed.

The sharp decline in response previously observed with methoxychlor was not seen here due to the ample sample available for active site deactivation. Furthermore, the thermogram for dieldrin was a smooth curve (less maxima/minima phenomena), than was obtained with lower concentrations of dieldrin. This showed that larger sample sizes were effective in hiding adsorptive effects of supports.

## 3.4 COMPARISON OF ADSORPTIVE PROPERTIES OF CHROMOSORB SUPPORTS

### 3.4.1 Chromosorb 750 and Chromosorb W Supports - Dieldrin as the Test Sample - FID



Figure 39 Thermograms for High Concentrations of Dieldrin, 50  $\mu\text{g}$

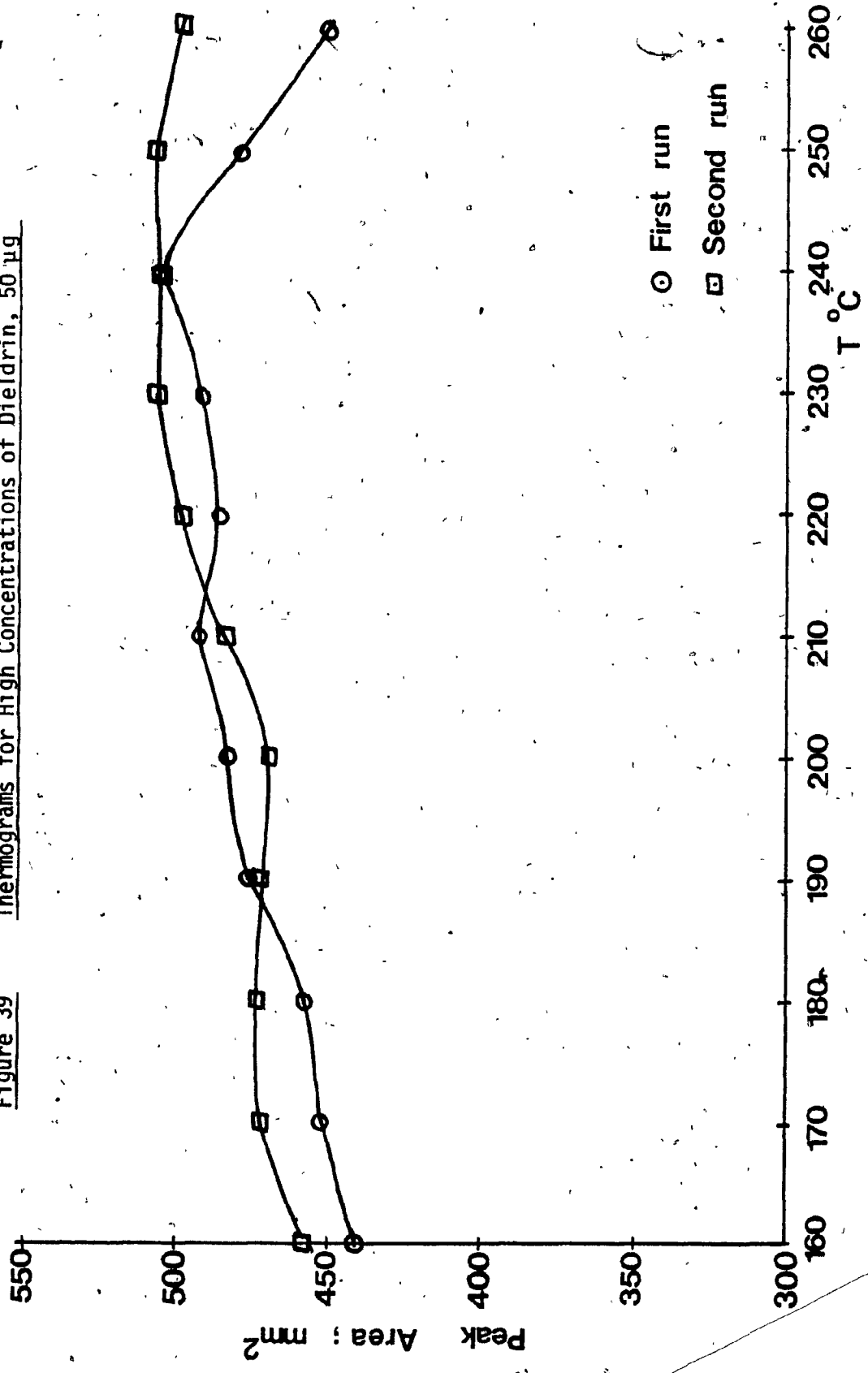
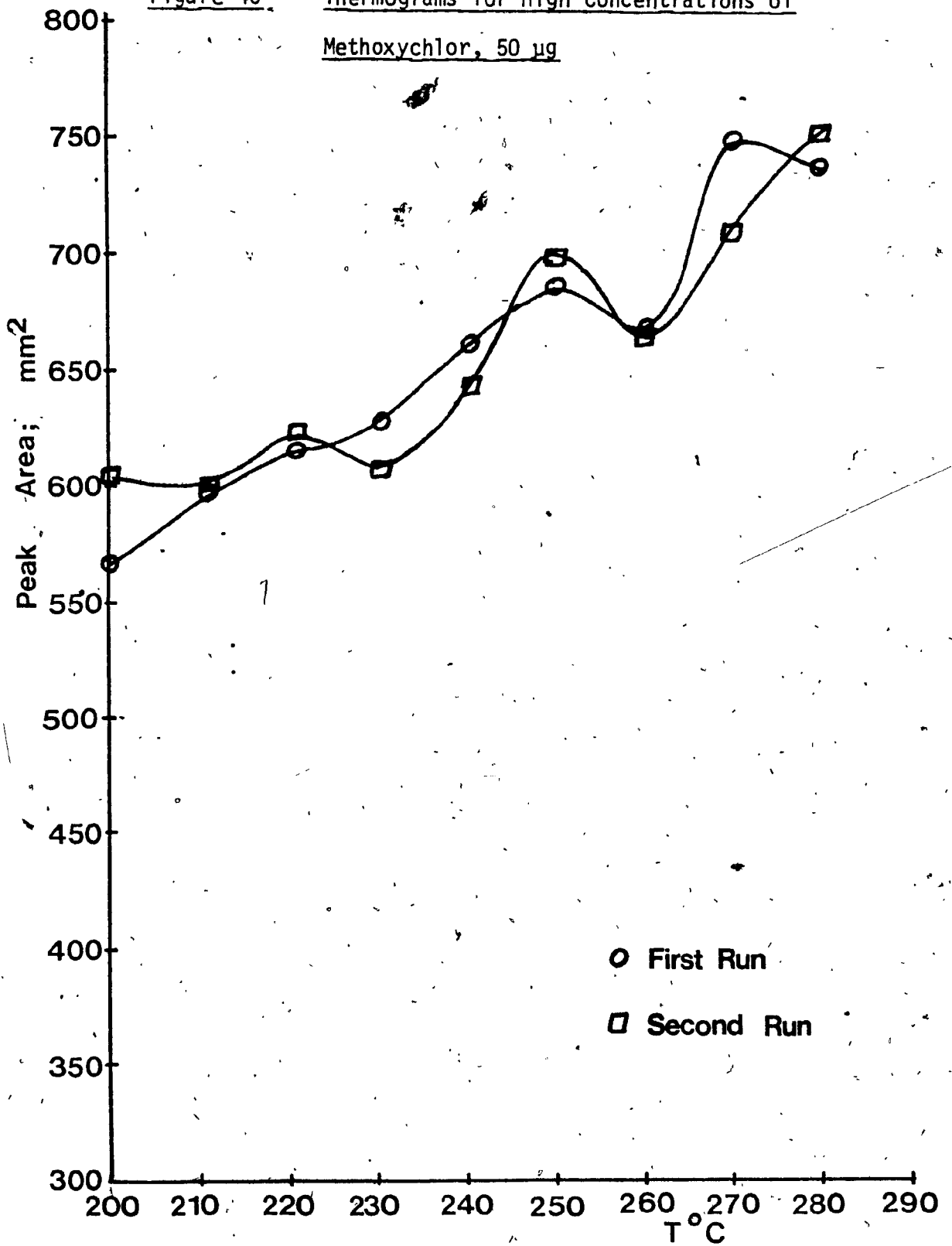


Figure 40. Thermograms for High Concentrations of  
Methoxychlor, 50  $\mu\text{g}$



Figures 41 and 42 contain the thermograms (first and second runs respectively) of all the Chromosorb W supports, including Chromosorb 750. From these Figures it was observed that there was a larger variation among the adsorptive properties of the different supports throughout the second runs than during the first runs. This was attributed to the priming effects of the first run, which resulted in an increase in response for some supports during the second run, and to the bleeding of the liquid phase during the first run, which resulted in an increase in the adsorptive properties of other supports during the second run (due to an increased number of active sites). The extent to which sample priming and liquid phase bleeding effects cancelled each other determined the overall effect on adsorptivity of the supports. Generally, the tendency was to render surface activity of all the supports more closely the same.

It was decided that more emphasis should be placed on the second runs, in evaluating the adsorptive properties of these supports. Once column priming and liquid phase bleed had had a chance to occur, it was thought that a more precise evaluation of the supports was possible in terms of how they would behave during regular use.

From Figure 42 it was concluded that for the W supports, in the temperature range of  $160^{\circ}$  to  $200^{\circ}\text{C}$ , Chromosorb W NAW was, very marginally, the least adsorptive of all the Chromosorb W supports while W AW, W AW-DMCS and W HP showed more adsorption, but were similar to one another. For example, at  $180^{\circ}\text{C}$ , Chromosorb W HP was slightly less adsorptive than the other two, while at  $200^{\circ}\text{C}$ , Chromosorb W AW showed an increase in response compared to the other two. Overall, these differences, as they are unlikely to be reproducible, are not significant. In this tempera-

Figure 41 Comparison of Thermograms for Dieldrin on Various Chromosorbs W. First Runs Using the FID.

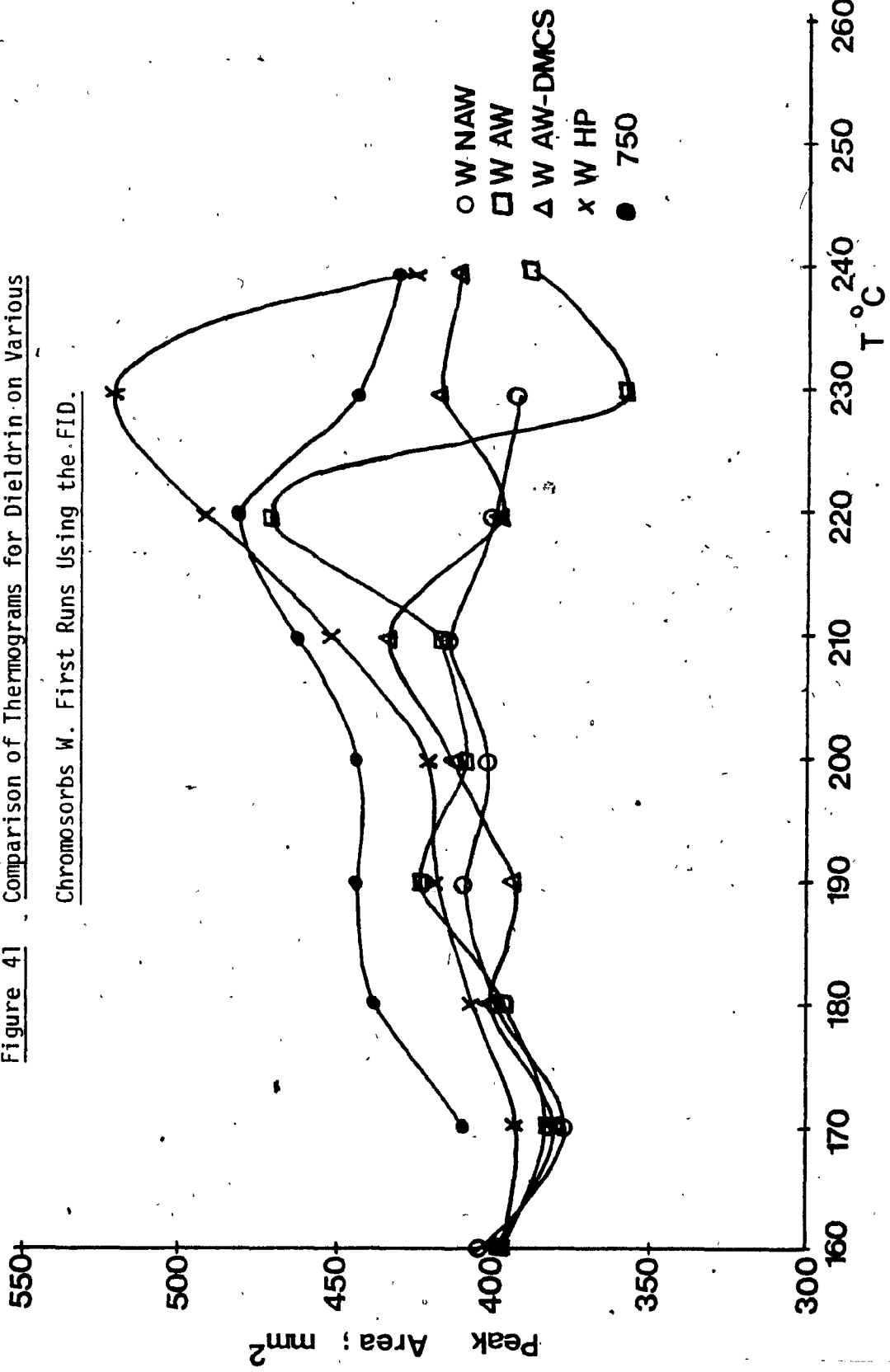
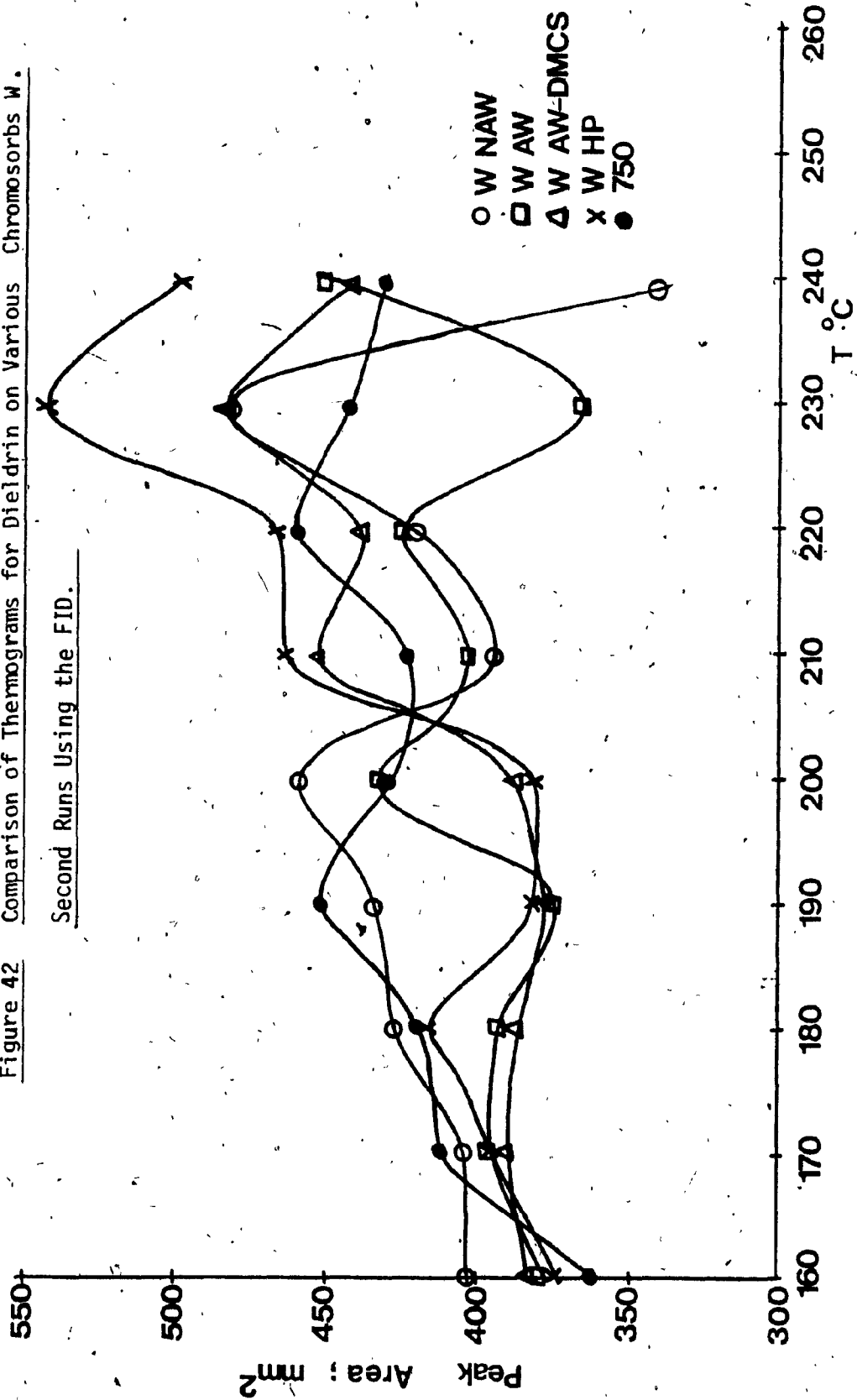


Figure 42 Comparison of Thermograms for Dieldrin on Various Chromosorbs W.  
 Second Runs Using the FID.



ture range the support deactivation treatments, acid washing and AW-DMCS, appear to have been of little benefit. Also, in the temperature range of 160<sup>0</sup> to 200<sup>0</sup>C, there was no discernible difference between Chromosorbs 750 and W NAW. Overall, 750 was slightly better than W AW, W AW-DMCS and W HP. In the temperature range of 210<sup>0</sup> to 240<sup>0</sup>C, W HP was, by far, the least adsorptive support and W AW-DMCS, W AW and W NAW were about the same.

It seemed that the silanized supports, 750, W HP and even W AW-DMCS, became relatively less adsorptive at the higher column temperatures. Deactivation treatments by silanization became important in reducing adsorption at the higher column temperatures where liquid phase bleeding may have been extensive enough to leave many parts of all support surfaces uncoated. The extra treatment that W HP receives, compared to W AW-DMCS, was reflected in its excellent performance at high temperatures.

Comparison with the first run thermograms confirmed the fact that in the temperature range of 160<sup>0</sup> to 200<sup>0</sup>C, there was no discernible difference among WNAW, W AW, W AW-DMCS and W HP. Furthermore, Chromosorb 750 was slightly less adsorptive than any of the W's, making it virtually equivalent to Chromosorb W HP. The first run also confirmed that W HP was the least adsorptive support at the higher column temperatures. The only differences between the first runs and the second runs in this temperature range were the increased response for W NAW during the second run and the improved performance of W AW-DMCS. For example, at higher temperatures, it became better than 750. It was very difficult from the results presented in Figures 41 and 42 to draw general conclusions, but it can be stated that at low column temperatures (160<sup>0</sup> to 200<sup>0</sup>C) 750 was slightly better than the W supports, based on Run 1, and all

supports tested were equivalent in the second run. At higher column temperatures (210<sup>0</sup> to 240<sup>0</sup>C), Chromosorb W HP displayed the least adsorptive behaviour. Over the entire temperature range covered (Runs 1 and 2), 750 was, marginally, the least adsorptive support. For high temperature work, W HP was better. Summarizing, adsorptivity towards dieldrin was:

$$750 \lesssim W \text{ HP} < W \text{ NAW} \approx W \text{ AW-DMCS} \approx W \text{ AW}$$

### 3.4.2 Chromosorb 750 and Chromosorb W Supports - Methoxychlor

#### As the Test Sample - FID

Figures 43 and 44 consist of the thermograms obtained for methoxychlor, first and second runs respectively, on Chromosorb W and Chromosorb 750 supports.

According to the second runs, Figure 44, W AW was the most adsorptive support with 750 only slightly less adsorptive. W NAW was about the least adsorptive support at temperatures of 200<sup>0</sup> to 240<sup>0</sup>C, but at higher temperatures it behaved as one of the more adsorptive supports. Overall, Chromosorb W HP was the least adsorptive support, except at high temperatures where W AW-DMCS was equivalent to it, or even better. The responses obtained for W AW-DMCS were very similar to those for W AW. In both cases, adsorption decreased drastically with increase in temperature.

According to the first runs, Figure 43, W AW was the most adsorptive support overall, with 750, and W NAW only slightly less adsorptive. W HP and W AW-DMCS were the least adsorptive supports. Chromosorb W AW-DMCS gave higher responses at column temperatures in the 220<sup>0</sup> to 260<sup>0</sup>C range, while W HP gave higher responses above 260<sup>0</sup>C. The results obtained from

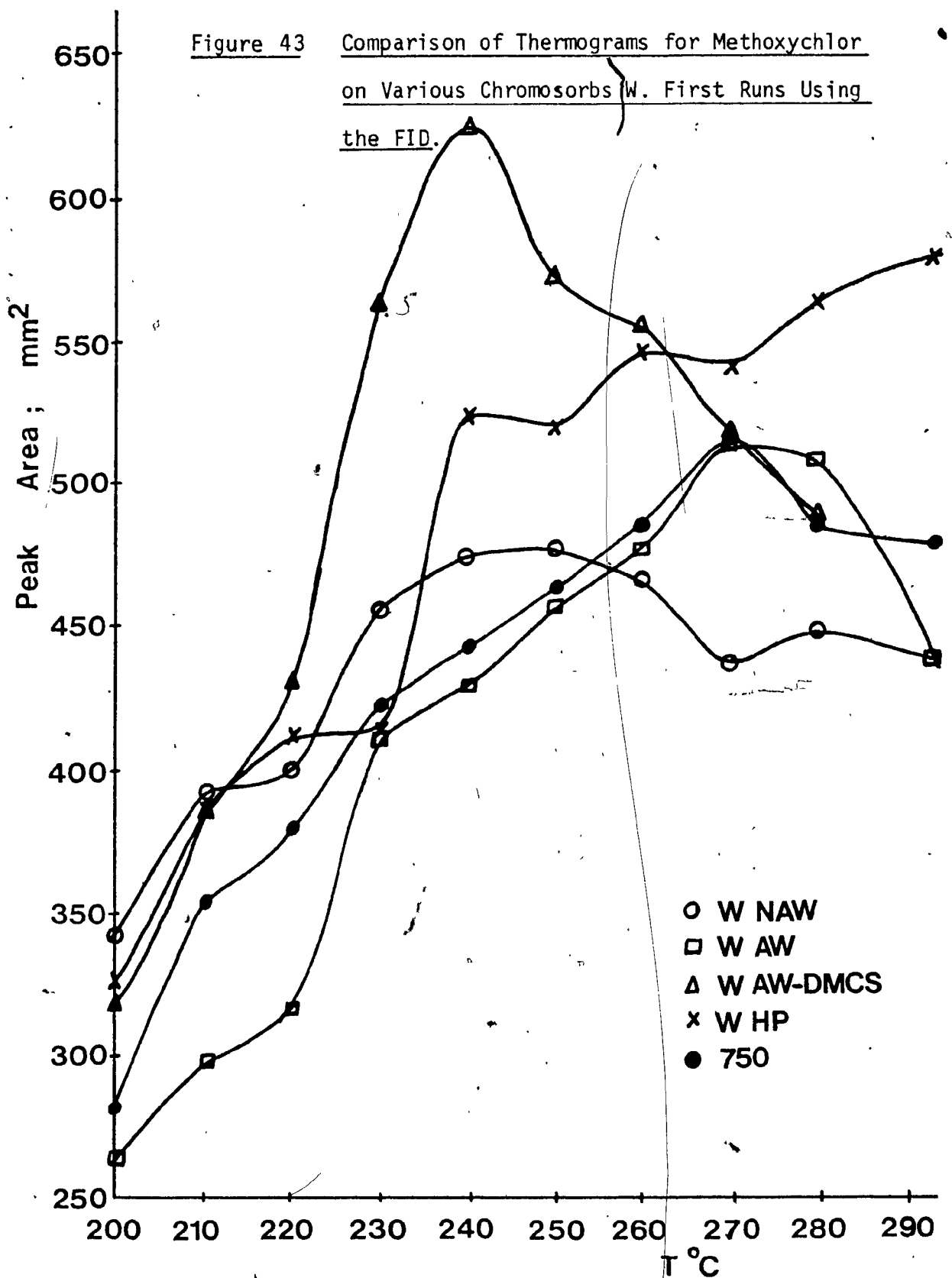
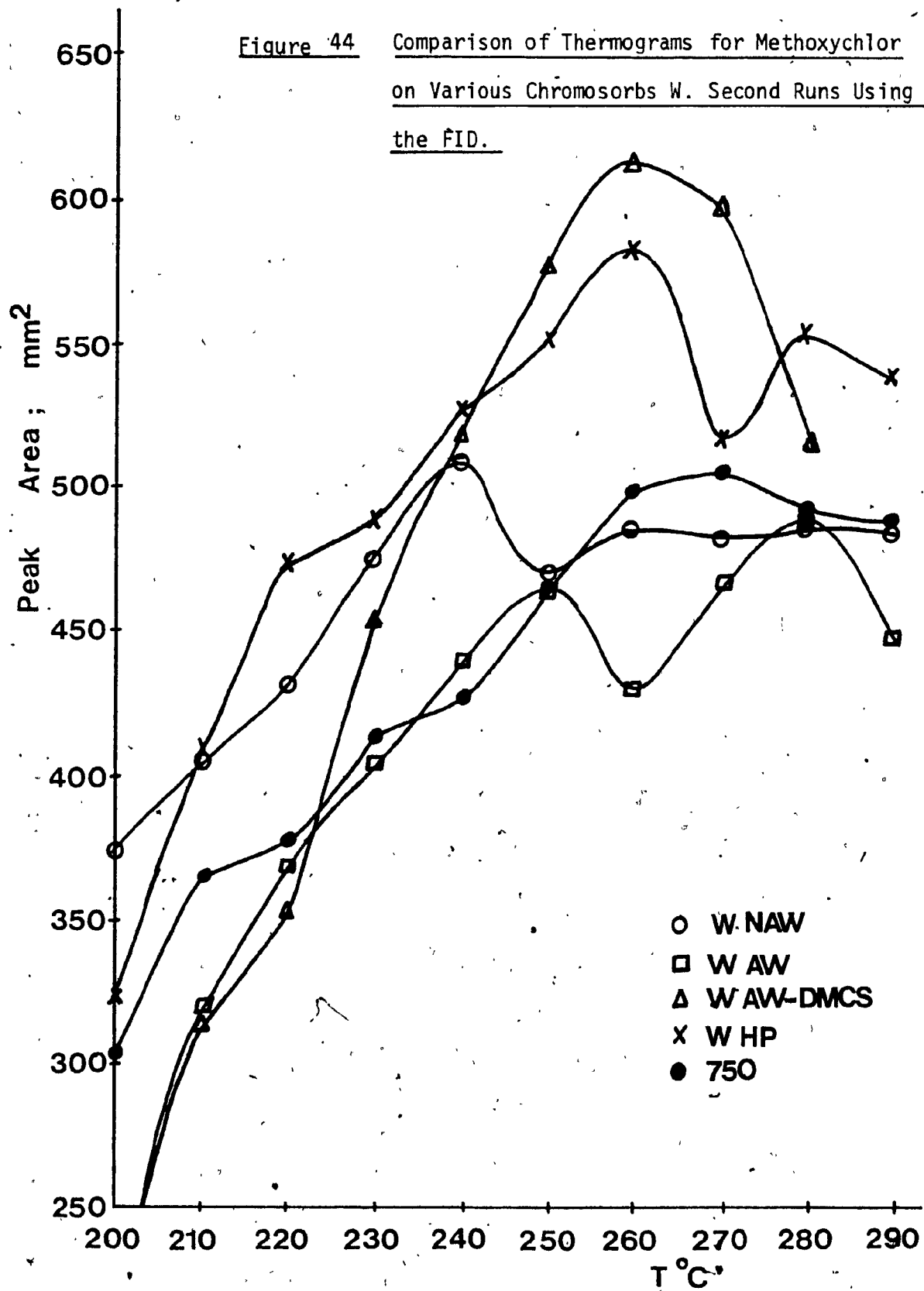




Figure 44 Comparison of Thermograms for Methoxychlor on Various Chromosorbs W. Second Runs Using the FID.



the second runs were, in fact, in good agreement with those from the first runs.

Chromosorb W NAW had been expected to be the most adsorptive support since this support had received no deactivation treatment. It was surprising, therefore, to find that W AW and 750 were both more adsorptive than Chromosorb W NAW. This might reflect a greater tenacity of W NAW to hold on to its liquid phase coating. Possible reasons for the poor behaviour of AW supports have already been described. The very poor behaviour of Chromosorb 750 was most unexpected and could be attributed only to severe loss of its liquid phase.

The high responses obtained on W NAW, at the lower column temperatures, compared to those on silanized supports (W AW-DMCS, W HP and 750) were an indication of the difficulty of effectively coating silanized supports with even somewhat polar liquid phases such as OV-17. As mentioned before, only at high column temperatures where bleeding of liquid phases is likely from all supports, was adsorption due to silanized supports markedly improved compared to that of nonsilanized supports. The levelling off of the responses obtained on W NAW at the high column temperatures was an indication of increased adsorption because of liquid phase bleeding, or, degradation of methoxychlor on this untreated support. Small extraneous peaks were detected at high column temperatures, Figure 17.

Generally speaking, whenever a decline in response at high column temperatures was observed, it could be attributed to the exposure of new active sites by increased liquid phase bleed. In conclusion, the overall adsorptive properties of the supports towards methoxychlor were as follows:

$$W \text{ AW-DMCS} \leq W \text{ HP} < W \text{ NAW} \leq 750 \approx W \text{ AW}$$

### 3.4.3 Chromosorb G Supports - Dieldrin as the Test Sample -

#### FID

Figures 45 and 46 consist of the thermograms of the first and second runs, respectively, obtained with the Chromosorb G supports, using dieldrin as the test sample.

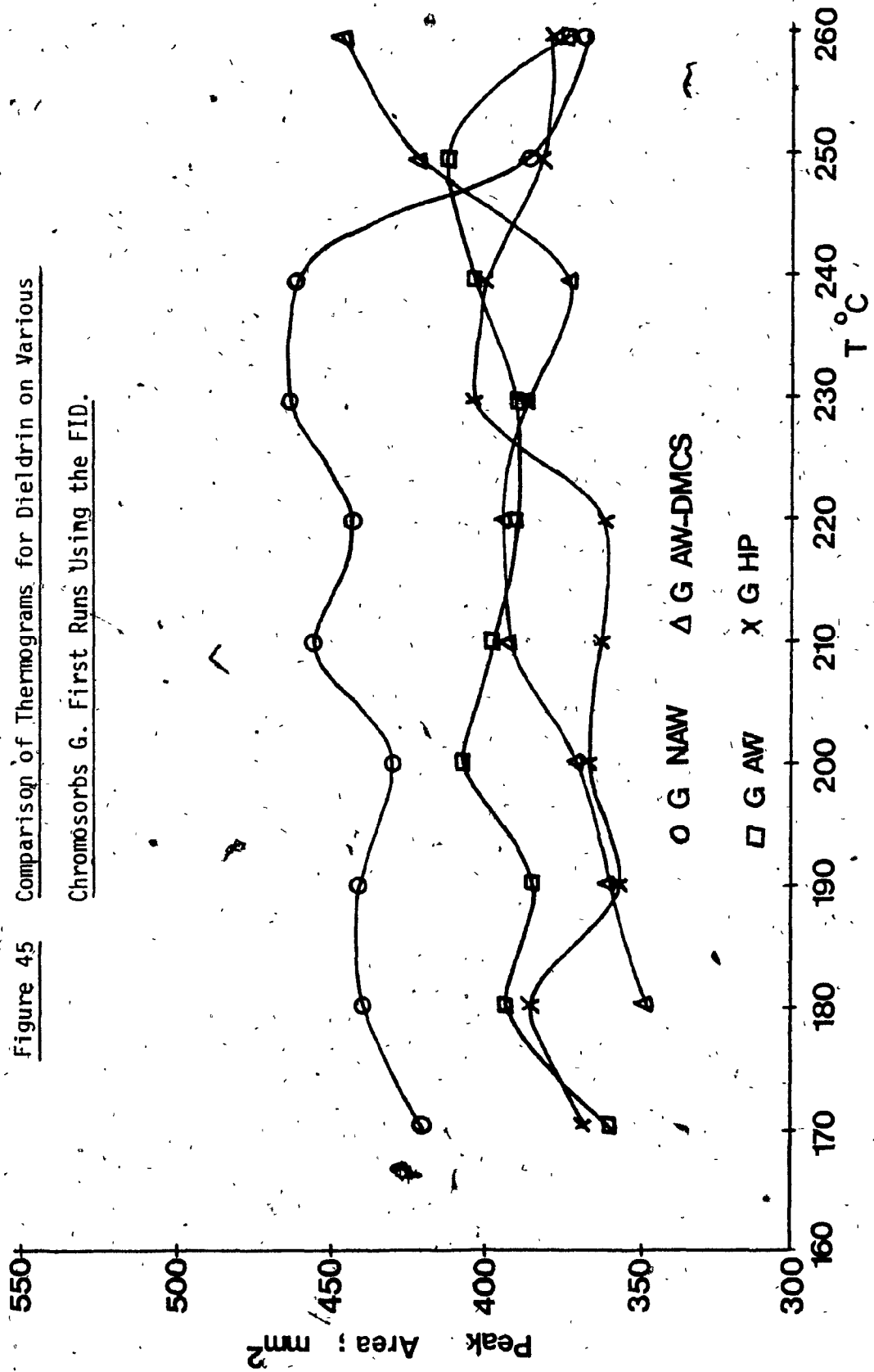
Both first and second runs showed no discernible differences in adsorption among G AW, G AW-DMCS and G HP at the various column temperatures used. The many maxima of the thermograms which changed with repeated runs, and with change in the column temperature, because of changing column conditions, were responsible for the frequently changing order of responses of the supports from temperature to temperature.

Both first and second runs indicated that Chromosorb G NAW was the least adsorptive of all the G supports. This support consistently showed the highest response for dieldrin at all temperatures except at 250°C, where a sharp drop in response occurred. It was also noted that the overall response for dieldrin on the Chromosorb G supports remained quite constant with increase in column temperature. In other words, the Chromosorb G supports did not decrease in adsorptivity with increasing column temperature, as had been observed with the W and Chromosorb 750 supports.

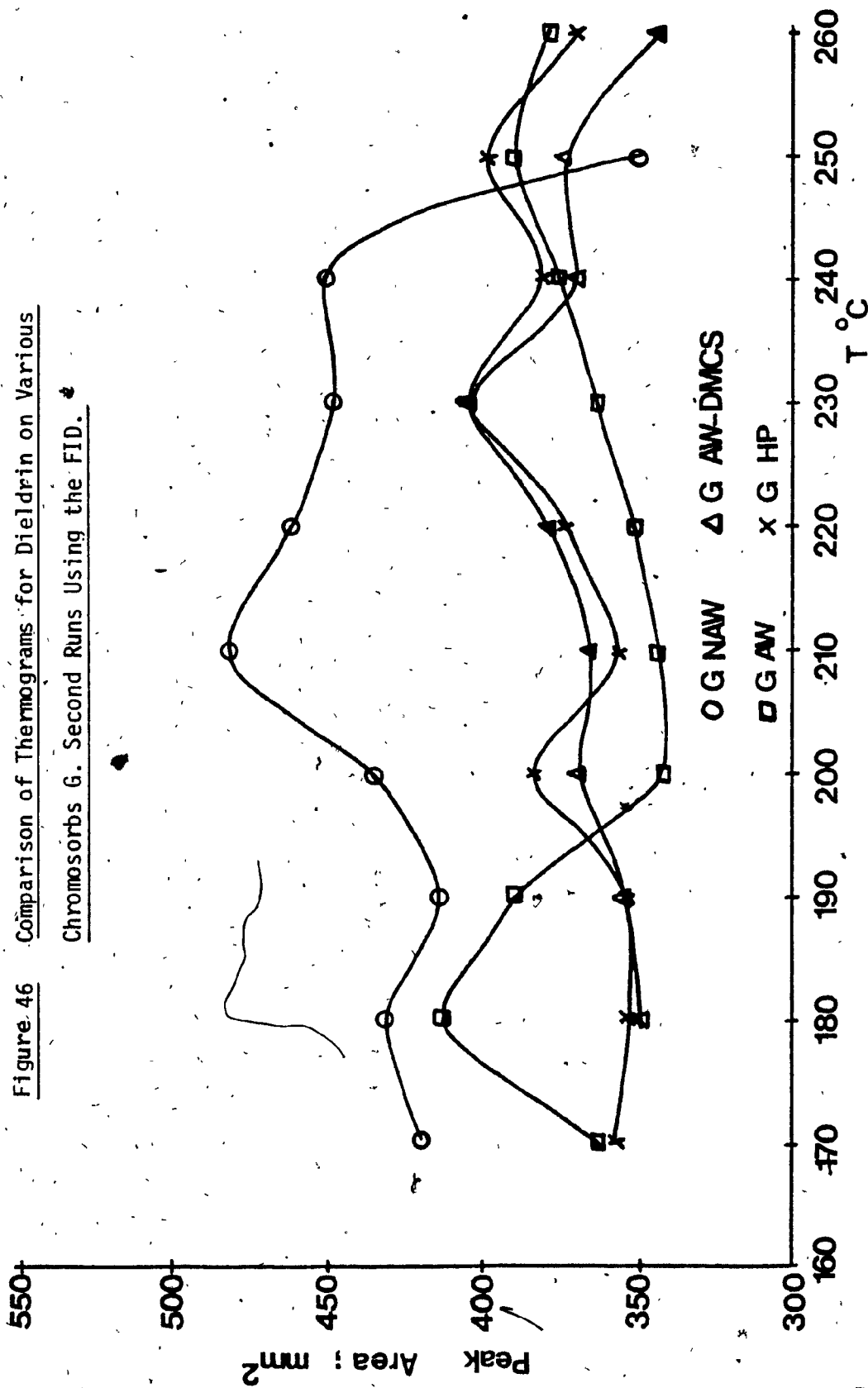
The poor performance of G AW-DMCS and G HP could be attributed either to ineffective silanization or to poor coating by the OV-17 liquid phase, because of non-wetting problems (Section 1.7.11, p. 36).

The G AW support was slightly better than the G AW-DMCS and G HP treated supports based on first run thermograms but not based on the second runs. Loss of liquid phase by bleeding during the first run left a more adsorptive surface for the AW support, compared to the silanized

Figure 45 Comparison of Thermograms for Dieldrin on Various Chromosorbs G. First Runs Using the FID.



**Figure 46** Comparison of Thermograms for Dieldrin on Various Chromosorbs G. Second Runs Using the FID. \*



supports.

The general conclusion was that, with respect to dieldrin, the order of adsorptivities was:

$$G \text{ NAW} < G \text{ AW} \leq G \text{ HP} \approx G \text{ AW-DMCS}$$

#### 3.4.4 Chromosorb G Supports - Methoxychlor as the Test Sample

-FID

Figures 47 and 48 contain the thermograms, first and second runs respectively, obtained using the various Chromosorb G supports. Both runs on the G supports showed G NAW to be the least adsorptive support. Only at a column temperature of 290°C did the response on G NAW show a dramatic drop. According to the second run, G AW, G AW-DMCS and G HP showed slight differences in adsorption only, with G HP being slightly less adsorptive.

From the first runs, no distinguishable differences were observed among G AW, G AW-DMCS and G HP. In fact, the two runs gave very similar results. The reasons for the best performance of Chromosorb G NAW, with methoxychlor, as well as for dieldrin, must be related to differences in efficiencies of applying liquid phase coatings to G NAW and G-"deactivated" supports, and possibly to other factors already discussed.

Summarizing, the order of adsorptivity with respect to methoxychlor was:

$$G \text{ NAW} < G \text{ HP} \leq G \text{ AW-DMCS} \approx G \text{ AW}$$

#### 3.4.5 Chromosorb P Supports - Dieldrin as the Test Sample -

FID

Figures 49 and 50 contain the thermograms, first and second runs respectively, for P NAW, P AW and P AW-DMCS.

The second runs gave no discernible differences among the adsorp-

Figure 47 Comparison of Thermograms for Methoxychlor on  
 Various Chromosorbs G. First  
 Runs Using the FID.

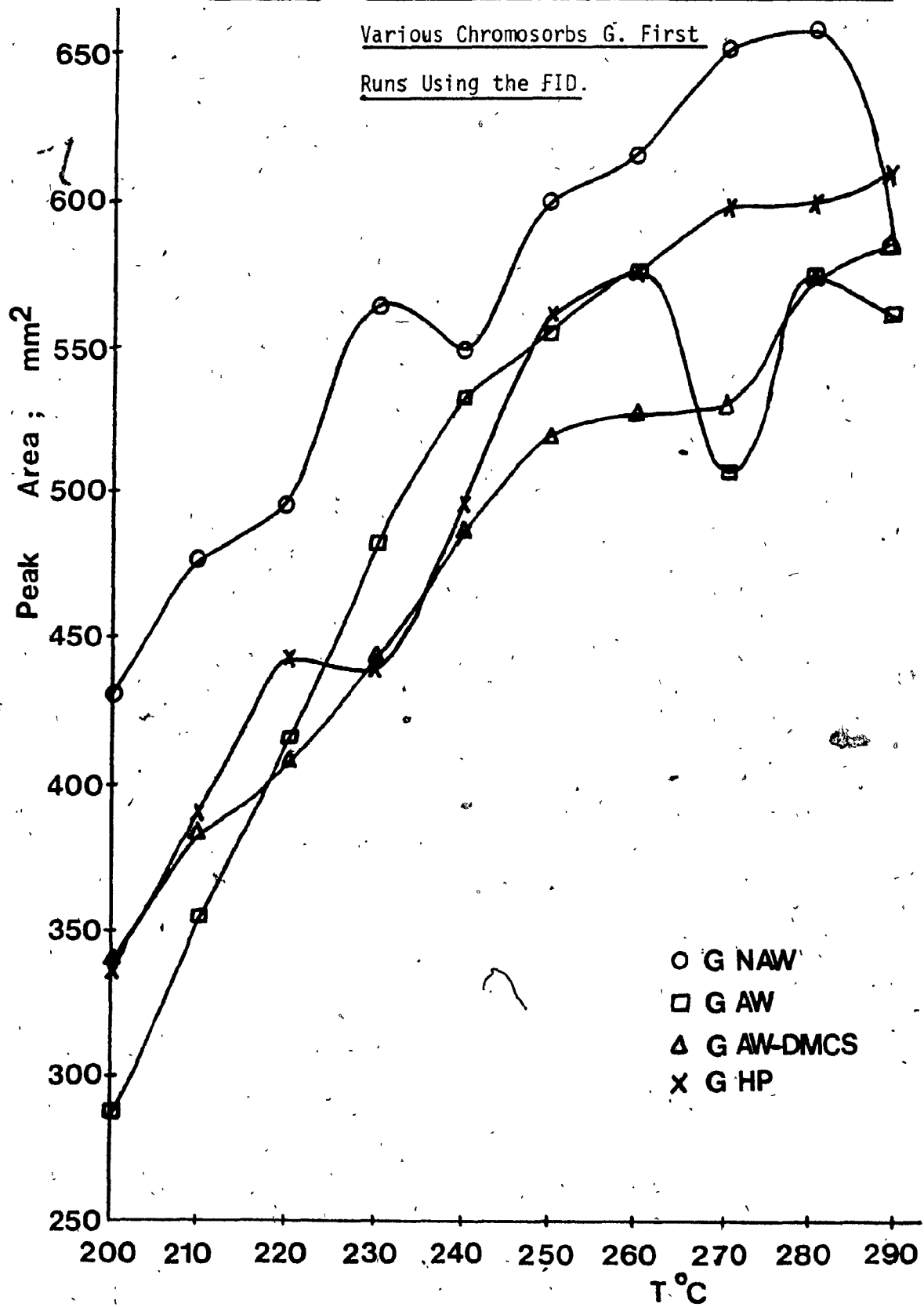


Figure 48 Comparison of Thermograms for Methoxychlor on Various Chromosorbs G. Second Runs Using the FID.

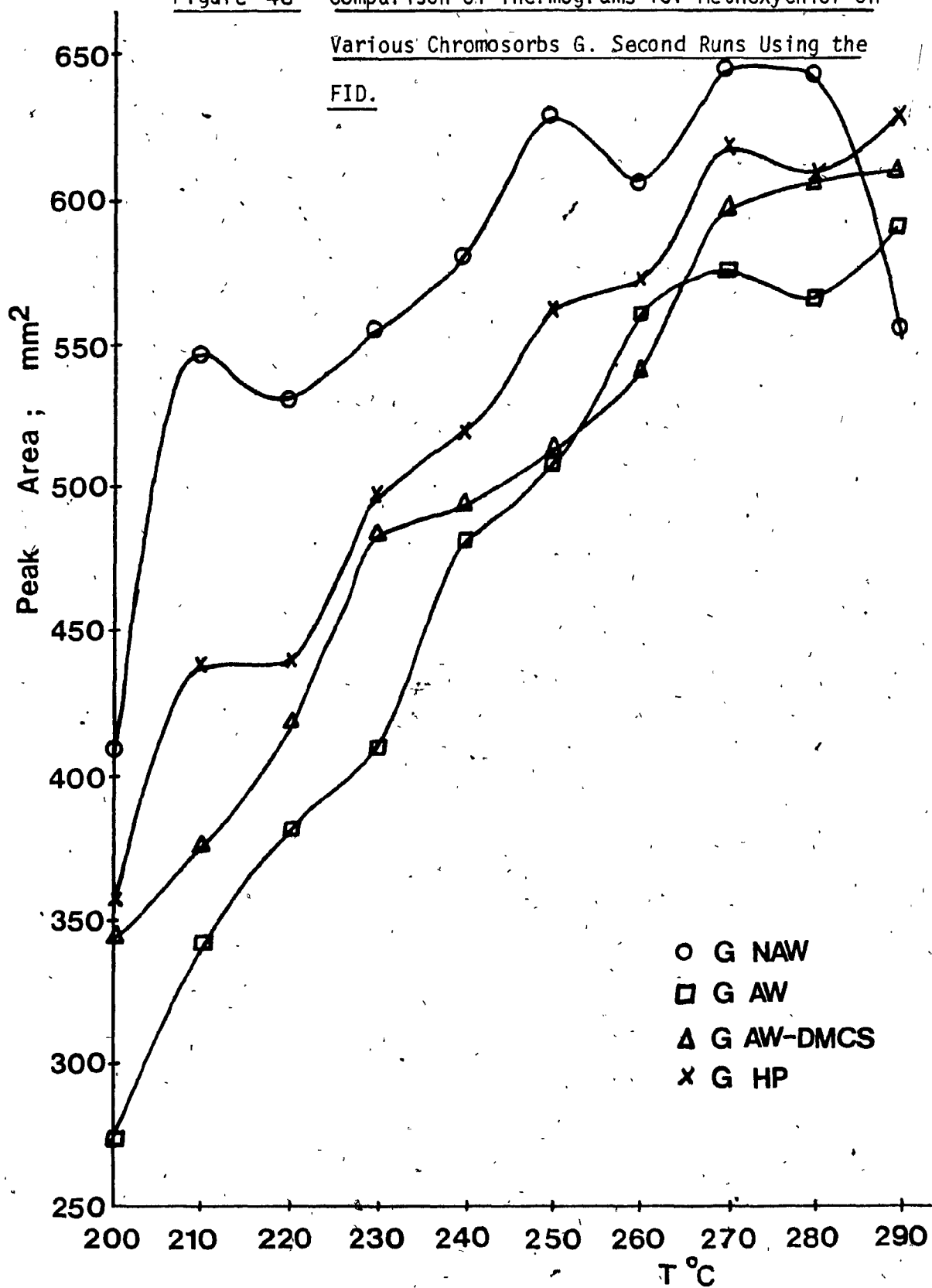




Figure 49 Comparison of Thermograms for Dieldrin on Various Chromosorbs P. First Runs Using the FID.

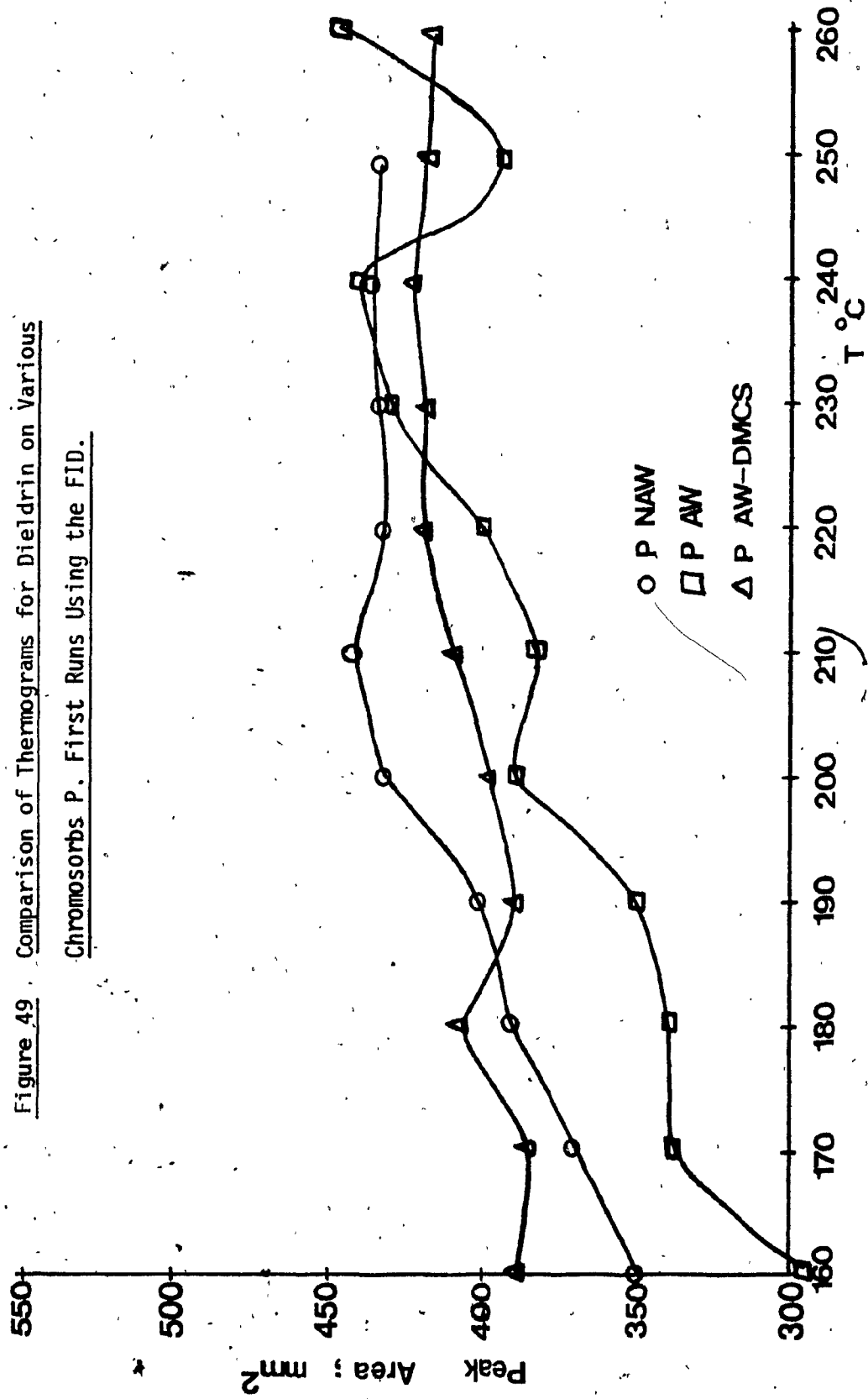
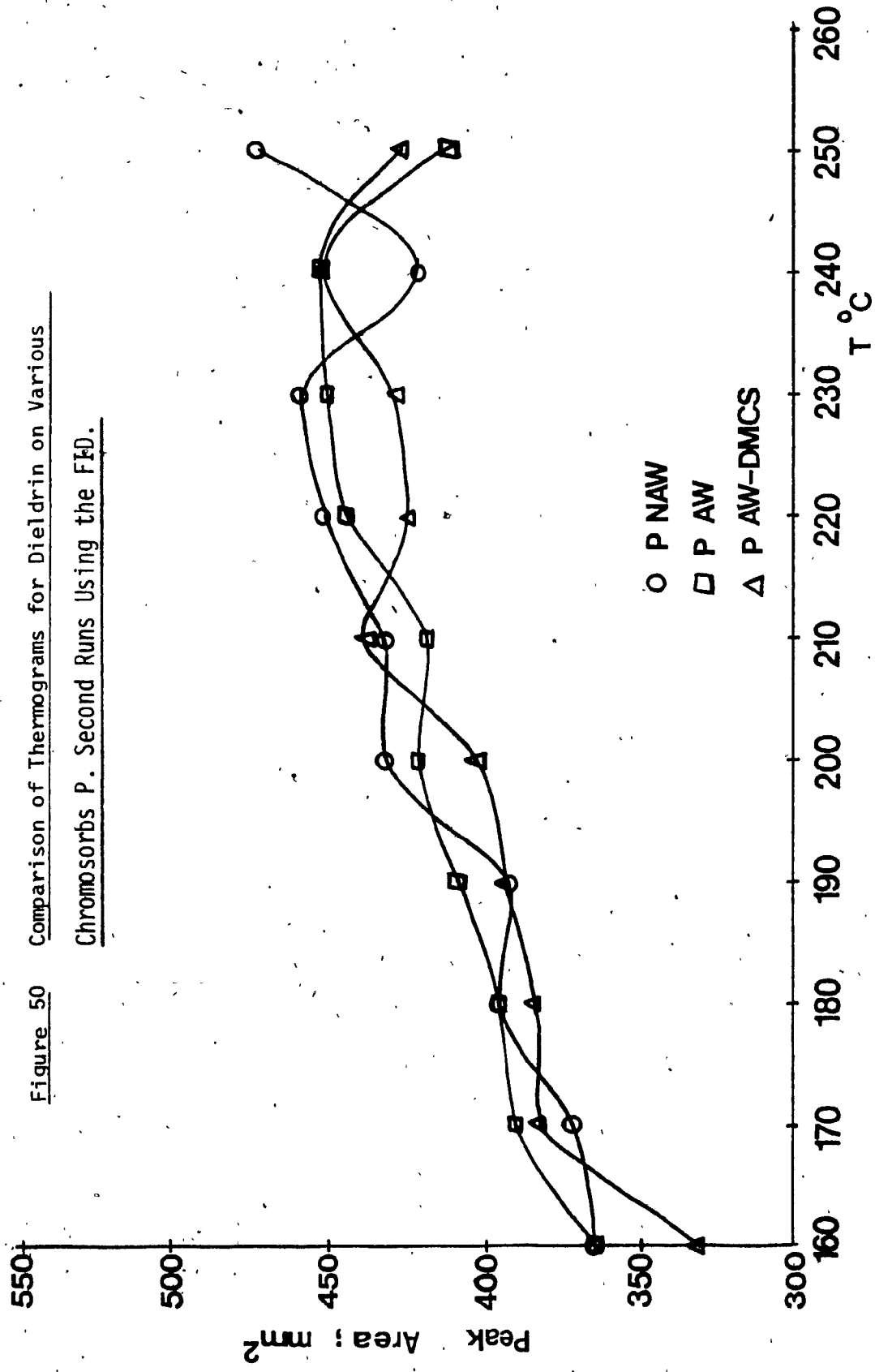


Figure 50 Comparison of Thermograms for Dieldrin on Various Chromosorbs P. Second Runs Using the FFD.



D

tive properties of the various P supports. However, from the first runs, it was observed that, overall, P AW was the most adsorptive support. The adsorptive order between P NAW and P AW-DMCS was temperature dependent. Below 180°C, P NAW was more adsorptive. At temperatures above 190°, P AW-DMCS was more adsorptive.

The discrepancy between the results of the first and second runs was due to the fact that priming effects during the first runs had changed the column conditions. The effects of sample priming were very clear with the P AW column, its performance definitely improving in going from the first to the second run. The fact that the second runs resulted in no discernible differences among the P supports suggested that neither acid washing nor a combined AW-DMCS treatment were of much use in reducing adsorption. It may be that the high surface area of P supports, and their very fine pore structure, makes them very difficult to deactivate.

#### 3.4.6 Chromosorb P Supports - Methoxychlor as the Test Sample -

##### FID

Methoxychlor could not be analyzed on any of the Chromosorb P supports due to decomposition of the compound at all temperatures studied. Column priming was not effective in reducing the degradation of methoxychlor. No change in the degradation pattern was observed after fifteen successive injections, each consisting of 20 µg of methoxychlor.

Figures 51 to 53 show examples of the chromatograms of methoxychlor obtained on Chromosorbs P AW-DMCS, P AW and P NAW.

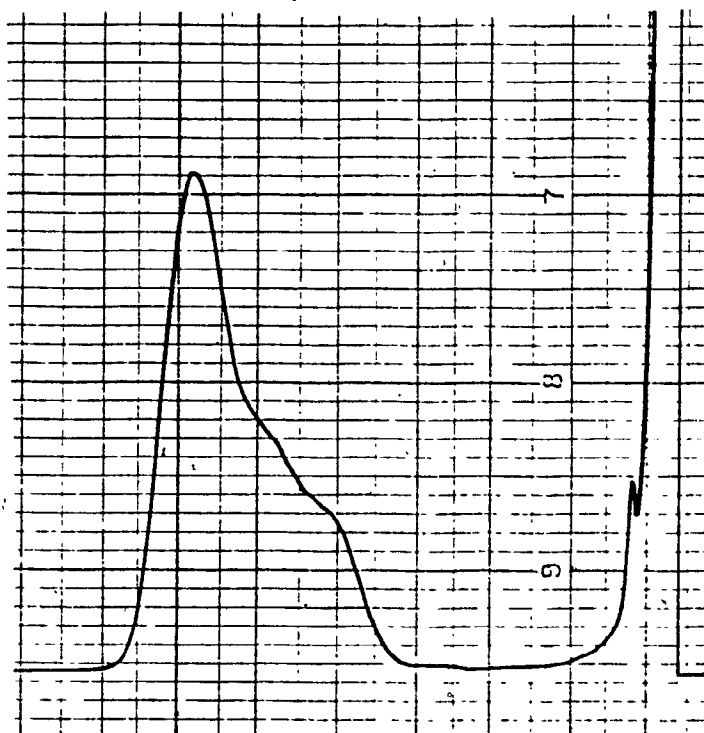


Figure 51    Analysis of Methoxychlor, 20  $\mu$ g,  
on 3.5% w/w OV-17 Coated on  
Chromosorb P AW-DMCS at 240 $^{\circ}$ C.

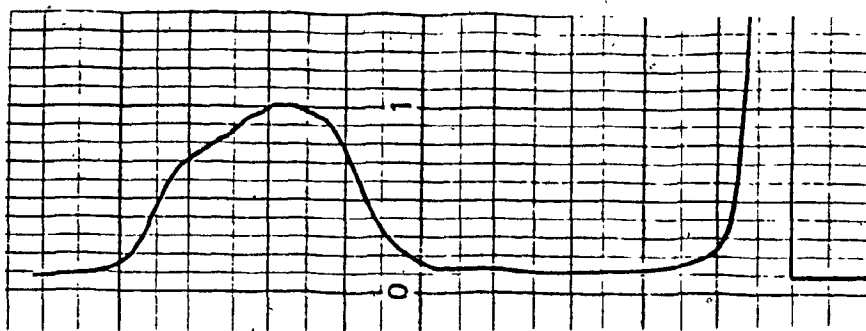


Figure 52 Analysis of Methoxychlor, 20  $\mu$ g, on 3.5% w/w  
OV-17 Coated on Chromosorb P AW at 230°C.

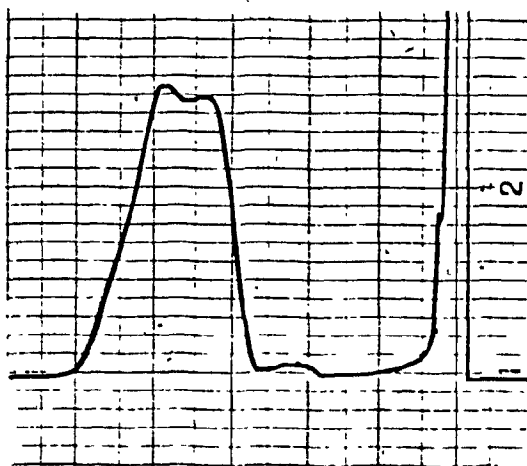


Figure 53 Analysis of Methoxychlor, 20  $\mu$ g, on 3.5% w/w  
OV-17 Coated on Chromosorb P NAW at 230°C.

3.5 COMPARISON OF THE ADSORPTIVE PROPERTIES OF CHROMOSORB W, P  
AND G SUPPORTS, USING VARIOUS CONCENTRATION LEVELS OF DIELDRIN  
AND METHOXYCHLOR - FID

The thermograms already discussed all gave strong evidence that the physical properties of the coated supports changed continuously from temperature to temperature, and run to run. Hence, the validity of any conclusions reached was very much subject to the immediate prior history of the columns. To eliminate any possible effects of liquid phase bleeding on relative adsorptivities observed, tests were carried out at a single temperature on each coated support and at two different concentration levels. They were 1 to 5  $\mu\text{g}$ , and 10 to 50  $\mu\text{g}$ . Linear regression analysis was used to show that the concentration plots obtained were linear, and to calculate both slopes and intercepts of the plots.

It was expected that very adsorptive supports might result in calibration curves having smaller slopes than less adsorptive supports. Concentration runs, in duplicate, were performed on columns A to L listed in Table VI, p. 83.

In the lower concentration range, each run consisted of making multiple (3 to 5) 2  $\mu\text{l}$  injections of each of the following pesticide solutions:

0.5, 1.0, 1.5, 2.0, and 2.5  $\mu\text{g}/\mu\text{l}$ ,  
dieldrin or methoxychlor, as the case may be.

In the higher concentration range, each run consisted of making multiple injections (3 - 5) of each of the following volumes of a 10  $\mu\text{g}/\mu\text{l}$  pesticide solution

1.0, 2.0, 3.0, 4.0, and 5.0  $\mu\text{l}$ .

All runs were started by injecting the smallest amount first. The column temperature was held constant during the runs at 230°C for dieldrin, and 240°C for methoxychlor.

Results obtained are summarized in Tables XVII to XXI. In each Table, comparisons are shown of peak area response factors for 1, 4, 10 and 40 µg samples, and of slopes of the calibration curves. Figure 54 illustrates a typical sample calibration curve, and is included to show the linearity of the plot. In all cases, the correlation coefficient was greater than 0.998.

### 3.5.1 Comparison of Chromosorb W and 750 Supports Using Various Concentration Levels of Dieldrin

The results of Table XVII, both first and second runs, indicated that at the 1 µg level, there were very little differences in the adsorptive properties of the W supports. Chromosorb W NAW was slightly more adsorptive than the other W and 750 supports during both runs, but this difference diminished during the second run.

At the 4 µg level, the following order of adsorptivity was observed among the supports:

First Run: W HP  $\leq$  W AW  $\leq$  W AW-DMCS < 750 < W NAW

Second Run: W HP  $\leq$  W AW-DMCS  $\leq$  W AW  $\leq$  750 < W NAW

The first and second runs were generally in good agreement. Chromosorbs W NAW and 750 were the most adsorptive, W NAW being more adsorptive than 750. Chromosorb W HP was definitely the least adsorptive support at this concentration level. Although the order of adsorptivity between W AW and W AW-DMCS varied from first to second runs, these supports were second only to Chromosorb W HP.

At the 10 µg level, the following order of adsorption was obtained:

Figure 54 Sample Calibration Curve for Methoxychlor on Chromosorb G AW Using the FID.

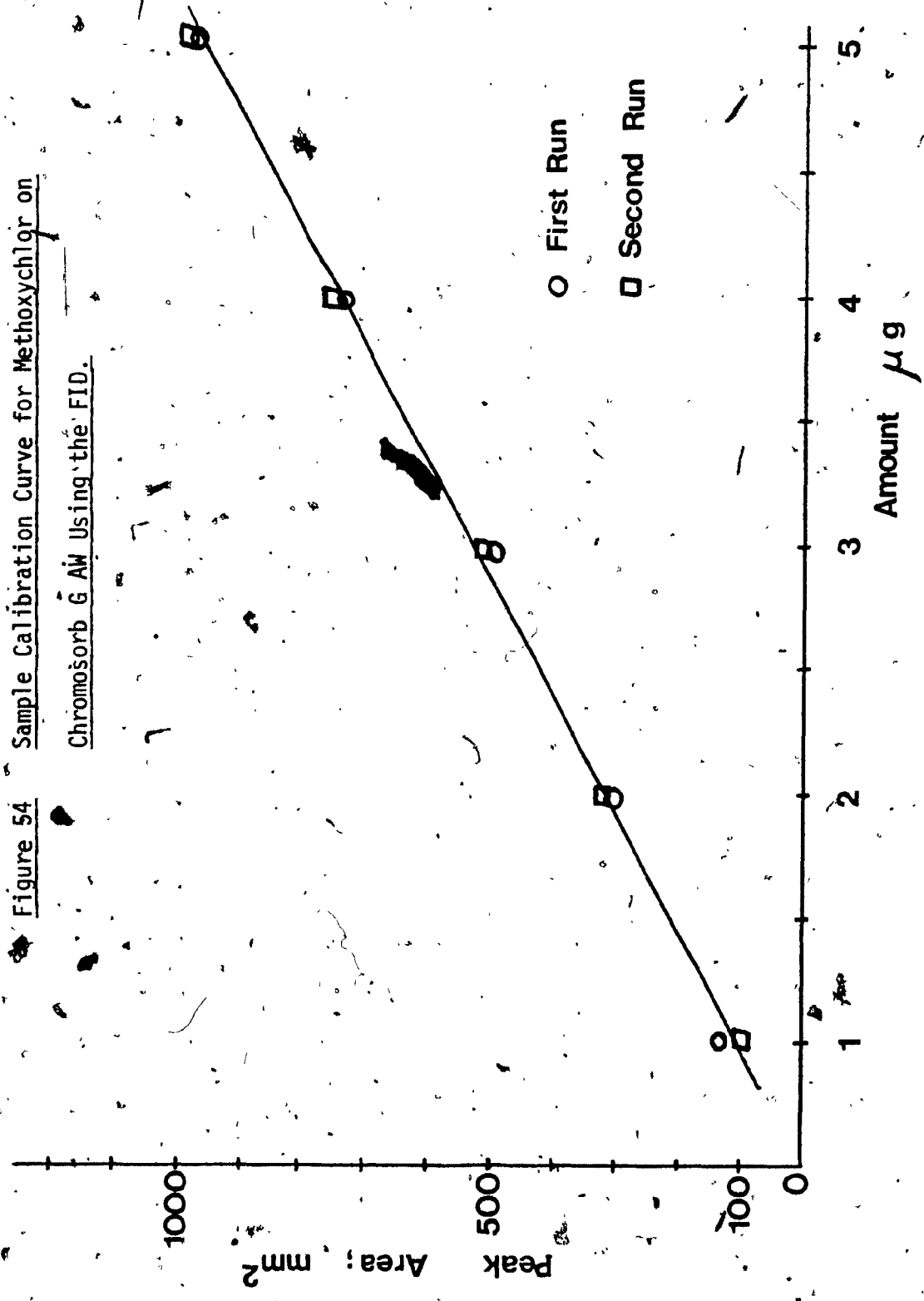




TABLE XVII  
 COMPARISON OF THE ADSORPTIVE PROPERTIES OF CHROMOSORB W AND 750 SUPPORTS  
 USING VARIOUS CONCENTRATION LEVELS OF DIELDRIN

SUPPORT	PEAK AREA RESPONSES*, mm <sup>2</sup>					HIGH CONC. SLOPE mm <sup>2</sup> /deg.	LOW CONC. SLOPE mm <sup>2</sup> /deg.
	1 µg	4 µg	10 µg	40 µg			
W NAW	153	612	131	849		23.8	147
W AW	175	741	166	870		24.2	181
W AW-DMCS	175	729	179	1063		29.7	188
W HP	185	776	223	1057		28.4	195
750	183	667	168	943		26.7	167
			SECOND RUN				
W NAW	162	598	120	799		23.0	164
W AW	175	731	175	884		23.5	187
W AW-DMCS	172	751	167	1061		30.0	186
W HP	187	777	204	1064		28.3	194
750	179	713	160	896		24.8	189

\*The precision of the peak area measurements was ±5%.

First Run:  $W \text{ HP} < W \text{ AW-DMCS} \lesssim 750 \approx W \text{ AW} < W \text{ NAW}$

Second Run:  $W \text{ HP} < W \text{ AW} \lesssim W \text{ AW-DMCS} \approx 750 < W \text{ NAW}$

Both first and second runs were in excellent agreement. Chromosorb W NAW was the most adsorptive support and Chromosorb W HP was the least adsorptive at this concentration level. There were no discernible differences among Chromosorbs 750, W AW and W AW-DMCS.

At the 40  $\mu\text{g}$  level, the adsorptive order among the supports was:

First Run:  $W \text{ AW-DMCS} \approx W \text{ HP} < 750 < W \text{ AW} \lesssim W \text{ NAW}$

Second Run:  $W \text{ HP} \approx W \text{ AW-DMCS} < 750 \approx W \text{ AW} < W \text{ NAW}$

Again, both first and second runs were in good agreement. Chromosorb W NAW was the most adsorptive support, and Chromosorbs W AW-DMCS and W HP were the least adsorptive. Although there was a difference between Chromosorbs W AW and 750 in the first runs, this difference was negligible in the second runs.

In conclusion, at all the concentration levels, Chromosorb W NAW was found to be the most adsorptive W support and Chromosorb W HP the least adsorptive. The adsorptive order among Chromosorbs W AW, W AW-DMCS and 750 varied with the concentration of sample used. However, the relatively mediocre performance of Chromosorb 750, a supposed high performance support, was clearly evident.

From the results of Table XVII the slopes of the calibration curves, based on linear regression analysis followed the order below:

(i) 10-50  $\mu\text{g}$  Range

First and Second Runs:  $W \text{ AW-DMCS} > W \text{ HP} > 750 > W \text{ AW} \gtrsim W \text{ NAW}$

(ii) 1-5  $\mu\text{g}$  Range

a) First Run:  $W \text{ HP} \gtrsim W \text{ AW-DMCS} \gtrsim W \text{ AW} > 750 > W \text{ NAW}$

b) Second Run:  $W \text{ HP} \gtrsim 750 \gtrsim W \text{ AW} \gtrsim W \text{ AW-DMCS} > W \text{ NAW}$

It was observed that there was good correlation between the adsorptive order of the supports obtained at various concentration levels of dieldrin and the slopes of the corresponding calibration curves.

Comparing the results here with those obtained from the thermograms, it was observed that there was some agreement, i.e.

Concentration:  $W\ HP < W\ AW-DMCS \lesssim 750 \approx W\ AW < W\ NAW$

Thermograms:  $750 \approx W\ HP < W\ NAW \approx W\ AW-DMCS \approx W\ AW$

Overall, W HP was clearly the least adsorptive support towards dieldrin, and 750 and W AW-DMCS were next best. W NAW was the poorest. The small differences in peak area responses obtained for W AW-DMCS, 750 and W AW led to the conclusion that any differences among these supports were small. The improved behaviour of W NAW observed in the second run of the temperature study was not seen in the concentration work.

### 3.5.2 Comparison of Chromosorb W and 750 Supports Using Various Concentration Levels of Methoxychlor

From the results of Table XVIII, both first and second runs, it was seen that at the 1  $\mu$ g level, the adsorptive order of the supports towards methoxychlor was as follows:

First Run:  $750 \lesssim W\ AW-DMCS < W\ HP$

Second Run:  $750 \lesssim W\ AW-DMCS \lesssim W\ AW \lesssim W\ NAW \lesssim W\ HP$

Both runs indicated the high adsorptive behaviour of Chromosorb W HP towards methoxychlor.

At the 4  $\mu$ g level, the following adsorptive order was found among the supports:

First Run:  $750 \lesssim W\ AW-DMCS \lesssim W\ HP$

Second Run:  $W\ AW < W\ AW-DMCS \lesssim W\ HP < W\ NAW \lesssim 750$

TABLE XVIII  
COMPARISON OF THE ADSORPTIVE PROPERTIES OF CHROMOSORB W AND 750 SUPPORTS USING  
VARIOUS CONCENTRATION LEVELS OF METHOXYCHLOR

SUPPORT	PEAK AREA RESPONSES* $\text{mm}^2$				HIGH CONC. SLOPE $\text{mm}^2/\text{deg.}$	LOW CONC. SLOPE $\text{mm}^2/\text{deg.}$
	1 $\mu\text{g}$	4 $\mu\text{g}$	10 $\mu\text{g}$	40 $\mu\text{g}$		
			FIRST RUN			
W NAW			171	1204	35.8	-
W AW			165	1327	40.9	-
W AW-DMCS	137	765	219	1372	36.7	214
W HP	82	717	151	1174	36.5	229
	145	784	185	1043	29.1	214
			SECOND RUN			
W NAW	103	686	207	1272	34.9	199
W AW	109	826	188	1299	38.3	235
W AW-DMCS	120	798	193	1395	38.7	235
W HP	90	780	208	1249	36.1	232
	129	664	192	1136	30.1	198

\* The precision of the peak area measurements was  $\pm 5\%$ .

At the 10  $\mu\text{g}$  level, the adsorptive order of the supports was:

First Run:  $W \text{ AW-DMCS} < 750 \lesssim W \text{ NAW} \approx W \text{ AW} \lesssim W \text{ HP}$

Second Run:  $W \text{ HP} \approx W \text{ NAW} \lesssim W \text{ AW-DMCS} \approx 750 \approx W \text{ AW}$

At the 40  $\mu\text{g}$  level, the adsorptive order of the supports was:

First Run:  $W \text{ AW-DMCS} < W \text{ AW} < W \text{ NAW} < W \text{ HP} < 750$

Second Run:  $W \text{ AW-DMCS} < W \text{ AW} < W \text{ NAW} < W \text{ HP} < 750$

It was clearly evident that the adsorptive properties of the supports largely depended on the sample size. Furthermore, the adsorptive order for the same sample size changed from run to run, and the change was so drastic for the 10  $\mu\text{g}$  sample that these results had to be ignored. Only at the 40  $\mu\text{g}$  level was there agreement between first and second runs.

While the order of adsorptivity towards methoxychlor was rather erratic, the general trend of adsorptivity was as follows:

$W \text{ AW-DMCS} < W \text{ AW} < W \text{ NAW} < W \text{ HP} < 750$

In comparison, thermogram data gave the following results:

$W \text{ AW-DMCS} \lesssim W \text{ HP} < W \text{ NAW} \lesssim 750 \approx W \text{ AW}$

Therefore, towards methoxychlor,  $W \text{ AW-DMCS}$  was the least adsorptive support, and 750 the poorest.  $W \text{ NAW}$  was moderately adsorptive. The behaviour of  $W \text{ HP}$  and  $W \text{ AW}$  was erratic from test to test, and appeared to be especially dependent on the history of the columns.

According to the results of Table XVIII, the slopes of the calibration curves, based on linear regression, followed the order:

(i) 10-50  $\mu\text{g}$  Range

a) First Run:  $W \text{ AW} > W \text{ AW-DMCS} \approx W \text{ HP} \gtrsim W \text{ NAW} > 750$

b) Second Run:  $W \text{ AW-DMCS} \gtrsim W \text{ AW} > W \text{ HP} > W \text{ NAW} > 750$

(ii) 1-5  $\mu\text{g}$  Range

a) First Run:  $W \text{ HP} > W \text{ AW-DMCS} \approx 750$

b) Second Run:  $W_{AW-DMCS} \approx W_{AW} \approx W_{HP} > W_{NAW} \approx 750$

There was some correlation between the slope data, and the results obtained from the comparison of peak area responses at various sample sizes.

### 3.5.3 Comparison of Chromosorb G Supports Using Various Concentration Levels of Dieldrin

According to the results of Table XIX, the adsorptive order of the Chromosorb G supports at the 1  $\mu$ g level was as follows:

First Run:  $G_{NAW} \leq G_{AW-DMCS} \leq G_{AW} < G_{HP}$

Second Run:  $G_{NAW} \leq G_{AW-DMCS} \leq G_{HP} \leq G_{AW}$

Although the differences in peak area responses among the supports were small, there was a definite increase in response for the above supports in going from right to left.  $G_{NAW}$  was definitely the least adsorptive G support at this concentration level.

At the 4  $\mu$ g level, the adsorptive order of the supports was found to be the following:

First Run:  $G_{NAW} < G_{AW-DMCS} < G_{AW} \approx G_{HP}$

Second Run:  $G_{NAW} < G_{AW-DMCS} < G_{AW} \leq G_{HP}$

Chromosorb G  $NAW$  was clearly the least adsorptive support at this concentration level. Chromosorbs G  $HP$  and G  $AW$  had very similar adsorptive properties and were the most adsorptive supports here. Differences between supports were greater than at the lower concentration levels.

At the 10  $\mu$ g level, the adsorptive order of the supports was:

First Run:  $G_{AW} \leq G_{AW-DMCS} \approx G_{NAW} < G_{HP}$

Second Run:  $G_{AW-DMCS} < G_{AW} \leq G_{NAW} \approx G_{HP}$

TABLE XIX  
 COMPARISON OF THE ADSORPTIVE PROPERTIES OF CHROMOSORB & SUPPORTS USING VARIOUS  
 CONCENTRATION LEVELS OF DIELDRIN

SUPPORT	PEAK AREA RESPONSES*, mm <sup>2</sup>				HIGH CONC. SLOPE mm <sup>2</sup> /deg.	LOW CONC. SLOPE mm <sup>2</sup> /deg.
	1 µg	4 µg	10 µg	40 µg		
			FIRST RUN			
G NAW	168	702	166	885	26.5	170
G AW	148	579	177	850	21.5	130
G AW-DMCS	156	627	166	879	23.7	162
G HP	122	576	128	869	24.5	150
			SECOND RUN			
G NAW	185	714	153	974	27.8	166
G AW	157	595	163	866	23.1	151
G AW-DMCS	177	668	193	1005	26.6	170
G HP	166	585	151	850	22.8	133

\*The precision of the peak area measurements was ±5%.

Chromosorb G HP was the most adsorptive support at this concentration level and Chromosorb G AW-DMCS, the least. However, there was no agreement between the first and second runs as to the relative positions of G NAW and G AW.

At the 40  $\mu\text{g}$  level, the following adsorptive order among the G supports was observed for the second run:

$$G \text{ AW-DMCS} \lesssim G \text{ NAW} < G \text{ AW} \approx G \text{ HP}$$

The first run results showed almost no differences.

In conclusion, the adsorptive order of the supports changed with the sample size and sometimes from run to run. In general, Chromosorbs G HP and G AW were more adsorptive than Chromosorbs G AW-DMCS and G NAW. G NAW appeared to be the least adsorptive G support at the lower concentrations, while G AW-DMCS was better for higher concentrations. The good behaviour of G NAW confirms the findings of the thermogram studies using dieldrin, i.e.:

$$G \text{ NAW} < G \text{ AW} \lesssim G \text{ HP} \approx G \text{ AW-DMCS}$$

According to Table XIX, the slopes of the calibration curves, based on linear regression analysis, followed the order:

(i) 10-50  $\mu\text{g}$  Range

a) First Run:  $G \text{ NAW} > G \text{ HP} \gtrsim G \text{ AW-DMCS} > G \text{ AW}$

b) Second Run:  $G \text{ NAW} > G \text{ AW-DMCS} > G \text{ AW} \approx G \text{ HP}$

(ii) 1-5  $\mu\text{g}$  Range

a) First Run:  $G \text{ NAW} \gtrsim G \text{ AW-DMCS} \gtrsim G \text{ HP} > G \text{ AW}$

b) Second Run:  $G \text{ AW-DMCS} \gtrsim G \text{ NAW} > G \text{ AW} > G \text{ HP}$

In general, there was good agreement between size of slope and adsorptivity of the support, a large value of slope suggesting low adsorptivity.



Summarizing, amongst the G supports, G NAW was determined to be the least adsorptive support towards dieldrin from all methods of evaluation. Furthermore, there was no discernible difference between Chromosorbs G AW and G HP. The only exception was Chromosorb G AW-DMCS, which was found to be less adsorptive than G AW and G HP in the concentration runs, while the thermogram studies showed it to be rather adsorptive.

#### 3.5.4 Comparison of Chromosorb G Supports Using Various Concentration Levels of Methoxychlor

The results of Table XX indicated that at the 1 and 4  $\mu\text{g}$  levels there were small differences only, among the adsorptive properties of the G supports. The differences in the peak area responses were often greater between runs on the same support than among the various G supports. For example, for 1  $\mu\text{g}$  methoxychlor,

First Run:  $G\ AW \lesssim G\ NAW < G\ HP \lesssim G\ AW-DMCS$

Second Run:  $G\ NAW \lesssim G\ HP \lesssim G\ AW-DMCS \lesssim G\ AW$

and for 4  $\mu\text{g}$  methoxychlor,

First Run:  $G\ HP \lesssim G\ NAW \approx G\ AW-DMCS \lesssim G\ AW$

Second Run:  $G\ AW \lesssim G\ NAW \approx G\ AW-DMCS \approx G\ HP$

The only thing consistent about this data was that G NAW, in every case, looked like a good choice of support. Other supports showed very erratic adsorptivity behaviour.

At the 10  $\mu\text{g}$  level, the order of adsorptivity of the G supports was:

First Run:  $G\ NAW < G\ AW \lesssim G\ AW-DMCS \lesssim G\ HP$

Second Run:  $G\ NAW < G\ HP \approx G\ AW \lesssim G\ AW-DMCS$

TABLE XX  
 COMPARISON OF THE ADSORPTIVE PROPERTIES OF CHROMOSORB G SUPPORTS USING VARIOUS  
 CONCENTRATION LEVELS OF METHOXYCHLOR

SUPPORT	PEAK AREA RESPONSES*, mm <sup>2</sup>			HIGH CONC. SLOPE mm <sup>2</sup> /deg.	LOW CONC. SLOPE mm <sup>2</sup> /deg.
	1 µg	4 µg	10 µg		
	FIRST RUN				
G NAW	114	757	221	35.9	213
G AW	129	729	173	35.4	212
G AW-DMCS	84	748	155	32.7	222
G HP	97	780	132	34.0	225
			SECOND RUN		
G NAW	136	735	232	34.3	217
G AW	96	765	174	35.0	222
G AW-DMCS	107	732	160	34.8	207
G HP	121	730	179	35.8	201

\*The precision of the peak area measurements was ±5%.

Clearly Chromosorb G NAW was the least adsorptive support here. There were no discernible differences among Chromosorbs G HP, G AW-DMCS and G AW.

At the 40  $\mu\text{g}$  level, the following order in adsorptivity was obtained:

First Run:  $G \text{ NAW} \lesssim G \text{ AW} < G \text{ HP} \approx G \text{ AW-DMCS}$

Second Run:  $G \text{ NAW} < G \text{ AW-DMCS} \approx G \text{ HP} \approx G \text{ AW}$

Again, Chromosorb G NAW was the least adsorptive support. The adsorptivities of the other G supports changed from run to run and differed but little from one to the other.

Overall, it was clear that G NAW was the least adsorptive support towards methoxychlor, and that the differences between the other G's were small. This agreed quite well with thermogram results.

A comparison of the slopes, based on linear regression analyses, of the calibration curves, Table XX, showed the following order:

(i) 10-50  $\mu\text{g}$  Range

First Run:  $G \text{ NAW} \approx G \text{ AW} > G \text{ HP} > G \text{ AW-DMCS}$

Second Run:  $G \text{ HP} \gtrsim G \text{ AW} \gtrsim G \text{ AW-DMCS} \gtrsim G \text{ NAW}$

(ii) 1-5  $\mu\text{g}$  Range

First Run:  $G \text{ HP} \approx G \text{ AW-DMCS} \gtrsim G \text{ NAW} \approx G \text{ AW}$

Second Run:  $G \text{ AW} \approx G \text{ NAW} \gtrsim G \text{ AW-DMCS} \approx G \text{ HP}$

At first glance, it appeared that the slope data did not support the argument that a large slope is indicative of low adsorptivity. In fact, the differences among slopes were small enough that no definite conclusions could be reached. But slope data here did not confirm G NAW as being the least adsorptive support.

### 3.5.5 Comparison of Chromosorb P Supports Using Various Concentration Levels of Dieldrin

From the results of Table XXI, it was concluded that at the four different concentration levels studied, differences in the adsorptive properties of the various Chromosorb P supports were very small, which was precisely what was previously found to be the case, based on the thermogram study. The only slight trend was that, in some cases, P NAW seemed to show the least adsorptivity by a very slight margin.

Similarly, slope data confirmed this virtual equivalence of adsorptivities of the P supports.

### 3.6. THERMOGRAMS OBTAINED USING LOW CONCENTRATIONS OF DIELDRIN AND METHOXYCHLOR AS TEST SAMPLES AND THE ELECTRON CAPTURE DETECTOR, ECD

The adsorptive properties of Chromosorbs W NAW, W HP, G NAW, G HP and P AW-DMCS were studied using the electron capture detector, and low concentrations of dieldrin and methoxychlor as test samples. The columns (A, D, E, H and K), were previously employed in the tests with dieldrin and methoxychlor using the FID and hence had been subjected to considerable use. The column temperature range used with dieldrin was from 160<sup>o</sup> to 250<sup>o</sup>C for the W supports, and from 170<sup>o</sup> to 260<sup>o</sup>C for the G and P supports. With methoxychlor, the column temperature range used was from 200<sup>o</sup> to 280<sup>o</sup>C for all the supports.

Duplicate temperature runs were performed with each pesticide on all the supports tested. Each temperature run consisted of making multiple injections (3 to 5) of the pesticide at ten degree intervals starting at the lowest column temperature first. At each column temperature, the peak area of each peak eluted was calculated, results were accepted

TABLE XXI COMPARISON OF THE ADSORPTIVE PROPERTIES OF CHROMOSORB P SUPPORTS USING VARIOUS CONCENTRATION LEVELS OF DIELDRIN

SUPPORT	PEAK AREA RESPONSES* $\text{mm}^2$				HIGH CONC. SLOPE $\text{mm}^2/\text{deg.}$	LOW CONC. SLOPE $\text{mm}^2/\text{deg.}$
	1 $\mu\text{g}$	4 $\mu\text{g}$	10 $\mu\text{g}$	40 $\mu\text{g}$		
P NAW	172	722	178	1079	30.4	179
P AW	148	705	202	1050	28.4	184
P AW-DMCS	146	702	193	1065	28.7	180
			FIRST RUN			
			SECOND RUN			
P NAW	171	730	208	1063	28.4	186
P AW	163	684	196	1064	28.3	179
P AW-DMCS	149	707	207	1061	29.0	170

\*The precision of the peak area measurements was  $\pm 5\%$ .

or rejected on the basis of the Q test and the average peak area response determined.

Plots of average peak area response versus column temperature were made for both first and second runs for each pesticide and each support studied. Results are shown in Figures 55 to 58.

Figures 55 and 56 indicated that, on all supports, the response for dieldrin decreased as the column temperature increased. The decrease in response for all the supports tested was quite drastic, ranging from a factor of about 3 to 10. It was also noted that there was very little difference between the first and second run results on the same support. Another characteristic of the thermograms obtained here was the overall smoothness of the curves. There were very few noticeable maxima and minima.

Figures 57 and 58 also showed that the thermograms obtained for methoxychlor were not much different from those obtained for dieldrin. The same pattern, a decreasing response with an increasing column temperature, was obtained with no evidence of maxima/minima effects. The curves were generally quite smooth. Differences between the first and second runs were insignificant. Considerable degradation of methoxychlor was observed above 240°C on W NAW. Decomposition was also evident on W HP, G NAW and G HP, but not to the same extent as on W NAW. Figures 59 to 62 are examples of the type of chromatograms that were obtained on Chromosorb HP, W NAW, G HP and G NAW respectively, illustrating the amount of decomposition in each case. Decomposition of methoxychlor on Chromosorb supports was discussed in Section 3.1, p. 94.

The ECD thermograms differed from the FID thermograms already described in that, with the latter, either more or less constant responses,

Figure 55 Comparison of Thermograms for Dielsin on Various

Chromosorb Supports. First Runs Using the ECD.

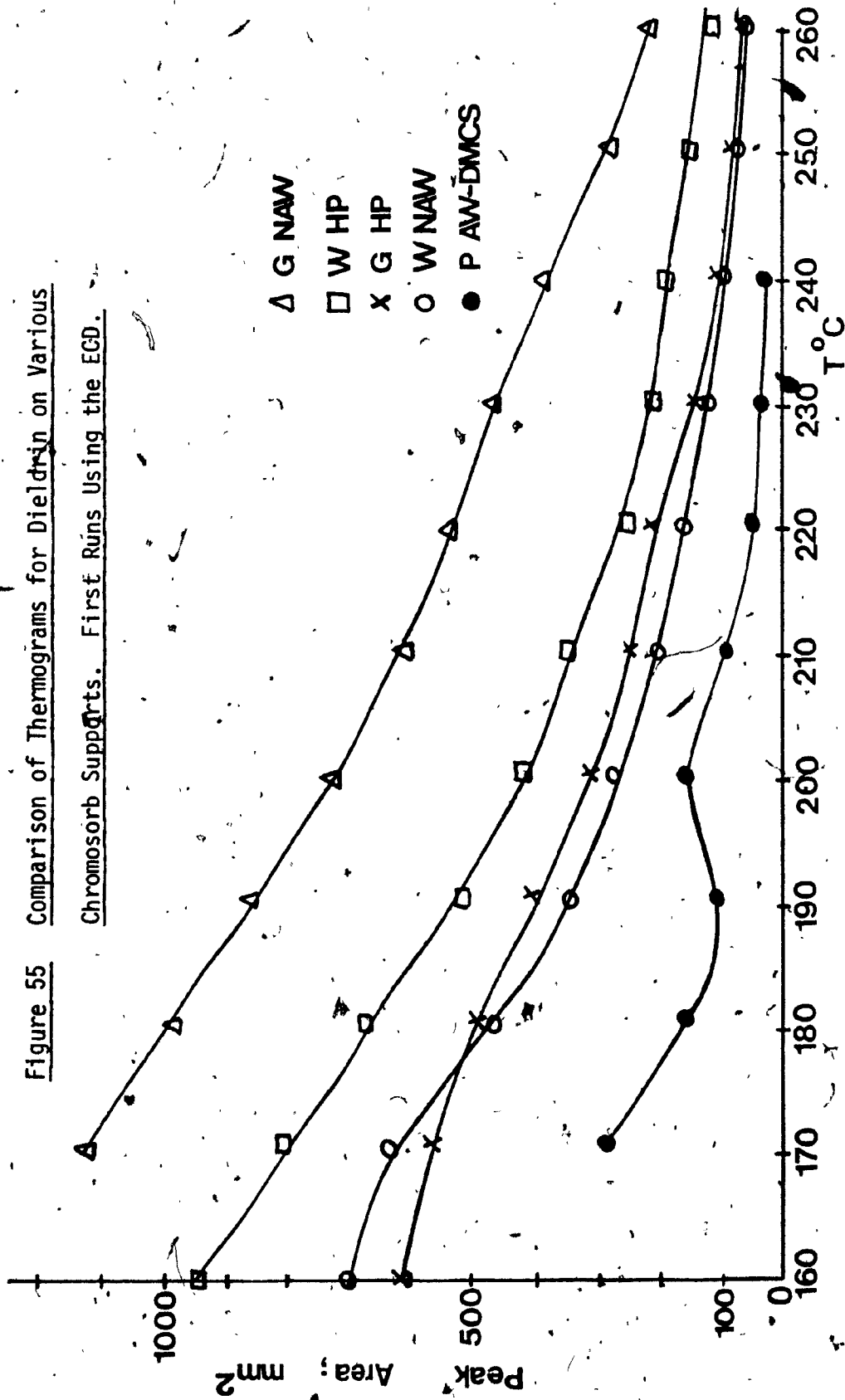


Figure 56 Comparison of Thermograms for Dieldrin on Various

Chromosorb Supports. Second Runs Using the ECD.

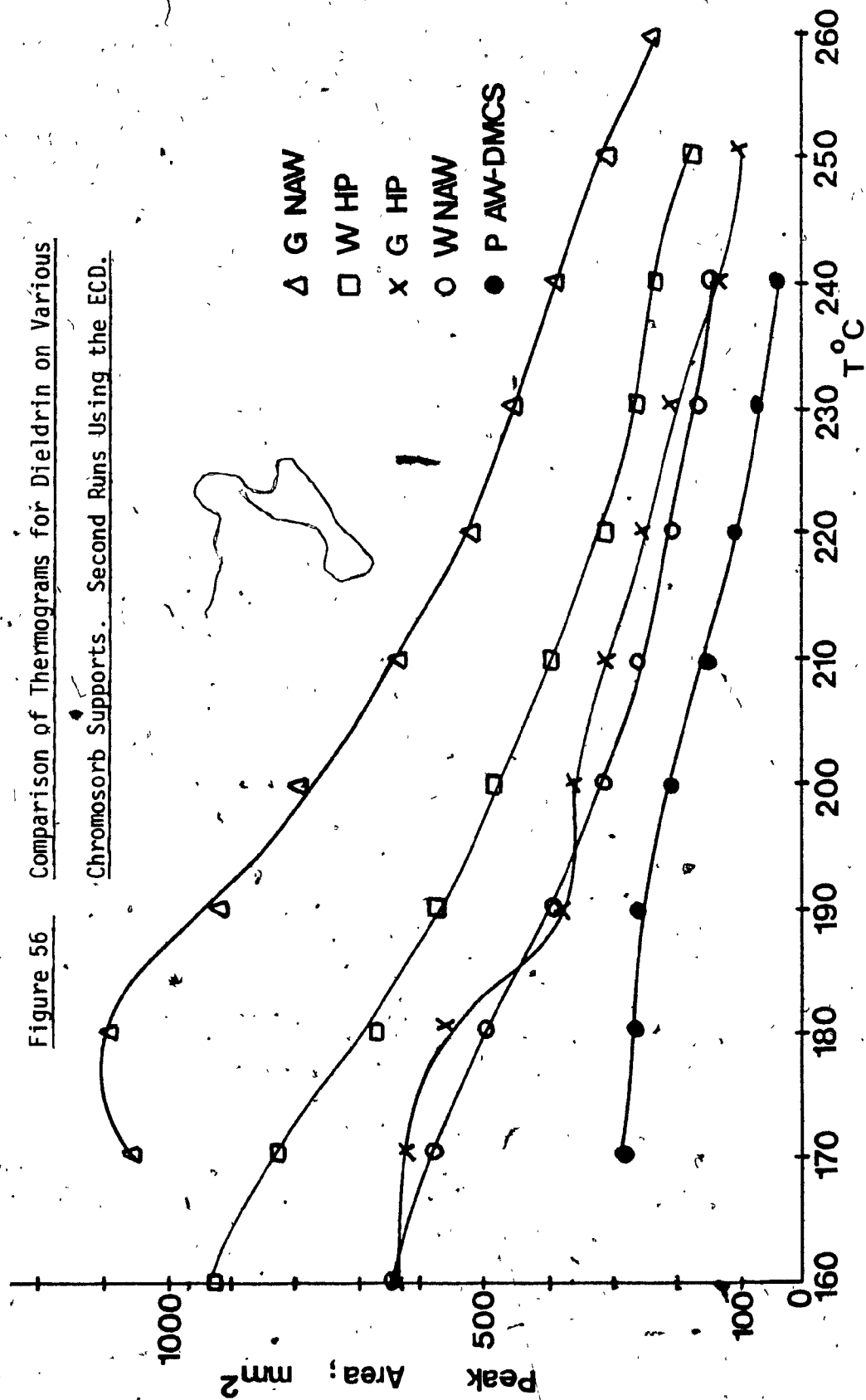




Figure 57 Comparison of Thermograms for Methoxychlor on Various Chromosorb Supports. First Runs Using the ECD.

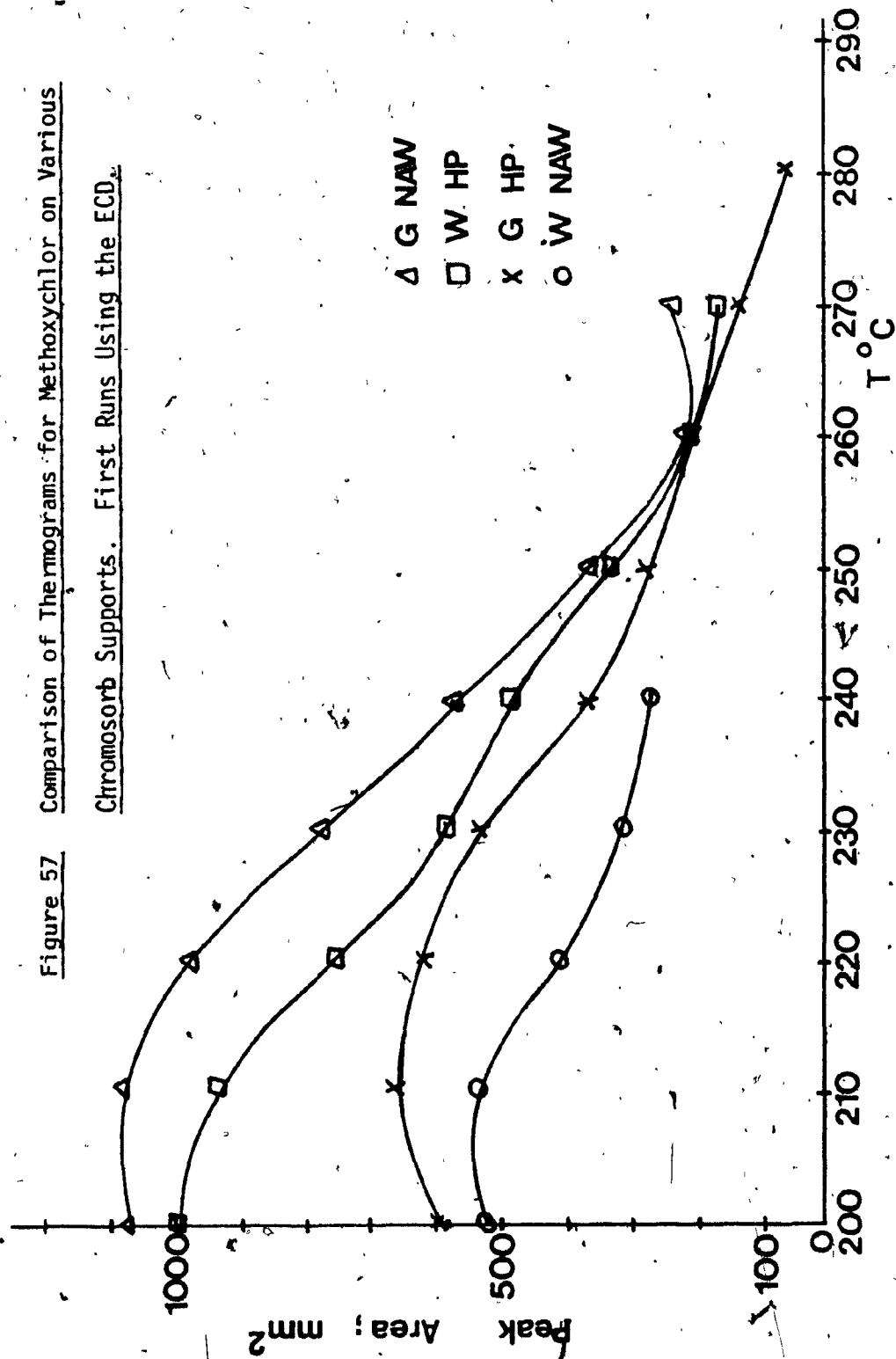
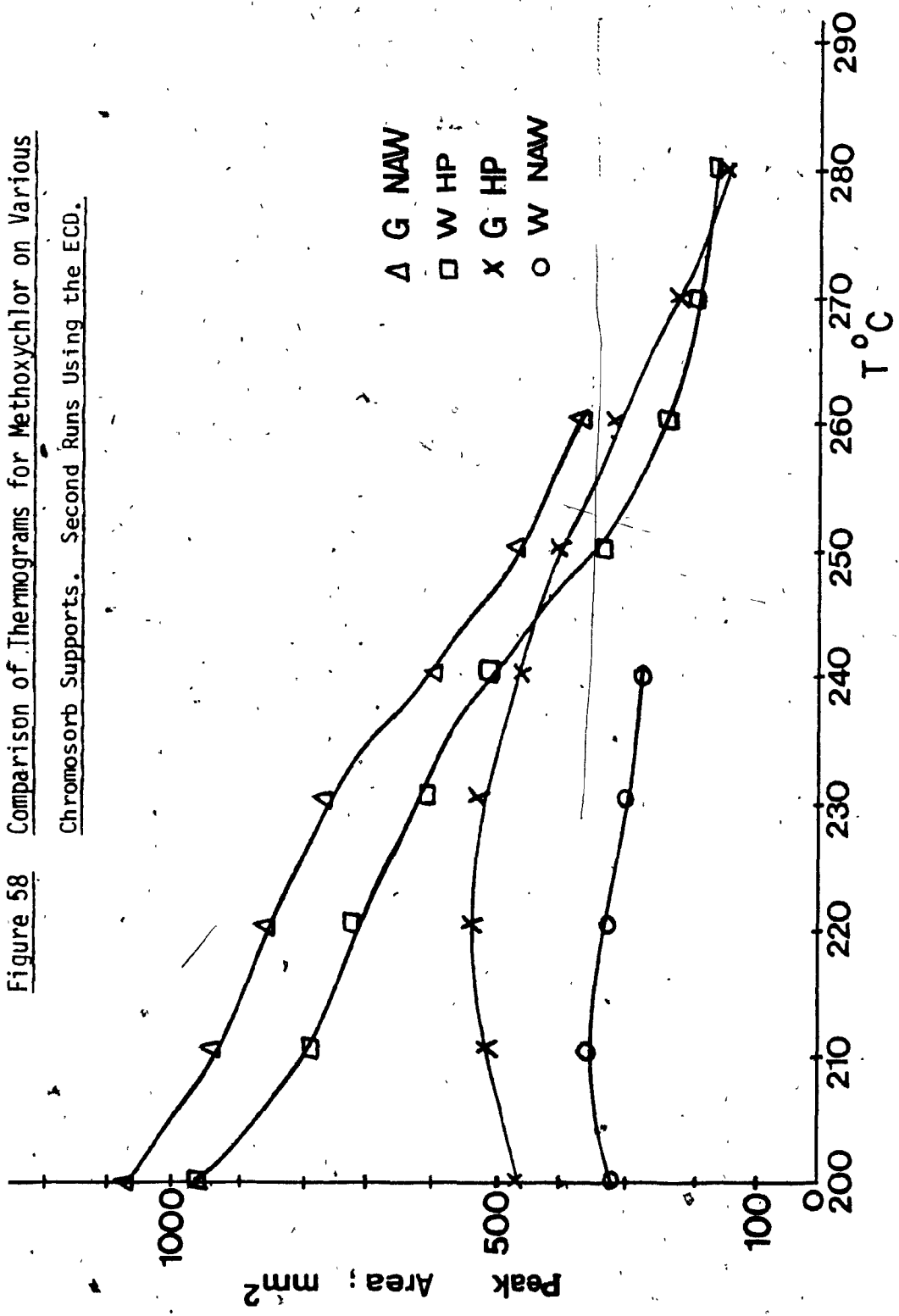


Figure 58 Comparison of Thermograms for Methoxychlor on Various Chromosorb Supports. Second Runs Using the ECD.



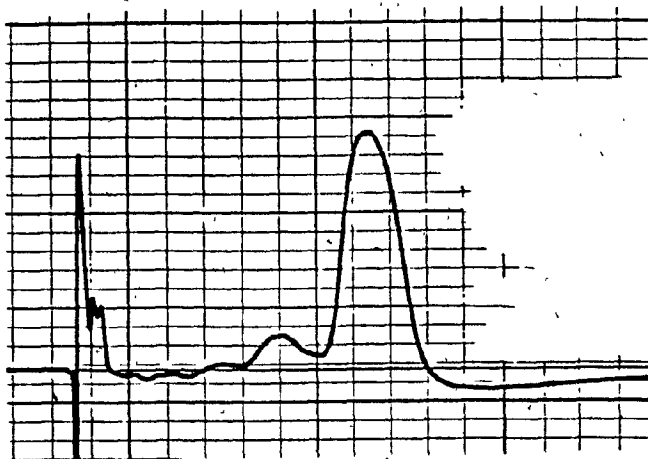


Figure 59 Methoxychlor, 10 ng, Analyzed on  
3.5% w/w OV-17 Coated on Chromosorb  
W HP at 230°C.

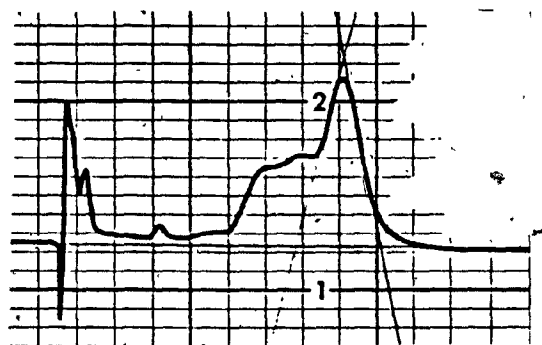


Figure 60 Methoxychlor, 10 ng, Analyzed on  
3.5% w/w OV-17 Coated on Chromosorb  
W NAW at 230°C.

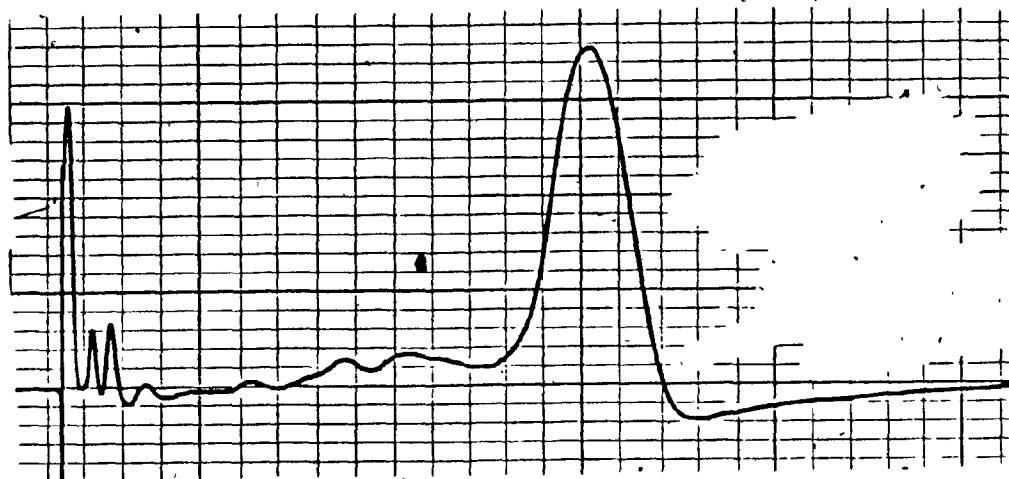


Figure 61 Methoxychlor, 10 ng, Analyzed on 3.5% w/w OV-17  
Coated on Chromosorb G HP at 230°C.

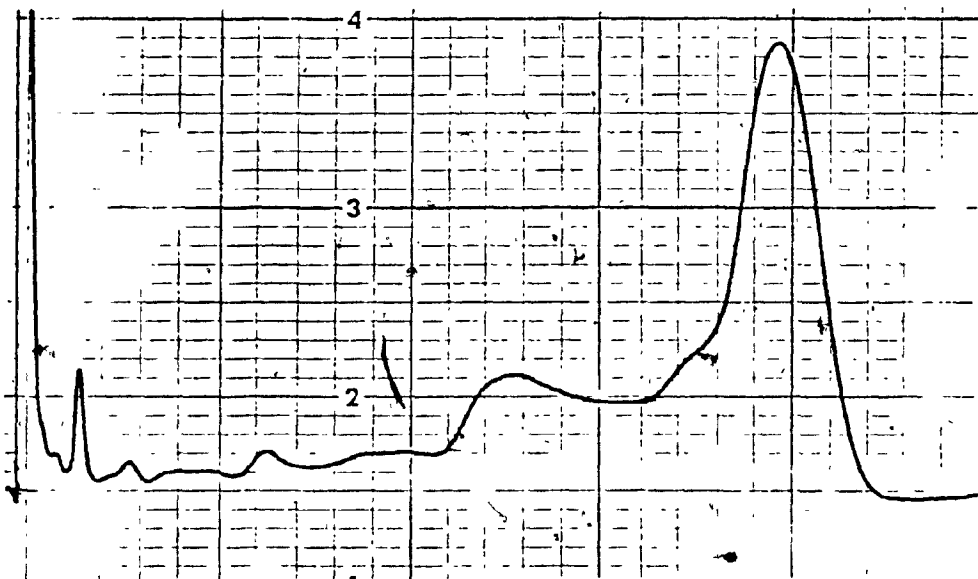


Figure 62 Methoxychlor, 10 ng, Analyzed on 3.5% w/w OV-17  
Coated on Chromosorb G NAW at 230°C.

or overall increases in response with increase in the column temperature were observed, as well as large differences between the first and second runs on the same support, and a multimaxima pattern on all the plots.

Because the same columns were used with both detectors, it was possible, even likely, that what was observed with the ECD tests was, in fact, largely a detector phenomenon. The electron capture detector, being a very sensitive instrument, would be highly influenced by any impurities in the carrier gas, or by a bleeding or decomposing liquid phase, as was discussed in Sections 1.8.4 to 1.8.5, pp. 41 and 47.

The decreasing responses obtained for dieldrin with an increasing column temperature can be attributed to an increased bleeding and/or degradation of the electron affinitive liquid phase material as column temperature was increased. The liquid phase or degradation products, which entered the ECD competed with the sample for the free electrons, thereby lowering the ability of the detector to respond to the sample. The higher the column temperature, the more bleeding/degradation that occurred and the more it dominated the signal of the detector, which made it increasingly less sensitive towards the injected sample.

Figures 63 to 67 show the typical baseline shifts which occurred when the column temperature was raised during a single multi-temperature run. The rise in the baseline was an indication that as the column temperature increased, the liquid phase bled and was detected by the ECD. The resulting signal (the rise in the baseline) was actually a very "tailing peak" due to the liquid phase. After some time, the baseline slowly returned to its original position, an indication that the detector was slowly being purged of the liquid phase. Although no attempt was made to actually measure the time it took for the liquid

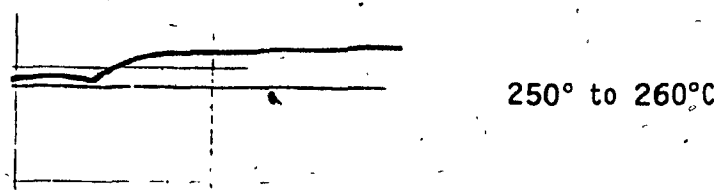
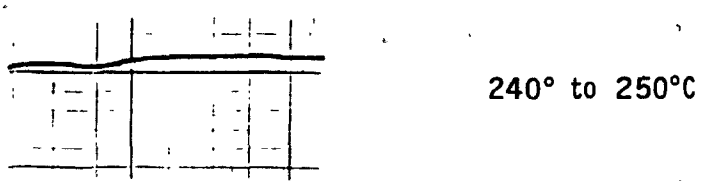
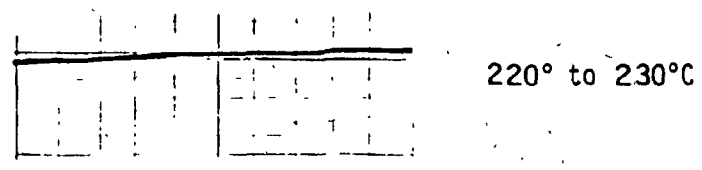


Figure 63 Bleeding of OV-17 Liquid Phase Coated on  
Chromosorb W HP, Recorder Baseline Changes.

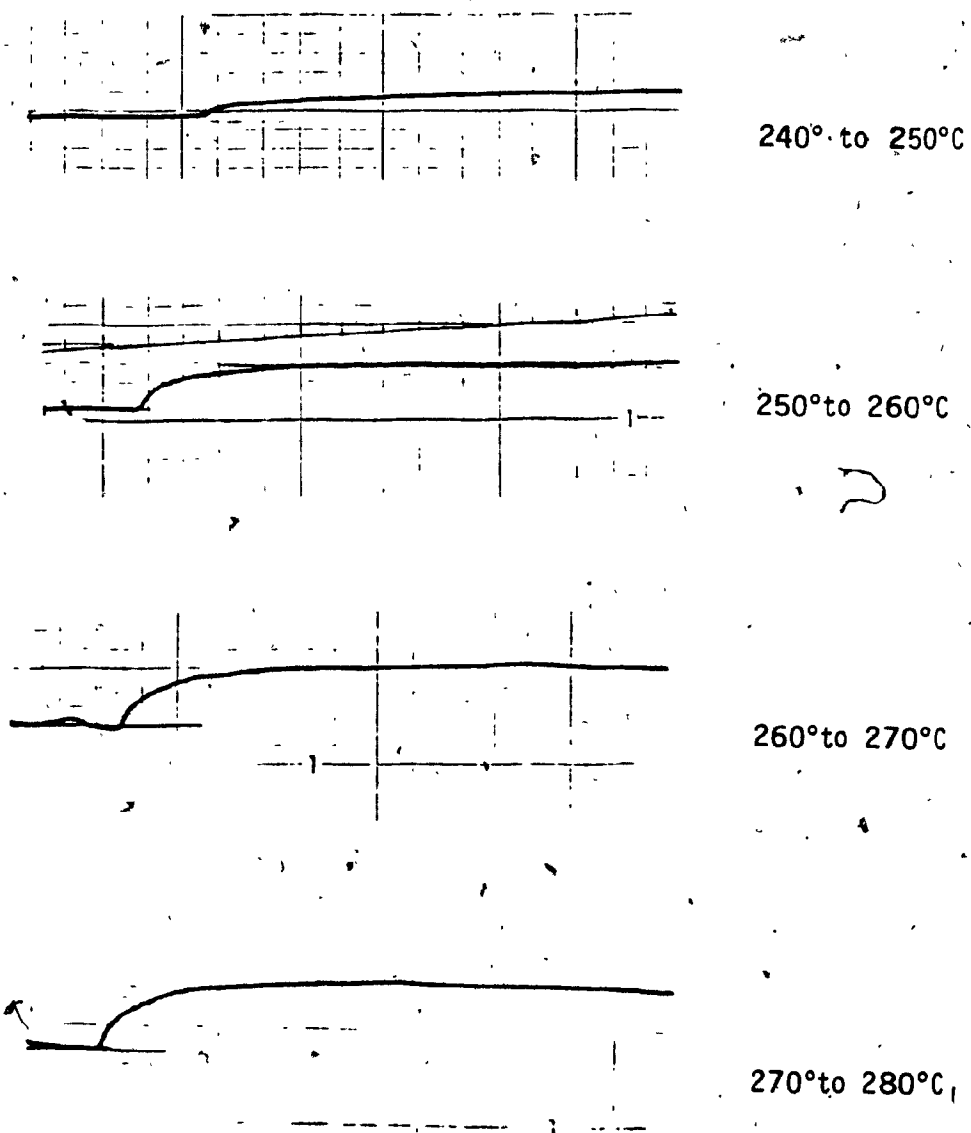


Figure 64 Bleeding of OV-17 Liquid Phase Coated on  
Chromosorb G NAW, Recorder Baseline Changes.

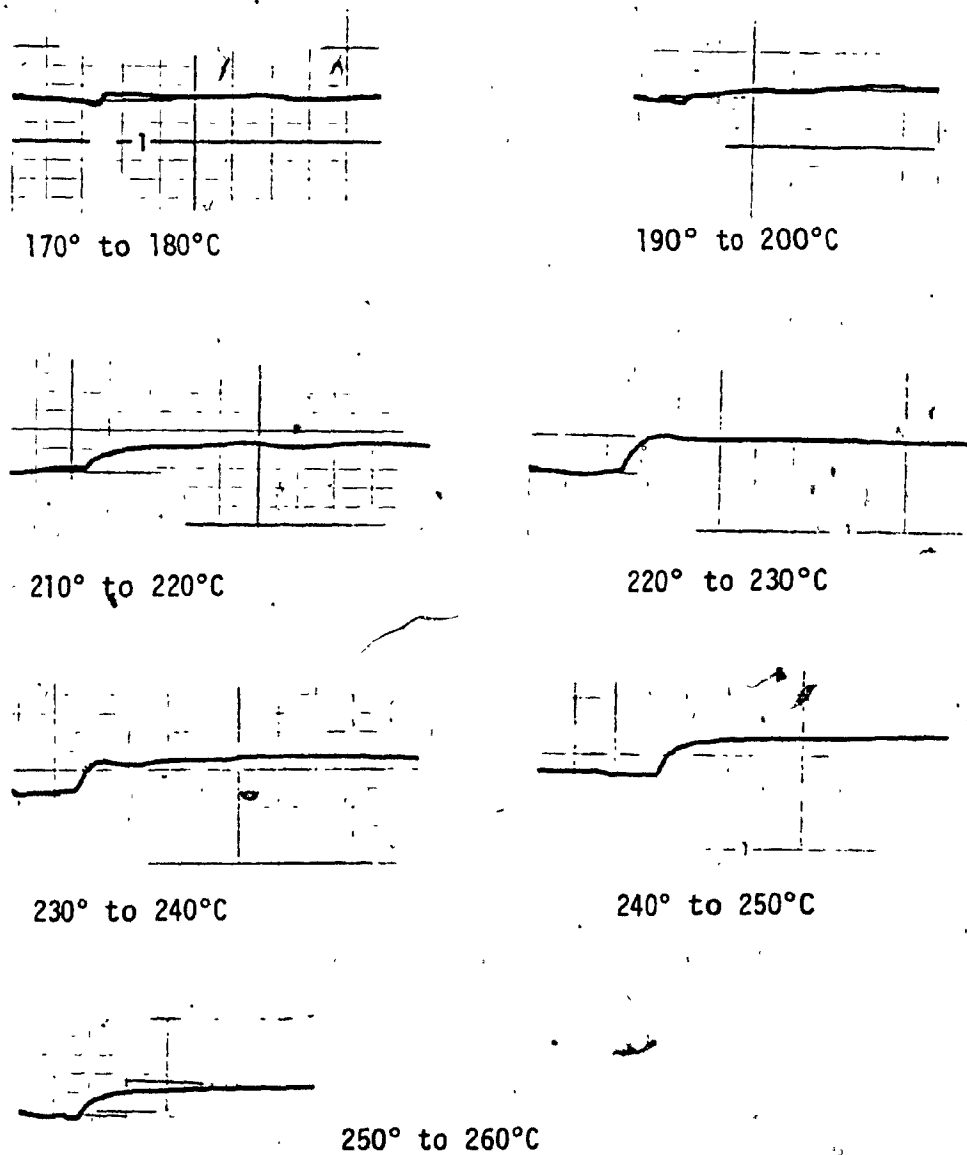


Figure 65 Bleeding of OV-17 Liquid Phase Coated on  
Chromosorb W NAW, Recorder Baseline Changes.



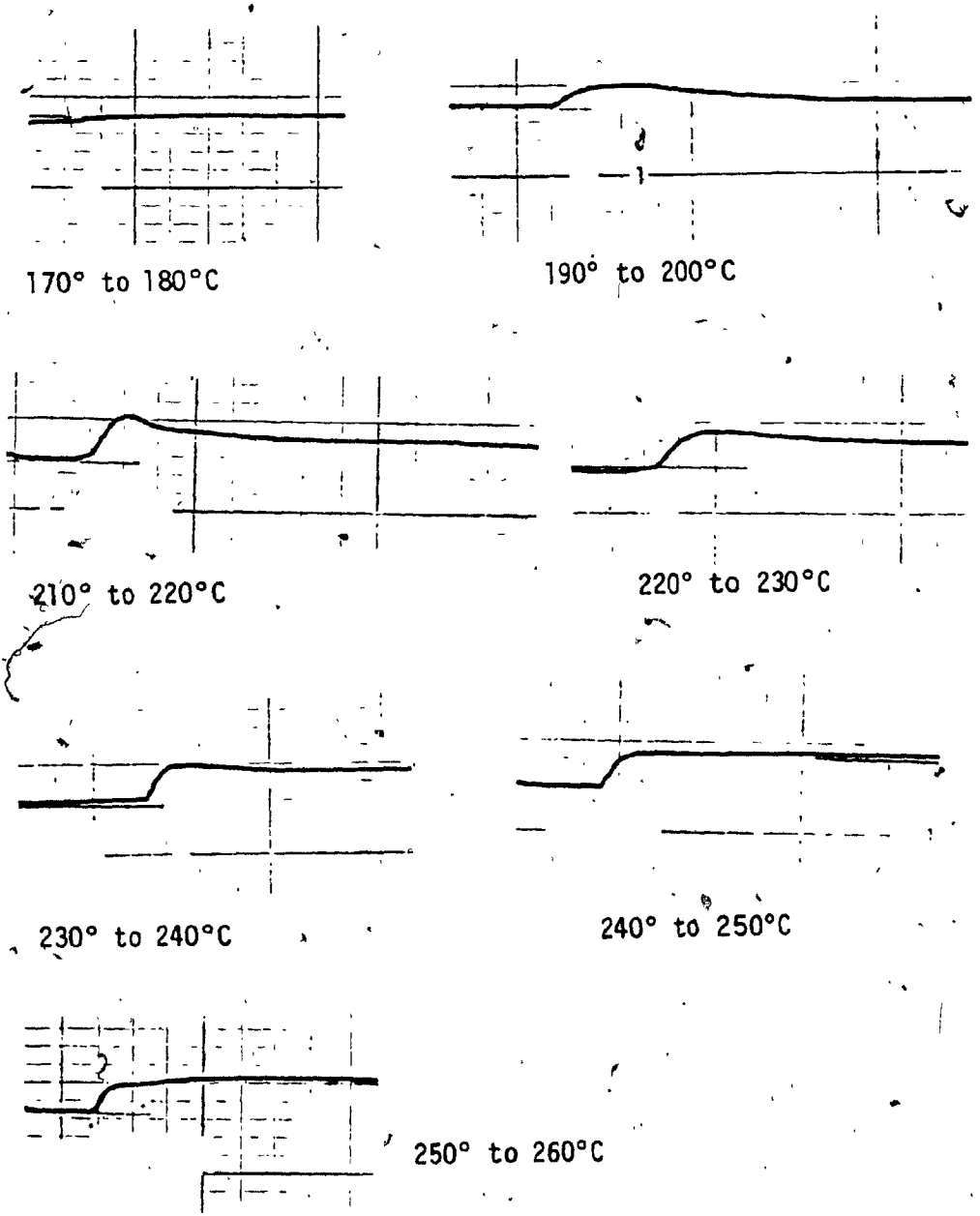


Figure 66 Bleeding of OV-17 Liquid Phase Coated on Chromosorb G HP, Recorder Baseline Changes.

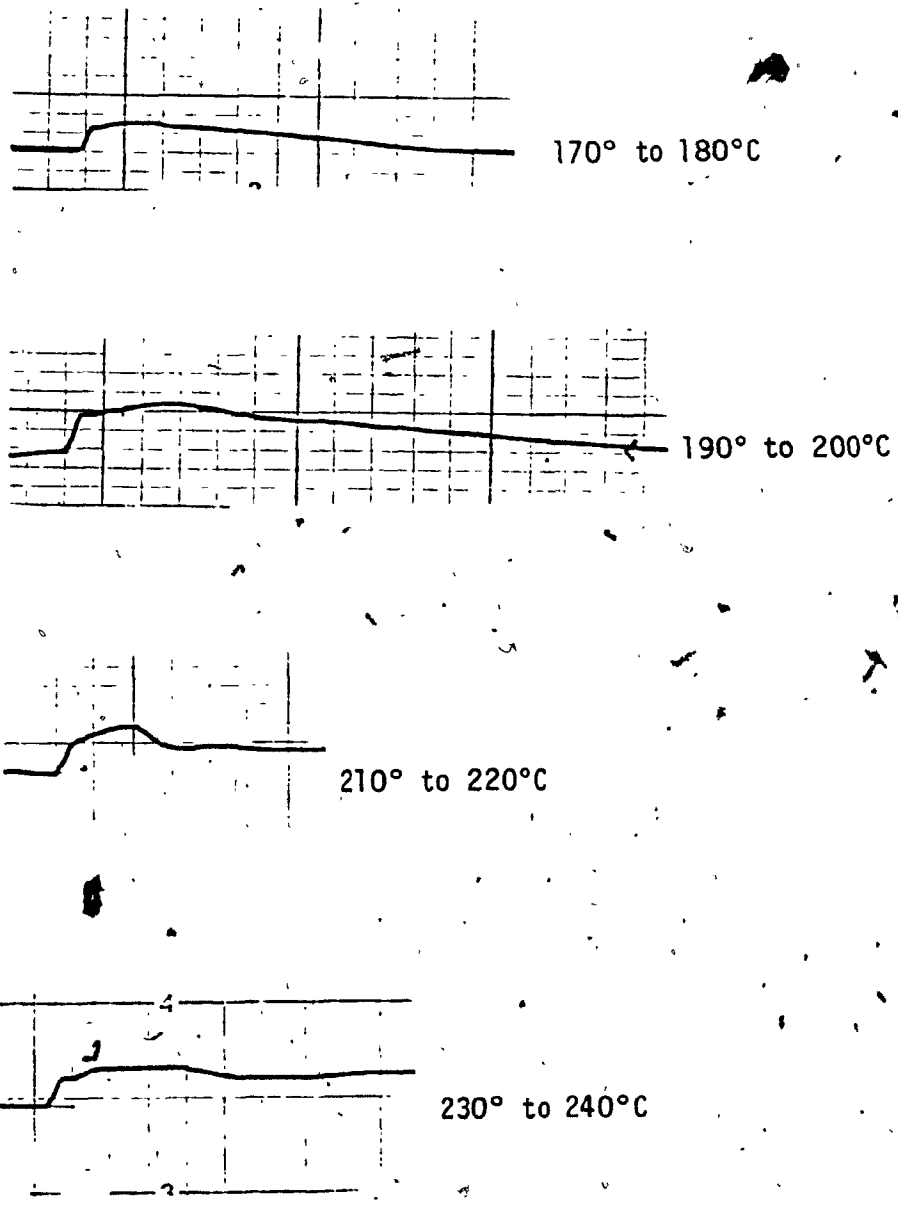


Figure 67 Bleeding of OV-17 liquid Phase Coated on  
Chromosorb P AW-DMCS, Recorder Baseline Changes.

phase to exit from the detector, there was evidence that even after an hour, the ECD sensitivity was still diminished towards the samples.

The thermograms obtained, decreasing response factors with increasing column temperature, were therefore a result of the decreasing sensitivity of the detector with increasing liquid phase bleed at the higher column temperatures. The column temperature at which liquid phase bleeding could be detected as a shift in recorder baseline varied from support to support. For columns containing Chromosorbs W NAW and G HP (Figures 65 and 66 respectively) liquid phase bleed was barely noticeable (a very slight baseline deflection) for the column temperature increase from 170° to 180°C, but became more apparent at higher column temperature changes. In contrast for the G NAW column, a baseline rise was barely noticeable even for a temperature change from 230° to 240°C (not shown in the Figure), but became apparent for the change from 240° to 250°C (Figure 64).

It was observed that the response to dieldrin on the various support materials decreased even at column temperatures where no baseline deflection was recorded. It is likely that even at these lower column temperatures, enough liquid phase bleed did occur to lower the sensitivity of the detector but not enough to cause an observable detector signal. The baseline deflection at almost every increase in the column temperature, the return of the baseline to its original position after a period of time, with a resulting straight baseline thereafter at a constant temperature, were all indications that liquid phase bleed was not continuous, but began to occur only when the column temperature was increased. Similar observations have been made by other workers, Section 1.8.4, p. 41.

### 3.6.1 Adsorptive Properties of Column Supports for Low Concentrations of Dieldrin, Using the ECD

While the ECD thermogram patterns were not descriptive of the behaviour of the different supports, the absolute peak area responses measured, should still have been indicative of relative support adsorptivities. Consideration of the thermograms for dieldrin (Figures 55 and 56, first and second runs respectively) showed exactly the same results for both runs. The order of adsorptivity was as follows:

G NAW < W HP < G HP  $\approx$  W NAW < P AW-DMCS.

Chromosorb W HP had also been found to be a very good support when the adsorptive properties of all the W supports were compared using dieldrin and methoxychlor and the FID, Section 3.4, p. 119.

For reasons already discussed, W NAW was more adsorptive than W HP.

A further explanation to account for the greater adsorptivity of Chromosorb W NAW is evident from Figures 63 and 65. From Figure 63, for the W HP column, only a very small amount of bleeding occurred, even at a column temperature of 230°C. In contrast, for the W NAW column, Figure 65, bleeding was seen even at as low a temperature as 180°C. At 230°C, the amount of bleeding was considerable as was indicated by the appreciable baseline rise. It was concluded that the amount of bleeding from the W NAW column was much more than the amount of bleeding from the W HP column and therefore, W NAW support will have far more uncoated surface active site regions than W HP support, after both have been preheated to the same temperatures.

The less adsorptive behaviour of Chromosorb G NAW compared to Chromosorb G HP is also in agreement with results of adsorptive studies of the G supports with higher concentrations of dieldrin and methoxychlor

and the FID (Sections 3.4.3 and 3.4.4, pp. 130 and 133).

It should be noted that again, for the G supports, there is a difference in the temperature at which bleeding became appreciable for the HP and NAW supports. In this case, bleeding from the G NAW column became noticeable only at a column temperature of about 250°C (Figure 64), while bleeding from the G HP column was observed at as low as 180°C, with considerable bleeding occurring at 220°C and higher (Figure 66).

The comparison of the W, P and G supports together was done, keeping in mind that the quantity of liquid phase layer varied from one type of support to another (Section 3.2, p. 105). Hence, the comparisons made are valid, only, keeping in mind, that each support W, P and G, was deactivated to a different extent by the liquid phase.

Chromosorb P AW-DMCS was found to be the most adsorptive support as expected. Other workers have also found this support to be very reactive due to its large surface area, and fine pore structure. According to the claims of the manufacturer, Chromosorb G should be less adsorptive and this was confirmed to the extent that G NAW was the least adsorptive of the five supports tested in this series of tests.

While the order of relative adsorptivities determined in the ECD tests confirmed findings with higher concentrations of dieldrin and methoxychlor using the FID, the results may have been somewhat fortuitous, because the order of decreasing response also followed closely the order of increasing liquid phase bleed. Below, the supports are listed in order of the column temperature at which bleeding was first noticed by a rise in the baseline which compares exactly with the ob-

served order of adsorptivity.

P AW-DMCS (below 180°C)	G HP (180°C)	W-NAW (180°C)	W HP (230°C)	G NAW (240°C)
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### 3.6.2 The Adsorptive Properties of Column Supports for Low Concentrations of Methoxychlor, Using the ECD

The thermograms obtained on the various supports using 10 ng methoxychlor, and the ECD, are given in Figures 57 and 58 (first and second runs respectively). The results obtained here were very similar to those observed with dieldrin. Overall, the adsorptive order of the supports was:

$$G\ NAW < W\ HP < G\ HP < W\ NAW$$

The same arguments and explanations presented for dieldrin also hold for methoxychlor. Note that methoxychlor could not be run on Chromosorb P AW-DMCS since it was expected that it would decompose.

### 3.7 ADSORPTIVE STUDIES OF COLUMN TUBING MATERIALS

The adsorptive properties of various column tubing materials (stainless steel, nickel, copper, aluminum and glass) towards dieldrin and methoxychlor were studied using the FID, and columns C, and M to P (Table XIII). The column temperature range used was from 160 to 240°C for dieldrin, and from 200 to 280°C for methoxychlor. Duplicate temperature runs were performed with each pesticide on all the columns. Each temperature run consisted of making multiple injections (3 to 5) of the pesticide at 10 degree intervals starting at the lowest column temperature and going upwards. The peak areas of peaks eluted at each tempera-

ture were measured and averages calculated.

Plots of average peak area response versus column temperature were made for each pesticide and each column used for both first and second runs. Figures 20, and 68 to 71 (Appendix E) contain the thermograms for dieldrin and Figures 32, and 72 to 74 (Appendix F) contain the thermograms for methoxychlor.

3.7.1 Thermograms Obtained Using Columns Packed in Various Tubing Materials

The thermograms for dieldrin on the Al, S.S., glass and Ni columns generally showed an increase in response with an increase in the column temperature as would be expected, since adsorption should decrease with temperature increase. There may also have been priming effects by the sample. Tubing materials, like the W AW-DMCS support which they contained, may have many active sites on their surface which can result in adsorption or even decomposition of the compounds analyzed. These active sites may be due to impurities in the composition of the metal, substances added to the material during its manufacturing process, oxides of the metal, or even dirt and grease contamination on the inside walls of the column tubings, although the latter is unlikely.

Glass, like diatomite supports, contains silanol groups on its surface and must be silanized to prevent or at least reduce adsorption.

The copper tubing column was an exception. The first run on the copper column showed an increasing response up to a column temperature of 200°C, above which response decreased (Figure 68). The second run showed a continuous decrease in response at all column temperatures, as temperature was increased. Copper is known to form oxides which can act as adsorbents, or, even as catalysts and cause decomposition. This effect was what was likely observed at temperatures of 200°C and over in the

first run, and throughout the second.

Although aluminum also forms oxides, the second run on the aluminum column did show higher responses than the first run due to sample priming (Figure 69). It may be that aluminum oxide is not as adsorptive as copper oxide, and does not catalyze any possible decompositions of samples as effectively.

The glass column also showed a slight improvement in response during the second run over the first run, a result of priming effects (Figure 70). Any silanol groups on the surface of the glass which were not converted to silyl esters during silanization of the tubing before use, would have caused adsorption during the first run. The lower response with glass during the second run at temperatures of 160° and 170°C was probably due to the loss of the injected sample to prime any fresh active sites formed because of liquid phase bleed at high temperatures during the first run.

The nickel column showed no discernible difference between the first and second runs (Figure 71).

For the stainless steel column, there was a slight decrease in adsorption during the second run at the higher column temperatures, 210° to 240°C. This was probably due to sample priming (Figure 20).

Figures 32, and 72 to 74 show that for methoxychlor, the expected thermograms were obtained, i.e. increasing at first and then decreasing peak area responses as column temperature was increased, using stainless steel tubing. The reasons for this behaviour have been discussed previously (Section 3.3, p. 108). There was less evidence for a meaningful decrease in response at high temperatures using the other column tubing materials.



The thermograms obtained using the aluminum tubing column (Figure 72) showed no discernible difference between the first and second runs. The thermograms obtained on the nickel column showed that the column was less adsorptive during the second run than during the first run (Figure 73). Again, this was attributed to sample priming of both the column tubing and contained solid support. An improved response on a nickel column with repeated injections of sample has also been observed by other workers (see Section 1.9, p. 50).

On the glass tubing column, an increased adsorption was observed from the first to the second and even to a third run. This could be attributed to changes in the solid support. Liquid phase bleed during the first run probably exposed enough new active sites on the support to cause this decrease in response. Sample priming was not effective enough in covering the new active sites (Figure 74).

Methoxychlor could not be analyzed using the copper column. The compound underwent degradation and gave a chromatogram containing three peaks, Figure 75. The copper oxides formed on the copper surface were probably responsible for the on-column decomposition of this substance. Sample priming was not effective in eliminating or reducing this decomposition. After two temperature runs involving about 50 injections of 10  $\mu$ g portions of methoxychlor, no improvement was observed in the degradation pattern.

It should be noted that it is not impossible that any differences between first and second runs shown in Figures 20, 32, and 68 to 74 actually reflected changes in the behaviour of the liquid phase coated supports as well as the tubing. But these differences should be taken as indications of tubing effects since whatever support changes occurred

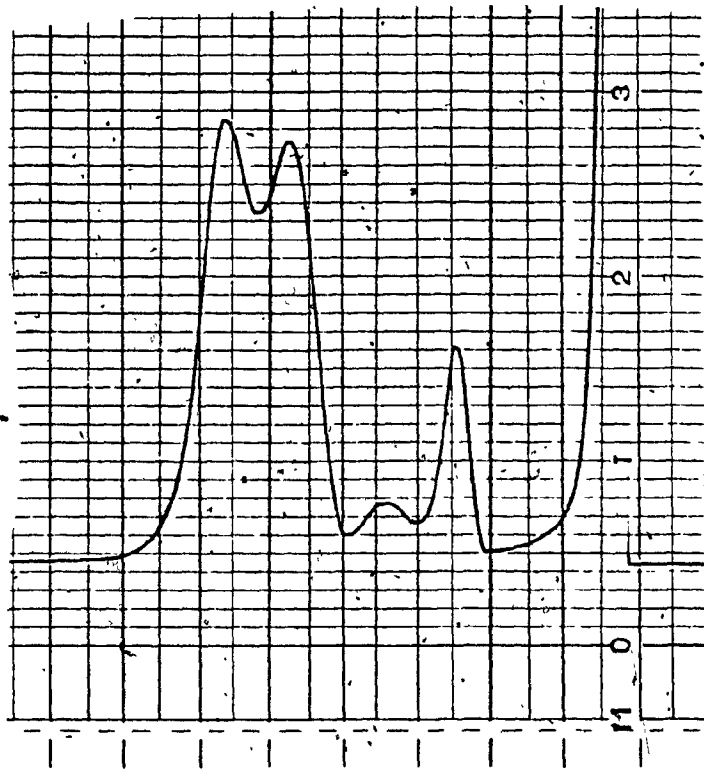


Figure 75 Analysis of Methoxychlor, 10 ng, on  
Copper Tubing Column at 230°C.

should have been the same regardless of the nature of the tubing.

### 3.7.2 Comparison of the Adsorptive Properties of Column Tubing

#### Materials Using Dieldrin as the Test Sample

Figures 76 and 77 consist of the thermograms for dieldrin, first and second runs respectively, obtained using various column tubing materials.

The second runs showed the glass tubing to be the least adsorptive followed by aluminum and then stainless steel. At column temperatures of 160° to 190°C, stainless steel and copper were very similar in their adsorptive properties. Also in this temperature range, the nickel tubing was the worst. From 200° to 240°C there was really no discernible difference between aluminum and stainless steel, but both of these tubings were better than nickel and copper. Also, in this temperature range, the nickel tubing was slightly better than copper.

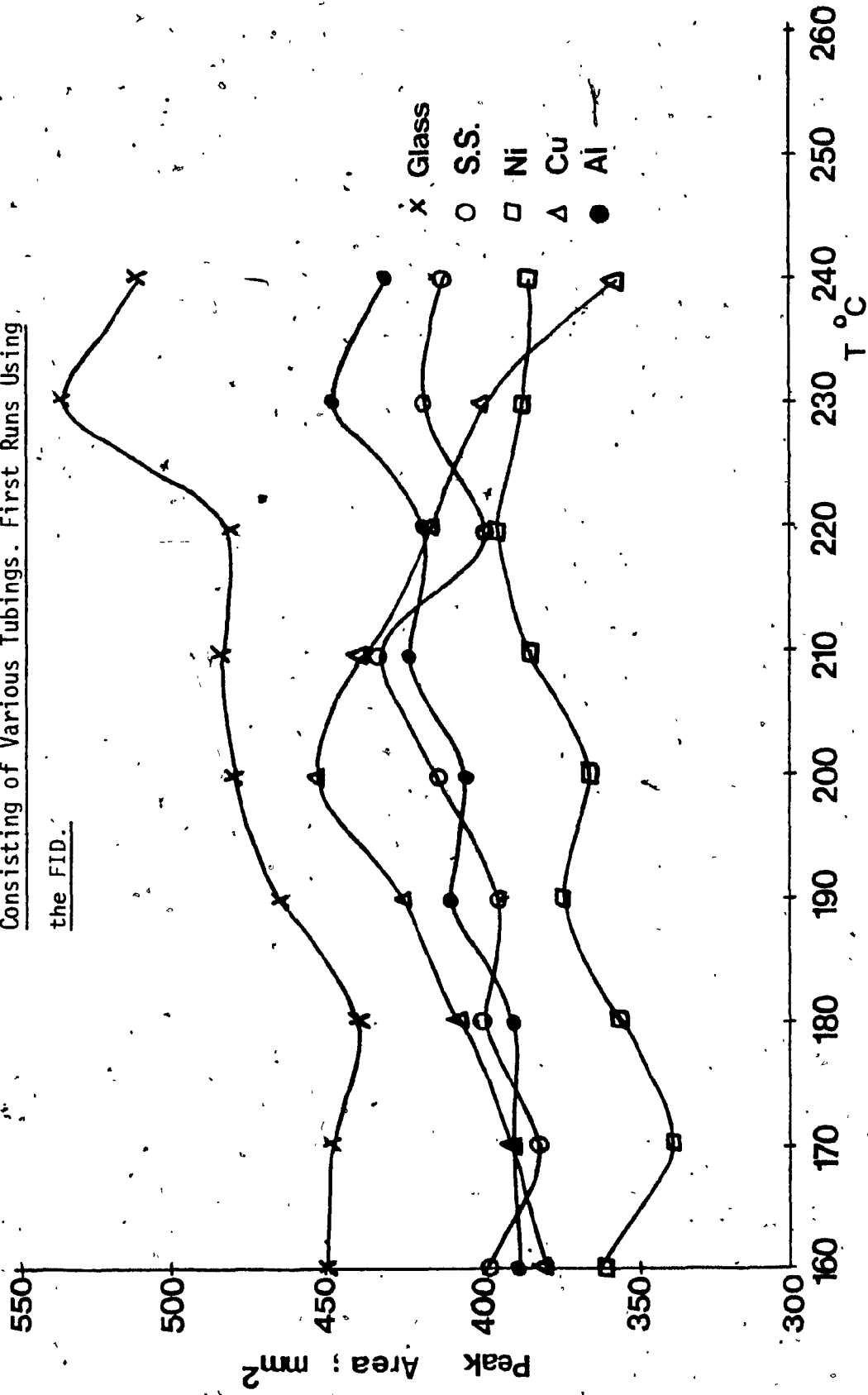
From the first runs it was also observed that the glass tubing was the least adsorptive and nickel the most adsorptive. There was no discernible difference among the copper, aluminum and stainless steel tubings.

There was no doubt that glass tubing was best for the analysis of dieldrin. All metal tubings were responsible for some adsorption, copper and nickel being the worst. Aluminum and stainless steel improved during the second runs but were still responsible for a fair amount of adsorption.

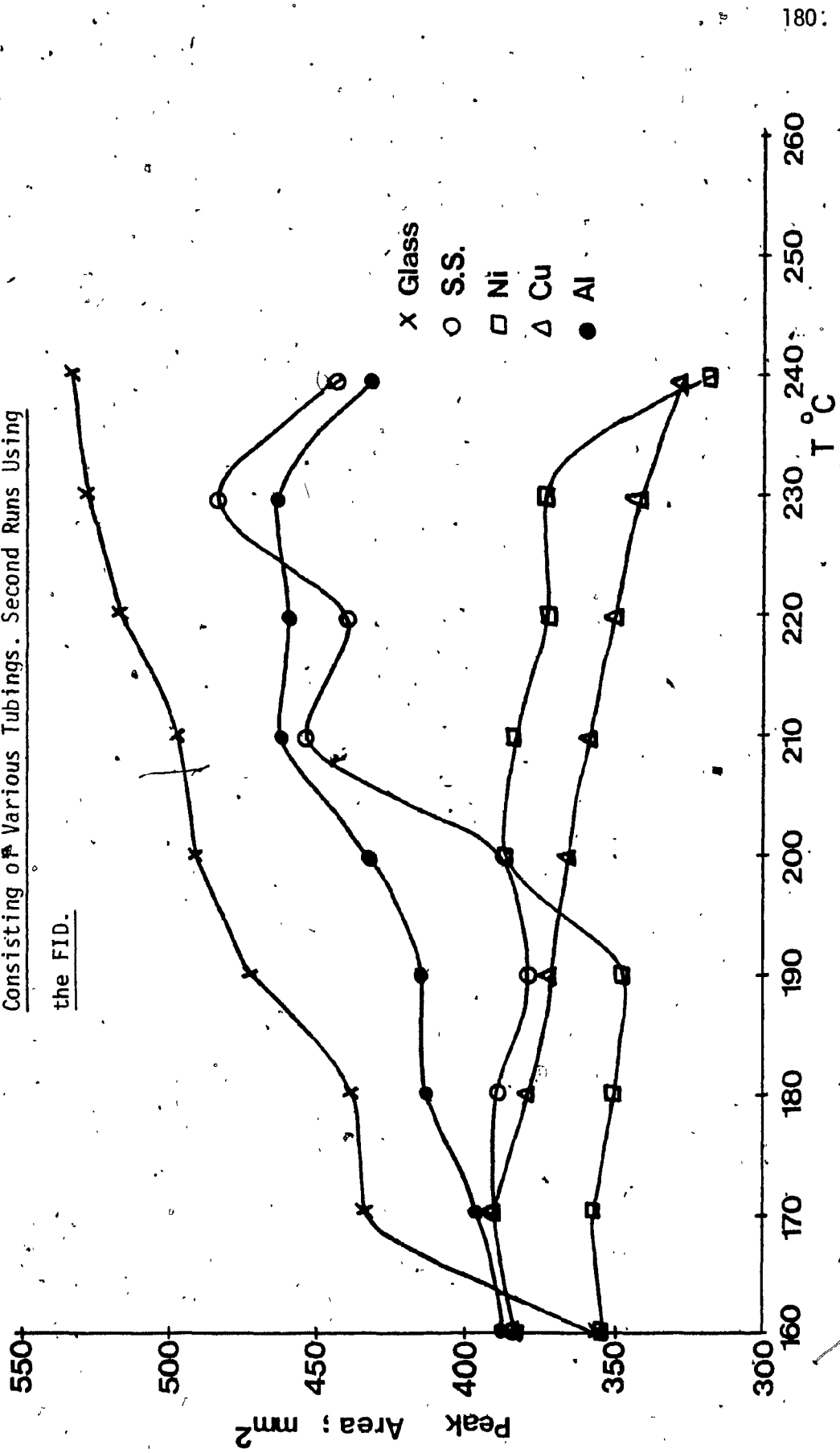
More emphasis was placed on the second runs since they more accurately indicated the adsorptive properties of the column tubing materials, once the effects of any oxide formation and sample priming had set in.

Note the better behaviour of the aluminum column compared to nickel and copper. Oxide formation on aluminum must have been less extensive

Figure 76 Comparison of Thermograms for Dieltrin on Columns Consisting of Various Tubings. First Runs Using the FID.



**Figure 77** Comparison of Thermograms for Dieltrin on Columns Consisting of Various Tubings. Second Runs Using the FID.



than on copper. Other workers have also reported that aluminum was slightly better than stainless steel for certain purposes (Section 1.9, p. 50).

### 3.7.3 Comparison of the Adsorptive Properties of Column Tubing Materials with Methoxychlor as the Test Sample

Figures 78 and 79 contain the thermograms for methoxychlor (first and second runs respectively) obtained by using various column tubing materials. The second runs showed the nickel column to be the least adsorptive followed by glass, then aluminum, and then stainless steel. Note that at column temperatures of 250<sup>0</sup>, 260<sup>0</sup> and 270<sup>0</sup>C, there was no discernible difference between aluminum and stainless steel. The copper column could not be used for the analysis of methoxychlor because of degradation problems.

Results of the first run, did not duplicate the second. According to the first run, nickel and glass were less adsorptive than aluminum and stainless steel. However, between 200<sup>0</sup> and 230<sup>0</sup>C there was no difference between nickel and glass. Above a column temperature of 230<sup>0</sup>C, the glass column became less adsorptive. On the other hand, stainless steel and aluminum showed no discernible difference above 230<sup>0</sup>C, but stainless steel, was more adsorptive below this temperature.

Overall, it can be concluded that glass and nickel are better than aluminum and stainless steel, which in turn are better than copper as far as methoxychlor analyses are concerned.

Considering adsorptivities towards both dieldrin and methoxychlor, all that could be concluded was that glass was less adsorptive than any of the metal tubings tested. Of the metal tubings, the behaviour of nickel was erratic, and copper was completely unacceptable. Aluminum was

Figure 78 Comparison of Thermograms for Methoxychlor on Columns Consisting of Various Tubings. First Runs Using the FID.

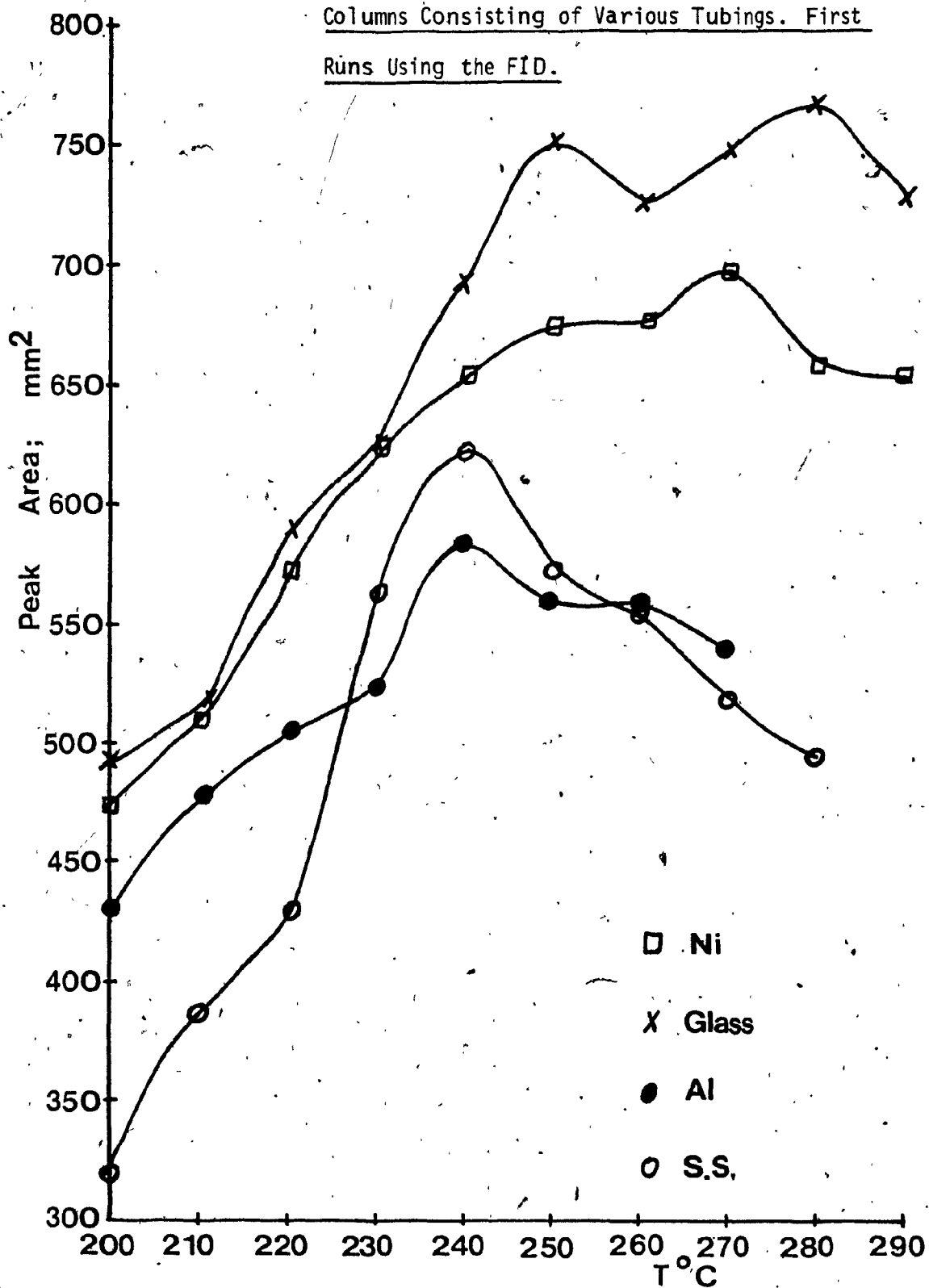
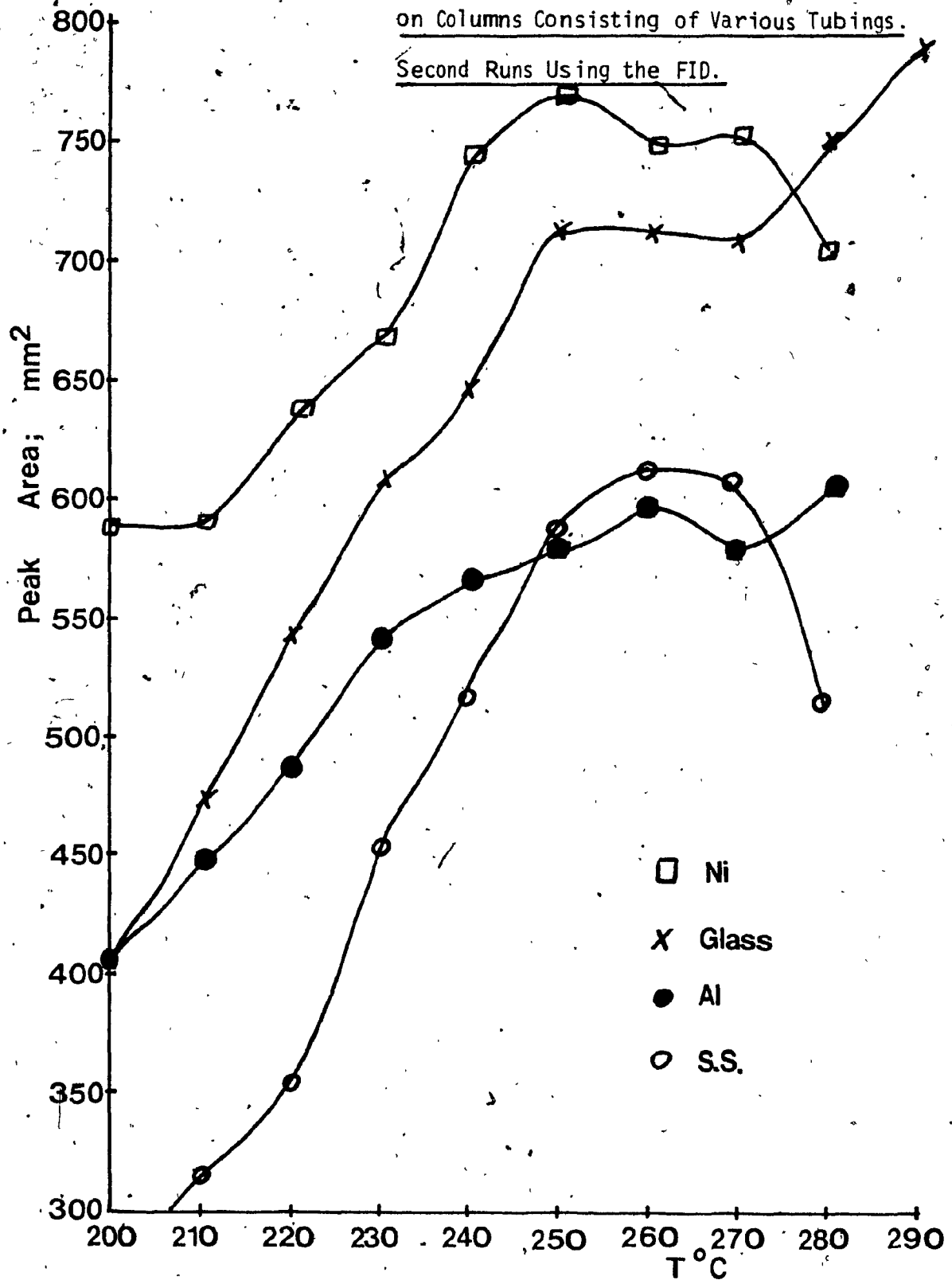


Figure 79 Comparison of Thermograms for Methoxychlor  
on Columns Consisting of Various Tubings.

Second Runs Using the FID.





less adsorptive than stainless steel.

### 3.8 COMPARISON OF THE ADSORPTIVE PROPERTIES OF COLUMN TUBING MATERIALS, USING VARIOUS CONCENTRATION LEVELS OF DIELDRIN AND METHOXYCHLOR - FID

The adsorptive properties of various column tubing materials (stainless steel, nickel, copper, aluminum and glass) were further evaluated by determining calibration curves within suitable concentration ranges, and comparing absolute peak area responses, and the slopes of the calibration curves obtained.

As in Section 3.5, p. 141, it was predicted that adsorptive column tubing materials would result in calibration curves having smaller slopes than less adsorptive column tubing materials.

The pesticides, dieldrin and methoxychlor, and columns M to P, Table XIII, p. 90, were used in this study.

The same procedure was followed, and the same experimental conditions and kinds of sample solutions were used as described in Section 3.5, p. 141.

Tables XXII to XXIII summarize the data obtained.

#### 3.8.1 Comparison of the Adsorptive Properties of Column Tubing Materials Using Various Concentration Levels of Dieldrin

From the results of Table XXII, the following increase in adsorptive properties of the various column tubing materials was obtained at the 1  $\mu$ g level.

First Run: Glass < S.S.  $\approx$  Al  $\approx$  Ni  $\approx$  Cu

Second Run: Glass < S.S.  $\approx$  Ni  $\approx$  Cu  $\approx$  Al

All metal tubings had very similar adsorptive properties and were considerably more adsorptive than glass.

TABLE XXII  
 COMPARISON OF THE ADSORPTIVE PROPERTIES OF COLUMN TUBING MATERIALS USING VARIOUS  
 CONCENTRATION LEVELS OF DIELDRIN

COLUMN TUBING MATERIALS	PEAK AREA RESPONSES* mm <sup>2</sup>				HIGH CONC. SLOPE, mm <sup>2</sup> /deg.	LOW CONC. SLOPE, mm <sup>2</sup> /deg.
	1 µg	4 µg	10 µg	40 µg		
			FIRST RUN			
Stainless Steel	175	729	179	1063	29.7	188
Aluminum	173	744	193	923	23.9	170
Nickel	170	698	219	1100	29.3	175
Copper	164	680	227	1142	28.6	170
Glass	210	890	253	1143	29.5	208
			SECOND RUN			
Stainless Steel	172	751	167	1061	30.0	186
Aluminum	165	672	203	919	23.4	159
Nickel	172	709	224	1100	29.4	176
Copper	168	668	219	1154	31.1	155
Glass	208	920	270	1161	29.8	220

\*The precision of the peak area measurements was ±5%.

At the 4  $\mu\text{g}$  level, the following adsorptive order was obtained:

First Run: Glass < Al  $\approx$  S.S.  $\approx$  Ni  $\approx$  Cu

Second Run: Glass < S.S.  $\leq$  Ni  $\leq$  Al  $\approx$  Cu

Glass was again the least adsorptive column tubing material. But no conclusions were reached as to the relative adsorptive properties of the various metal tubings. Differences were small and varied from run to run.

At the 10  $\mu\text{g}$  level, the following order of decreasing adsorptivity was obtained:

First Run: Glass  $\leq$  Cu  $\approx$  Ni  $\leq$  Al  $\approx$  S.S.

Second Run: Glass < Ni  $\approx$  Cu  $\leq$  Al < S.S.

Glass was again the least adsorptive column tubing. Differences among metal tubings were small and varied from run to run, except that stainless steel was slightly inferior.

At the 40  $\mu\text{g}$  level, the order of adsorptivity among tubings was the following:

First Run: Glass  $\approx$  Cu  $\leq$  Ni  $\leq$  S.S. < Al

Second Run: Glass  $\approx$  Cu  $\leq$  Ni  $\leq$  S.S. < Al

Glass was still the best tubing, but only by a small margin. The metal tubings had very similar adsorptivity behaviour.

The copper tubing was rather adsorptive at the low concentration levels (1 and 4  $\mu\text{g}$ ) but improved considerably at higher concentration levels (10 and 40  $\mu\text{g}$ ). This was attributed to a more complete coverage of the active sites on the column tubing (such as copper oxides) with larger sample sizes.

In contrast to this, the performance of stainless steel was marginally better for smaller sample sizes.

The slopes of the linear regressions performed on the calibration curves in the high concentration range, Table XXII, followed the following order:

First Run: S.S.  $\approx$  Glass  $\approx$  Ni  $\geq$  Cu  $>$  Al

Second Run: Cu  $>$  S.S.  $\approx$  Glass  $\approx$  Ni  $>$  Al

There was complete disagreement between the order of slopes and adsorptivities of the supports.

A comparison of the slopes of the calibration curves at the low concentration range, Table XXII, gave the following order of decreasing slopes for the various tubing materials:

First Run: Glass  $\geq$  S.S.  $\geq$  Ni  $\geq$  Al  $\approx$  Cu

Second Run: Glass  $\geq$  S.S.  $\geq$  Ni  $\geq$  Al  $\approx$  Cu

There was good agreement between the slope data and the comparison of peak area responses at various sample sizes which had showed that glass was the least adsorptive column tubing material for the analysis of dieldrin. Overall, the adsorptive properties of the metal tubings depended on the sample size. Furthermore, the differences among metal tubes were small and often varied from run to run on the same column. These results correlated well with the thermogram data. They confirmed the less adsorptive behaviour of glass compared to metal tubings, and the changing behaviour of the metal columns from run to run.

### 3.8.2 Comparison of the Adsorptive Properties of Column Tubings Using Various Concentration Levels of Methoxychlor

According to the results of Table XXIII, at the 1  $\mu$ g level, the order of increasing adsorption for the various column tubings was the following:

First Run: Ni  $\approx$  Glass  $<$  Al  $<$  S.S.

TABLE XXIII  
COMPARISON OF THE ADSORPTIVE PROPERTIES OF COLUMN TUBING MATERIALS USING VARIOUS  
CONCENTRATION LEVELS OF METHOXYCHLOR

COLUMN TUBING MATERIALS	PEAK AREA RESPONSES* $\text{mm}^2$				HIGH CONC. SLOPE $\text{mm}^2/\text{deg.}$	LOW CONC. SLOPE $\text{mm}^2/\text{deg.}$
	1 $\mu\text{g}$	4 $\mu\text{g}$	10 $\mu\text{g}$	40 $\mu\text{g}$		
Stainless Steel			FIRST RUN			
	137	765	219	1372	36.7	214
	159	804	220	1243	32.6	219
	186	944	247	1211	36.1	256
	-	-	-	-	-	-
Glass	180	940	257	1337	35.5	274
			SECOND RUN			
Stainless Steel	120	798	193	1395	38.7	235
	148	772	199	1221	34.6	227
Aluminum	186	924	241	1191	35.6	254
	-	-	-	-	-	-
Copper	202	925	238	1233	33.4	261

\*The precision of the peak area measurements was  $\pm 5\%$ .

Second Run: Glass < Ni < Al < S.S.

Glass and nickel had very similar adsorptive properties. It was also noted that aluminum was less adsorptive than stainless steel.

At the 4  $\mu$ g level, the following order of increasing adsorption was obtained:

First Run: Ni  $\approx$  Glass < Al < S.S.

Second Run: Ni  $\approx$  Glass < S.S.  $\approx$  Al

Again the less adsorptive behaviour of glass and nickel was evident.

At the 10  $\mu$ g level, the order of increasing adsorption was:

First Run: Glass  $\approx$  Ni  $\leq$  Al  $\approx$  S.S.

Second Run: Ni  $\approx$  Glass < Al  $\approx$  S.S.

Also at this concentration level, glass and nickel had very similar adsorptive properties and were less adsorptive than stainless steel and aluminum.

At the 40  $\mu$ g level, the order of increasing adsorption was:

First Run: S.S.  $\leq$  Glass < Al  $\approx$  Ni

Second Run: S.S. < Glass  $\approx$  Al  $\approx$  Ni

Stainless steel tubing was, surprisingly, the least adsorptive tubing at this sample size. Nickel was the most adsorptive.

From the slopes of the linear regressions performed on the calibration curves of the high concentration range, Table XXIII, the following order was obtained for the various column tubings:

First Run: S.S.  $\geq$  Ni  $\geq$  Glass > Al

Second Run: S.S. > Ni > Al > Glass

From Table XXIII, a comparison of the slopes of the linear regressions performed on the calibration curves of the low concentration range, gave the following order:

First Run: Glass  $\geq$  Ni  $>$  Al  $\approx$  S.S.

Second Run: Glass  $\approx$  Ni  $\geq$  S.S.  $\approx$  Al

The results obtained for slopes were in good agreement with those obtained by comparison of peak area responses at various sample sizes. Nickel and glass were less adsorptive than aluminum and stainless steel for the analysis of methoxychlor at small sample sizes, and stainless steel was less adsorptive for large sample sizes, and their corresponding calibration curves had large slopes.

The thermogram results obtained previously agreed with the above findings for adsorptivity towards methoxychlor. Glass and nickel were found to be less adsorptive than aluminum and stainless steel. The good performance of stainless steel for the higher concentrations had not been observed from the thermogram results since the sample size used there was only 10  $\mu$ g. It is possible that with large sample sizes (about 40  $\mu$ g), sample priming may have been very effective in deactivating whatever active sites existed on the inner surface of the stainless steel tubing.

In general, the concentration tests often gave conclusions about support adsorptivities which agreed with those based on thermogram studies. There were, however, exceptions. This is not surprising when one realizes that the thermogram runs showed that the nature of a column changes with every run, because of priming effects by the samples analyzed, and liquid phase bleeding or decomposition. Hence, the same results could not be realistically expected when concentration tests were performed using columns which had had considerable use already, and not each one to the same extent, as part of the preparation of the thermograms.

The work in this thesis has shown that it is not possible to obtain

meaningful adsorptivity determinations by carrying out a single set of tests under any one set of conditions. Long-ranging, detailed studies under various conditions are required to obtain useful adsorptivity results. To illustrate the degree to which erroneous results can be obtained using "short cut" methods, Appendices A and B show results of tests carried out over a two-day period using different supports and tubings, but at one temperature only, per set of tests. The results differed from what was obtained over the long term study, and which was more realistic of "true" adsorptivity data.

### 3.9 COLUMN BENDING EFFECTS

When a new column was prepared by packing 3.5% w/w OV-17 coated on Chromosorb G AW-DMCS in 2' x 1/8" o.d. stainless steel tubing, and fitted into the Shimadzu Gas Ghromatograph, after preconditioning, injection of 10  $\mu$ g of methoxychlor gave the chromatogram shown in Figure 80. Only one peak was evident. When a similar column which had been used successfully for dieldrin work was taken from the Shimadzu GC, and reshaped to fit the oven of the Microtek instrument, injection of the same amount of methoxychlor gave the chromatogram in Figure 81, (4 peaks). After considerable priming of this column with methoxychlor, the chromatogram in Figure 82 was obtained (one peak with minor degradation). Bending the column from a "U" shape ( in the Shimadzu ) to this form " } " (in the Microtek) resulted in the crushing of some of the support particles exposing new active site surfaces. These active sites caused the decomposition of methoxychlor that is seen in Figure 81. Considerable priming reduced the degradation to that shown in Figure 82. The fact that no degradation was observed on the newly packed column showed that the decomposition was not a result of a poorly prepared packing, but was



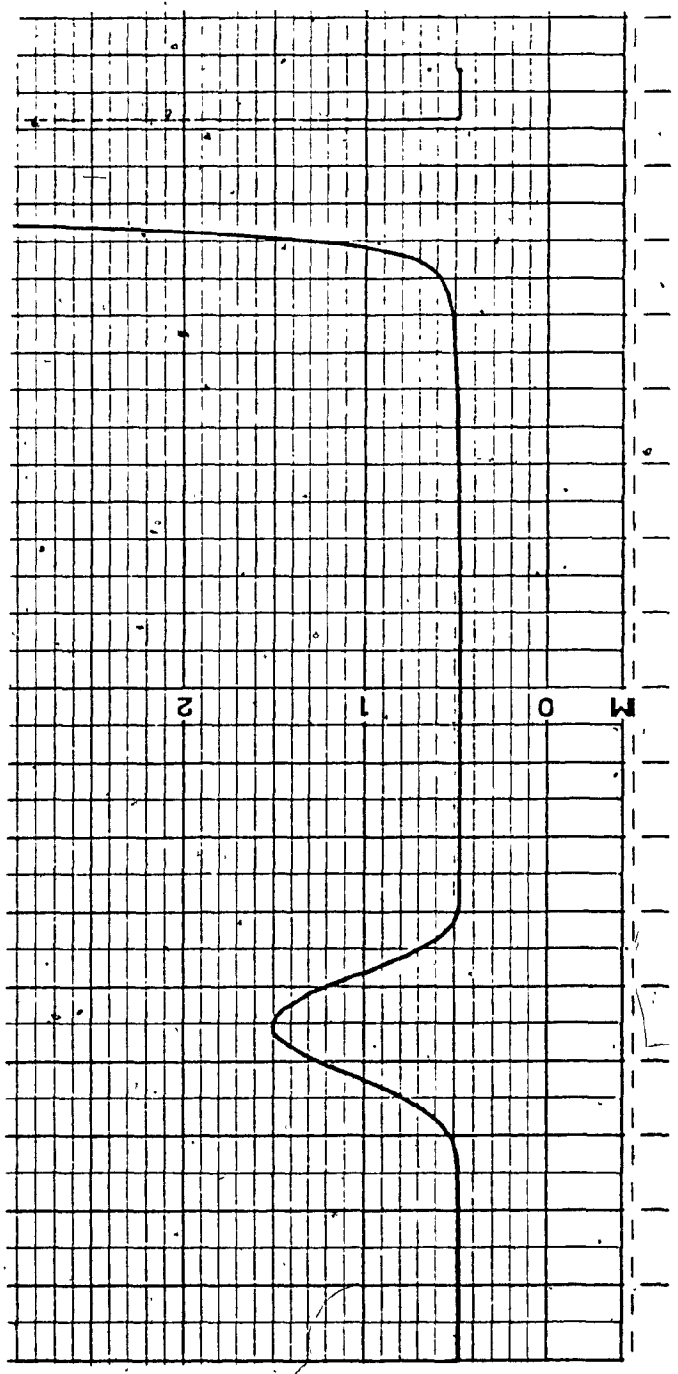


Figure 80 Chromatogram of Methoxychlor on a Newly Packed Column of 3.5% w/w OV-17  
Coated on Chromosorb G AW-DMCS at 230°C.

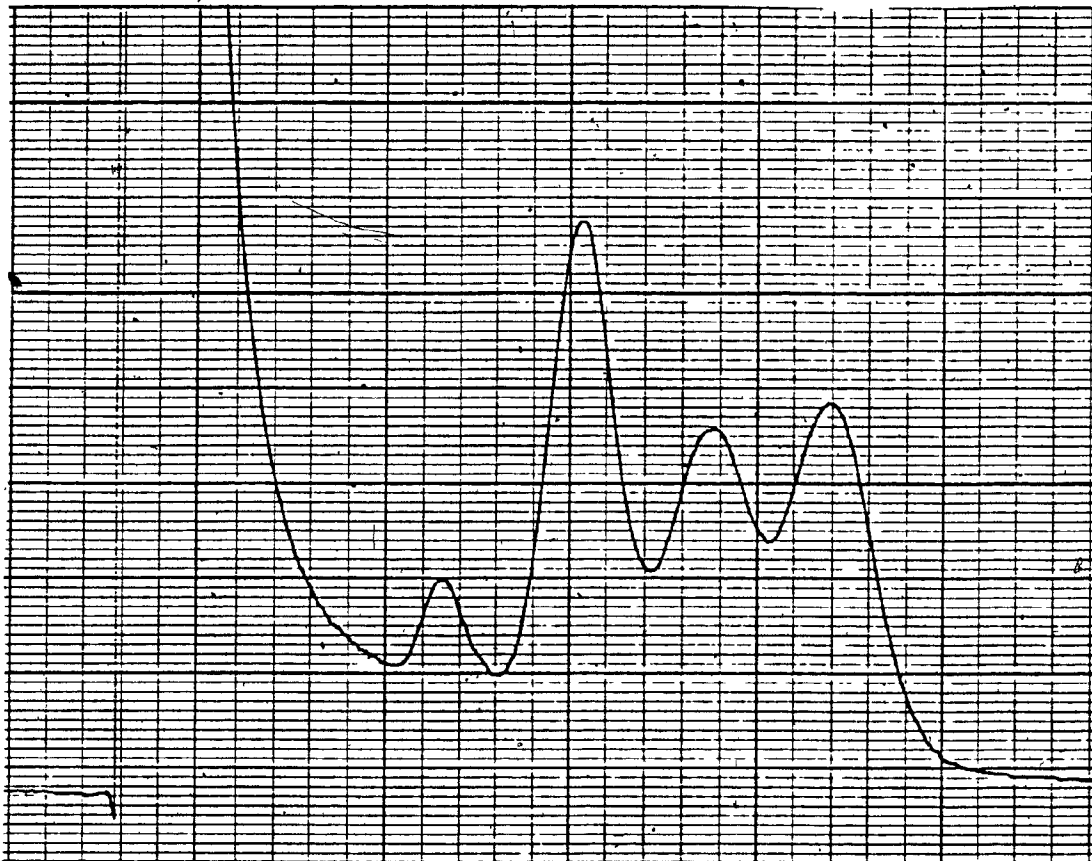


Figure 81 Chromatogram of Methoxychlor on 3.5% w/w OV-17  
Coated on Chromosorb G AW-DMCS at 230°C, After  
the Column Was Reshaped.

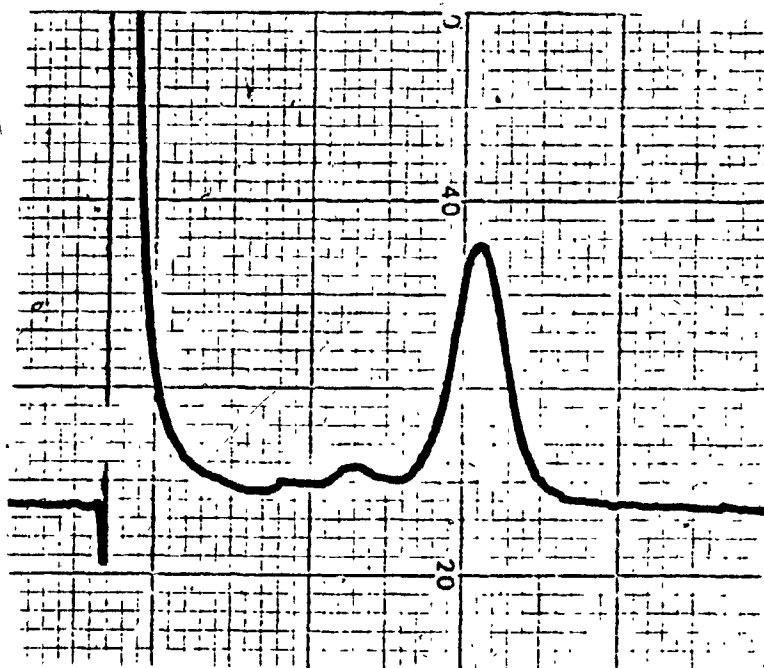


Figure 82 Chromatogram of Methoxychlor on 3.5%  
w/w OV-17 Coated on Chromosorb  
G-AW-DMCS at 240°C, After Reshaping  
and Priming

a consequence of column bending which damaged the packing.

#### 4.0 CONCLUSIONS

Chromosorb W HP was the best W support for the analysis of dieldrin, while W NAW was the poorest. Differences among Chromosorbs 750, W AW-DMCS and W AW were small and depended on column temperature, sample size and the history of the columns.

Chromosorbs W AW-DMCS and W HP were the least adsorptive supports towards methoxychlor from the temperature studies, but the good performance of W HP was not confirmed by the concentration tests. The 750 support was the poorest for the analysis of methoxychlor. W NAW was moderately adsorptive. The behaviour of W AW was erratic from test to test, and was dependent on the history of the column.

Chromosorb G NAW was the best G support for the analysis of dieldrin. There were no discernible differences among G AW, G HP and G AW-DMCS, except that G AW-DMCS was about equal to, or slightly better than G NAW for the highest concentration of dieldrin that was tested, i.e. 40 µg. Chromosorb G NAW was also the least adsorptive G support towards methoxychlor. Differences among G AW, G HP and G AW-DMCS were small.

All P supports were virtually equivalent in their adsorptive behaviour towards dieldrin. The P supports catalyzed the decomposition of methoxychlor, and as a result these supports could not be used for the analysis of this compound.

A good correlation was found between the slopes of calibration curves and adsorptivity of supports. This suggests the possibility of determining relative support adsorptivities by a comparison of the slopes of calibration curves.

The overall trends for the thermograms obtained with dieldrin, using the FID, were small increases in peak area responses with increasing column temperatures, with few exceptions. Similarly, the overall trends of the thermograms obtained with methoxychlor using the FID were increases in peak area responses with increasing column temperatures, but, the increases were more dramatic compared to what was obtained for dieldrin. The increase in response with column temperature must have been due to decreasing adsorptivity of the support active sites as well as sample priming effects.

The thermograms gave strong evidence that the physical properties of the coated supports changed continuously from temperature to temperature, and run to run. The validity of any comparisons of liquid phase coated supports depended on the immediate prior history of the columns.

The overall trends of the thermograms obtained with both dieldrin and methoxychlor using the ECD were large decreases in peak area responses with increasing column temperatures. This was not due to any column effects. It was attributed to saturation of the ECD response by the bleeding liquid phase. The ability of the ECD to respond to the sample was greatly influenced by bleeding or degradation of the electron affinitive liquid phase material used as stationary phase. At high column temperatures, the signal of the detector becomes dominated by the extraneous bleeding liquid phase entering the detector cell. The amount of bleeding of the liquid phase was affected by the type of support on which the liquid phase was coated. In fact, the order of

the column temperatures at which bleeding was first noticed as indicated by a rise in the recorder baseline, followed closely the order of adsorptivity. For columns heated to the same temperature, increased bleeding meant that new active sites were exposed resulting in increased adsorption.

Glass tubing was found to be less adsorptive than copper, aluminum, nickel or stainless steel tubings for both dieldrin and methoxychlor analyses. All metal tubings were relatively poor except for nickel, which was comparable to glass for the analysis of methoxychlor. Copper tubing caused degradation of methoxychlor.

It was shown that it is not possible to obtain meaningful comparison of supports by carrying out a single set of tests under any one set of conditions. Long ranging, detailed studies under various conditions are needed to obtain useful adsorptivity data.

Methoxychlor was shown to undergo catalytic decomposition on 3.5% w/w QV-17 coated Chromosorb supports. The decomposition can be reduced by considerable priming of the column with dieldrin and/or methoxychlor.

The results of this study differed from those obtained by Setiawan (125)\* for lindane and aldrin (Section 1.15, p. 70), but this is not surprising since:

- (i) the different pesticides tested could result in different solute - support - liquid phase interactions occurring,
- (ii) different sample size ranges used could have resulted in different column behaviour,
- (iii) dieldrin and methoxychlor were retained by the columns for longer times than lindane and aldrin which could

again have affected amounts of interactions that occurred between pesticides and supports/liquid phases.



## 5.0 SUGGESTIONS FOR FURTHER WORK

- (i) Since it was determined that the physical properties of the columns varied from temperature to temperature and run to run, due to liquid phase bleed and sample priming, it is suggested that instead of carrying out complete temperature runs on each column, all columns should be examined first at the lowest temperatures of interest before proceeding to higher temperatures. Furthermore, new columns should be used for each set of tests (temperature or concentration), and each compound examined. In this way, the "real" adsorptive properties of the columns, in the form in which they were prepared, would be examined and not the altered properties of the columns (due to liquid phase bleed and sample priming).
- (ii) The different families of supports should be compared to one another under conditions of equal liquid phase thicknesses on the support surfaces. This will ensure that any deactivation due to the liquid phase will be equal for all the different families of supports.
- (iii) The least polar liquid phase capable of efficient column operation should be used so that the adsorptive properties of the supports are not masked by liquid phase deactivation. Also glass tubing should be used in building the columns.
- (iv) The investigation of column effects on the GLC analysis of pesticides should be repeated using the ECD, under conditions where effect of liquid phase is negligible so that very small amounts of sample can be used. This will allow the detection of any

small amounts of sample degradation and column adsorption effects, which are masked by large sample sizes. Furthermore, to minimize the effect of liquid phase bleed on detector response, the lowest possible column temperatures should be used. Alternately, use should be made of a non-electron affinitive liquid phase.

- (v) Chromatographic conditions should be found to eliminate on-column decomposition of methoxychlor. The use of a tail reducer may be effective.
- (vi) Polymer coated supports are reported to be the most inert. A comparison should be made of these supports to diatomite supports for pesticide analyses.

REFERENCES

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1. Agro-Allied Industries and FAO, Pesticides in the modern world, New Gate Press, London, England, 1972, p.1.
2. J. Sherma, CRC Critical Reviews in Analytical Chemistry 3: 301(1973).
3. R.L. Metcalf, Pesticides in the environment, vol. 1, part 1, R.W. Stevens, ed. Marcel Dekker, New York, 1971, p. 83.
4. G.T. Brooks, Pesticide chemistry in the 20th century, J.R. Plimmer, ed. ACS Symposium Series 37, American Chemical Society, Washington D.C., 1977, p. 1.
5. N. Brenner and R.J. Olson, The practice of gas chromatography, L.S. Ettre, and A. Zlatkis, ed. John Wiley and Sons, New York, 1967, p. 3.
6. D. Ambrose, Gas chromatography, 2nd ed. Butterworths, London, England, 1971, p. 2.
7. O.E. Schupp, Technique of organic chemistry, vol. 13, E.S. Perry and A. Weissberger, ed. Interscience Publishers, Toronto, Canada, 1968, p. 3.
8. R.P.W. Scott and D.W. Grant, Analyst, 89: 179 (1964).
9. A.J.P. Martin and R.L.M. Synge, Biochem. J., 35: 1358 (1941).
10. A.T. James and A.J.P. Martin, Analyst, 77: 915 (1952).
11. A. Bevenue, Analytical methods for pesticides, plant growth regulators and food additives, vol. 1, A. Zweig, ed. Academic Press, New York, 1963, p. 190.
12. R.L. Grob, Modern practice of gas chromatography, John Wiley and Sons, New York, 1977, p. 71.

13. H. Purnell, Gas chromatography, John Wiley and Sons, New York, 1962, p. 71.
14. J.J. van Deemter, F.J. Zuiderweg and A. Klinkenberg, Chem. Eng. Sci., 5: 271 (1956).
15. J.C. Giddings, Anal. Chem., 34: 1186 (1962).
16. C. Horvath, The practice of gas chromatography, L.S. Ettre and A. Zlatkis, ed. John Wiley and Sons, New York, 1967, p. 152.
17. D.M. Ottenstein, Advances in chromatography, vol. 3, J.C. Giddings and R.A. Keller, ed. Marcel Dekker, New York, 1966, p. 137.
18. D.M. Ottenstein, J. of G.C., 1: 11 (1963).
19. D.M. Ottenstein, J. Chromatogr. Sci., 11: 136 (1973).
20. H.S. Knight, Anal. Chem., 30: 2030 (1958).
21. J.C. Giddings, Anal. Chem., 35: 1999 (1963).
22. R.G. Scholz and W.W. Brandt, Third international gas chromatography symposium, N. Brenner, J.E. Callin and M.D. Weiss, ed. Academic Press, New York, 1962, p. 7.
23. R. Roman, C.H. Yates, J.F. Millar, J. Chromatogr. Sci., 15: 555 (1977).
24. H. Brotell, H. Ehrsson, O. Gyllenhaal, J. Chromatog. 78: 293 (1973).
25. Johns-Manville Bulletin FF-102, Diatomite aggregates for gas chromatography, 22 East 40 St., New York, 10016.
26. A.I.M. Keulemans and A. Kwantes, Analysis of volatile organic compounds by means of vapour-phase chromatography, Proc., 4th, World Petrol. Congr. Rome, 1955.

27. M. Dimbat, P.E. Porter and F.H. Stross, Anal. Chem., 28: 290 (1956).
28. Johns-Manville Bulletin FF-121, Chromosorb G, 22 East 40 St., New York, 10016.
29. W.J. Baker, E.W. Lee and R.F. Wall, Gas chromatography, H. Nobels, R.F. Wall and N. Brenner, ed. Academic Press, New York, 1961, p. 21.
30. A.M. Filbert and M.L. Hair, Advances in chromatography, A. Zlatkis, ed. Preston Technical Abstracts, Evanston, Illinois, 1969, p. 51.
31. J.M. Harper and E.G. Hammond, Anal. Chem., 37: 490 (1965).
32. J.H. Purnell, Ann. N.Y. Acad. Sci., 72: 592 (1959).
33. R.H. Perrett and J.H. Purnell, J. Chromatog., 7: 455 (1962).
34. G. Blandenet and J.P. Robin, J. of G.C., 2: 225 (1964).
35. P.S. Roller and G. Ervin, J. Am. Chem. Soc., 62: 468 (1940).
36. R.K. Iler, The colloid chemistry of silica and silicates, Cornell Univ. Press, Ithaca, N.Y. 1955, p. 238.
37. L.J. Papa, Dissertation Abst., 24: 3078 (1964).
38. V. Kusy, Anal. Chem., 37: 1748 (1965).
39. B.L. Karger and W.D. Cooke, Advances in chromatography, vol. 1, J.C. Giddings and R.A. Keller, ed. Marcel Dekker, New York, 1965, p. 327.
40. R.A. Keller and G.H. Stewart; Anal. Chem., 34: 1834 (1962).
41. E. Cremer and H.F. Huber, Gas Chromatography, N. Brenner, J.E. Callen and M.D. Weiss, ed. Academic Press, New York, 1962, p. 169.

42. J. Tadmor, Anal. Chem., 36: 1565 (1964).
43. D.M. Ottenstein, J. of G.C., 6: 129 (1968).
44. E.D. Smith and R.D. Radford, Anal. Chem., 33: 1160 (1961).
45. E.C. Horning and W.J.A. Van den Heuvel, Advances in chromatography, vol. 1, J.C. Giddings and R.A. Keller, ed. Marcel Dekker, New York, 1966, p. 153.
46. A. Zlatkis, S.Y. Ling and H.R. Kaufman, Anal. Chem., 31: 945 (1959).
47. B.J. Gudzinowicz and S.J. Clark, J. of G.C., 3: 147 (1965).
48. J. Bohemen, S.H. Langer, R.H. Perrett and J.H. Purnell, J. Chem. Soc., 2444 (1960).
49. G.A. Howard and A.J.P. Martin, Biochem. J., 46: 532 (1950).
50. D.T. Sawyer and J.K. Barr, Anal. Chem., 34: 1518 (1962).
51. J.J. Kirkland, Gas chromatography, L. Fowler, ed., Academic Press, New York, 1963, p. 77.
52. F.J. Kabot and L.S. Ettre, J. of G.C., 2: 21 (1964).
53. G.V. Filonenko, V.A. Tertykh, V.V. Pavlov, G. Ya Guba and A.N. Korol, J. Chromatog., 209: 385 (1981).
54. E.C. Ormerod and R.P.W. Scott, J. Chromatog., 2: 65 (1959).
55. G. Blandenet and J.P. Robin, J. of G.C., 4: 288 (1966).
56. P.P. Wickramanayake and W.A. Aue, J. Chromatog., 210: 133 (1981).
57. W.J.A. Van den Heuvel, W.L. Gardinger and E.C. Horning, Anal. Chem., 35: 1745 (1963).
58. M.K. Withers, J. of G.C., 2: 345 (1964).
59. D.M. Ottenstein and D.A. Bartley, J. Chromatogr. Sci., 9: 673 (1971).

60. J.A. Jönsson, L. Mathiasson and Z. Suprynowicz, J. Chromatog., 207: 69 (1981).
61. J. Serpinet, Anal. Chem., 48: 2264 (1976).
62. E.R. Adlard, Vapour phase chromatography, D.H. Desty, ed. Butterworths, London, England, 1956, p. 98.
63. R.L. Martin, Anal. Chem., 33: 347 (1961).
64. N.C. Saha and J.C. Giddings, Anal. Chem., 37: 822 (1965).
65. J.C. Giddings, Anal. Chem., 34: 458 (1962).
66. O.E. Schupp, Technique of organic chemistry, vol. 13, E.S. Perry and A. Weissberger, ed., Interscience Publishers, Toronto, Canada, 1968, p. 200.
67. R.A. Keller, R. Bate, B. Costa and P. Forman, J. Chromatog., 8: 157 (1962).
68. W. Gerrard, S.J. Hawkes and E.F. Mooney, Gas Chromatography, 1960 symposium, R.P.W. Scott, ed. Butterworths, Washington, p. 199.
69. S.T. Preston, J. of G.C., 1: 8 (1963).
70. J.G. Keppler, G. Dijkstra and J.A. Schols, Vapour phase chromatography, D.H. Desty ed. Butterworths, London, England, 1956, p. 222.
71. G. Dijkstra, Vapour phase chromatography, D.H. Desty, ed. Butterworths, London, England, 1956, p. 275.
72. A. Kwantes, Vapour phase chromatography, D.H. Desty, ed., Butterworths, London, England, 1956, p. 274.
73. S. Dal Nogare and L.W. Safranski, Anal. Chem., 30: 894 (1958).
74. J.C. Hawkes, Vapour phase chromatography, D.H. Desty, ed. Butterworths, London, England, 1956, p. 266.

75. G.W. Taylor and A.S. Dunlop, Chromatography, V.J. Coates, H.J. Noebels and I.S. Fagerson, ed. Academic Press, New York, 1958, p. 73.
76. L. Guild, S. Bingham and F. Aul, Gas chromatography, D.H. Desty, ed. Butterworths, London, England, 1958, p. 226.
77. G.A.P. Tvey, Vapour phase chromatography, D.H. Desty, ed. Butterworths, London, England, 1959, p. 275.
78. H.S. Knight, Principles and practice of gas chromatography, John Wiley and Sons, 1959.
79. R. Komers and M. Cerny, J. Chromatog., 207: 345 (1981).
80. A.E. Coleman, J. Chromatogr. Sci., 11: 198 (1973).
81. A.F. Williams, Gas chromatography, 1960 symposium, R.P.W. Scott, ed. Butterworths, London, England, 1960, p. 210.
82. H. Rotzsche, Gas chromatography, 1960 symposium, R.P.W. Scott, ed. Butterworths, London, England, 1960, p. 210.
83. W.R. Supina, The packed column in gas chromatography, Supelco Inc., Bellefonte, Pennsylvania, 1974, p. 105.
84. D.C. Fenimore, J.H. Whiteford, C.M. Davis, and A. Zlatkis, J. Chromatogr., 104: 8 (1977).
85. H. Beckman and A. Bevenue, J. Chromatog., 10: 231 (1963).
86. H. Beckman and A. Bevenue, J. Chromatog., 12: 109 (1963).
87. K.I. Beyman and K.E. Elgar, Analyst, 91: 143 (1966).
88. J.E. Arnold and H.M. Fales, J. of G.C. 3: 131 (1965).
89. R.H. Groth and T.B. Doyle, J. of G.C., 6: 138 (1968).



90. A. Bevenue, Analytical methods for pesticides, plant growth regulators and food additives, vol. 5, G. Zweig; ed. Academic Press, New York, 1963, p. 7.
91. W.R. Supina, The packed column in gas chromatography, Supelco Inc., Bellefonte, Pennsylvania, 1974, p. 110.
92. D.E. Martire, Advances in analytical chemistry and instrumentation, vol. 6, J.H. Purnell, ed. Interscience Publishers, New York, 1967, p. 93.
93. W.R. Supina, The packed column in gas chromatography, Supelco Inc., Bellefonte, Pennsylvania, 1974, p. 22.
94. Johns-Manville Bulletin FF-114, Chromosorb P and Chromosorb W (AW-DMCS Treated), 22 E. 40 St., New York, 10016.
95. Johns-Manville Bulletin FF-149, High performance Chromosorb G and W for steroids, 22 E 40 St., New York, 10016.
96. Chromatographic Specialties Bulletin, Chromosorb 750, Brockville, Ontario.
97. A. Bevenue, J.N. Ogata and H. Beckman, J. Chromatog., 35: 17 (1968).
98. E.D. Smith, J.M. Oathout and G.T. Cook, J. Chromatogr. Sci. 8: 291 (1970).
99. J. Krupcik, K. Tesarik, O. Liska, J. Nemeč, Y.P. Duchesne, Chromatographia, 5: 252 (1972).
100. J.J. Sullivan, Modern practice of gas chromatography. R.L. Grob, e.d. John Wiley and Sons, New York, 1977, P. 244.
101. A. Karmen, Advances in chromatography, vol. 2, J.C. Giddings and A. Keller, ed. Marcel Dekker Inc., New York, 1966, p. 295.

102. Shimadzu Gas Chromatograph Instruction Manual, GC 6AM Series, Shimadzu Seisakusho Ltd., Kyoto, Japan.
103. B.J. Gudziniowicz, The practice of gas chromatography, L.S. Ettre and A. Zlatkis, ed., John Wiley and Sons, New York, 1967, p. 254.
104. E.R. Adlard, CRC Critical Reviews in Analytical Chemistry, 5: 1 (1975).
105. J.E. Lovelock, Anal. Chem., 35: 474 (1963).
106. C.F. Poole, Chem. Ind., 5: 479 (1976).
107. E.D. Pellizzari, Chromatog. Rev., 98: 324 (1974):
108. M. Krejcl and M. Dressler, Chromatog. Rev., 13: 1 (1970).
109. E.R. Adlard, CRC Critical Reviews in Analytical Chemistry, 5: 13 (1975).
110. Shimadzu Gas Chromatograph Instruction Manual, GC 6 AM Series, Shimadzu Seisakusho Ltd., Kyoto, Japan.
111. P. Devaux and G. Guiochon, Advances in gas chromatography, A. Zlatkis, ed., Preston Technical Abstracts, Evanston, Illinois, 1967, p. 64.
112. W.E. Wentworth and E. Chen, Advances in gas chromatography, A. Zlatkis, ed., Preston Technical Abstracts, Evanston, Illinois, 1967, p. 10.
113. W.A. Aue and S. Kapila, J. Chromatogr. Sci., 11: 255 (1973).
114. J. Novak, J.G. Ruzickova, S. Wicar, and J. Janak, Advances in chromatography, A. Zlatkis, e.d., Preston Technical Abstracts, Evanston, Illinois, 1971, p. 75.

115. M.J. de Faubert Maunder, H. Egan and J. Roburn, Analyst, 89: 157 (1964).
116. H.B. Pionke and G. Chesters, Soil Sci. Soc. Amer. Proc., 32: 749 (1968).
117. G. Zweig, ed. Analytical methods for pesticides plant growth regulators and food additives, vol. 1-10, Academic Press, New York, 1963-1978.
118. R.L. Grob, ed. Chromatographic analysis of the environment, Marcel Dekker Inc., New York, 1975.
119. E.J. Bonelli, H. Hartmann and K.P. Dimick, Publication W-110, Wilkens Instrument and Research, Inc., Walnut Creek, California, 1963.
120. J.F. Thompson, A.C. Walker and R.F. Mosemann, J. of AOAC., 52: 1263 (1969).
121. M. Suzuki, Y. Yamato and T. Watanabe, J. of AOAC, 58: 297 (1973).
122. M.L. Schafer, J.T. Peeler, W.S. Gardner and J.E. Campbell, Environ. Sci. Tech., 3: 1261 (1969).
123. J.F. Thompson, J.B. Mann and A.O. Apodaca, J. of AOAC., 58: 1037 (1973).
124. I.S. Taylor, J. Chromatogr., 52: 141 (1970).
125. B. Setiawan, M.Sc. Thesis, Concordia University, 1981.

APPENDIX A

COMPARISON OF THE ADSORPTIVE PROPERTIES OF THE CHROMOSORB  
SUPPORTS AT ONE COLUMN TEMPERATURE AND AT TWO DIFFERENT  
SAMPLE SIZES. ALL TESTS CARRIED OUT DURING A TWO-DAY PERIOD

The adsorptive properties of the Chromosorb W, P and G supports, and Chromosorb 750 were compared at one column temperature and at two different sample sizes, 1  $\mu\text{g}$  and 30  $\mu\text{g}$ , using the pesticides, dieldrin and methoxychlor.

The columns used for this study were columns A to L listed in Table VI, p. 83, which already had been used extensively. The column temperature used for methoxychlor was 250°C, and for dieldrin, 230°C. The experimental conditions are given in Table XXIV for methoxychlor and dieldrin.

All columns were studied within a period of two days. Multiple injections (3 - 5) of each pesticide were made. The peak area of each peak eluted was calculated and the average value was determined. The results for Chromosorbs W, P, G and 750 are given in Table XXV for dieldrin, and in Table XXVI for methoxychlor.

(a) W Supports - Dieldrin

According to the results given in Table XXV, at the 1  $\mu\text{g}$  level, the adsorptive properties of the W supports, including Chromosorb 750, increased in the following order:

W NAW = 750 < W AW-DMCS = W AW < W HP

At the 30  $\mu\text{g}$  level, the order of increasing adsorption was:

W AW  $\leq$  W AW-DMCS  $\leq$  750 = W HP = W NAW



TABLE XXV

COMPARISON OF ADSORPTIVE PROPERTIES OF CHROMOSORB  
SUPPORTS TOWARDS DIELDRIN - TWO DAY TESTS

SUPPORT	PEAK AREA, $\text{cm}^2$	
	1 $\mu\text{g}$ SAMPLE	30 $\mu\text{g}$ SAMPLE
W NAW	690	730
W AW	620	780
W AW-DMCS	620	760
W HP	520	730
750	680	730
G NAW	640	710
G AW	570	750
G AW-DMCS	620	700
G HP	570	730
P NAW	370	660
P AW	440	640
P AW-DMCS	480	650

TABLE XXVI      COMPARISON OF ADSORPTIVE PROPERTIES OF CHROMOSORB  
SUPPORTS TOWARDS METHOXYCHLOR - TWO DAY TESTS

SUPPORT	PEAK AREA, $\text{mm}^2$	
	1 $\mu\text{g}$ SAMPLE	30 $\mu\text{g}$ SAMPLE
W NAW	390	780
W AW	740	910
W AW-DMCS	720	850
W HP	580	940
750	620	790
G NAW	780	980
G AW	680	950
G AW-DMCS	710	870
G HP	550	950

There was no correlation between these results and those obtained previously (Section 3.5.1, p. 142). This was attributed to the changing column characteristics with continued use of the columns as had been shown to occur in Section 3.3, p. 108 in the thermogram results.

(b) W Supports - Methoxychlor

From the results given in Table XXVI, in the case of methoxychlor, the order of increasing adsorption for the Chromosorb W and 750 supports at the 1  $\mu$ g level was:

$$W \cdot AW \approx W \text{ AW-DMCS} \lesssim 750 \lesssim W \cdot HP < W \text{ NAW}$$

At the 30  $\mu$ g level the order of increasing adsorption was:

$$W \cdot HP \approx W \text{ AW} \lesssim W \text{ AW-DMCS} \lesssim 750 \approx W \text{ NAW}$$

Again here, there was little correlation between these results.

and those of Section 3.5.2. p. 146.

(c) G Supports - Dieldrin

From Table XXV it was seen that when dieldrin was used as the test sample, the order of increasing adsorption among the Chromosorb G supports at the 1  $\mu$ g level was:

$$G \text{ NAW} \lesssim G \text{ AW-DMCS} \lesssim G \text{ AW} \approx G \text{ HP}$$

At the 30  $\mu$ g level the order of increasing adsorption was:

$$G \text{ AW} \lesssim G \text{ HP} \lesssim G \text{ NAW} \lesssim G \text{ AW-DMCS}$$

At the 1  $\mu$ g level there was good agreement between the results above and those of Section 3.5.3, p. 149. In both series of tests, Chromosorbs G NAW and G AW-DMCS were found to be superior to Chromosorbs G AW and G HP. However, there was little agreement between the results at the 30  $\mu$ g level above and any previous findings.



## (d) G Supports-Methoxychlor

The results of Table XXVI indicated that when methoxychlor was used as the test sample, the order of adsorption among the Chromosorb G supports at the 1  $\mu$ g level was:

$$G \text{ NAW} \leq G \text{ AW-DMCS} \leq G \text{ AW} < G \text{ HP}$$

At the 30  $\mu$ g level, the order of adsorption was:

$$G \text{ NAW} \leq G \text{ AW} \approx G \text{ HP} \leq G \text{ AW-DMCS}$$

In both cases here, G NAW was found to be the least adsorptive of all the Chromosorb G supports, in agreement with previous results, Section 3.5.4, p. 152.

## (e) P Supports - Dieldrin

From Table XXV it was observed that when dieldrin was used as the test sample, the order of adsorption among the Chromosorb P supports at the 1  $\mu$ g level was:

$$P \text{ AW-DMCS} \leq P \text{ AW} \leq P \text{ NAW}$$

At the 30  $\mu$ g level the Chromosorb P supports displayed adsorptive properties very similar to one another. Since adsorption on the surface of the support is more likely to be detected for small sample sizes, the Chromosorb P supports displayed a difference in their adsorptive properties at the 1  $\mu$ g level.

The results at the 1  $\mu$ g level were not in agreement with those obtained in Section 3.5.5, p. 156;

APPENDIX BCOMPARISON OF THE ADSORPTIVE PROPERTIES OF COLUMN TUBING  
MATERIALS AT ONE COLUMN TEMPERATURE AND AT TWO SAMPLE SIZES  
- ONE DAY RUN

The adsorptive properties of various column tubing materials (glass, nickel, stainless steel, copper and aluminum) were compared at one column temperature and at two different sample sizes (1  $\mu\text{g}$  and 30  $\mu\text{g}$ ) using the pesticides dieldrin and methoxychlor. The columns used for this study were columns M to P, Table XIII, p. 90 and column C, Table VI, p. 83. The column temperature used for methoxychlor was 250°C, and for dieldrin, 230°C. The operating conditions are given in Table XXIV. All columns were studied in a period of one day. Multiple injections (3 - 5) of each pesticide were made of the sample sizes mentioned above. The results with both pesticides, for the various columns, are given in Table XXVII.

According to Table XXVII, the order of adsorption among the various column tubing materials, towards methoxychlor, at the 1  $\mu\text{g}$  level was:

Glass < Ni  $\leq$  Al  $\leq$  S.S.

At the 30  $\mu\text{g}$  level the order of adsorption was

Ni  $\approx$  Glass  $\leq$  Al  $\approx$  S.S.

There was good agreement between the above results and those of Section 3.8.2, p. 187. In both cases, glass and nickel tubings were found to be less adsorptive than aluminum and stainless steel.

When dieldrin was used as the test sample, the order of adsorption at the 1  $\mu\text{g}$  level was:

TABLE XXVII

COMPARISON OF ADSORPTIVE PROPERTIES OF COLUMN  
TUBING MATERIALS

COLUMN	PEAK AREA, mm <sup>2</sup>			
	METHOXYCHLOR		DIELDRIN	
	1 μg	30 μg	1 μg	30 μg
Glass	890	920	680	750
Nickel	760	940	700	740
Stainless Steel	720	850	620	760
Copper	-	-	710	750
Aluminum	720	870	640	710

Cu ≈ Ni ≈ Glass ≲ Al ≈ S.S.

At the 30 μg level, the order of adsorption was:

S.S. ≈ Cu ≈ Glass ≈ Ni ≈ Al

There was little correlation between these results and those of Section 3.8.1, p. 184.

APPENDIX CTHERMOGRAMS FOR DIELDRIN ON CHROMOSORBS W, P, G AND 750 COATED WITH3.5% W/W OV-17 USING THE FID

<u>Figure</u>		<u>Page</u>
18	Chromosorb W NAW	221
19	Chromosorb W AW	222
20	Chromosorb W AW-DMCS	223
21	Chromosorb W HP	224
22	Chromosorb 750	225
23	Chromosorb G NAW	226
24	Chromosorb G AW	227
25	Chromosorb G AW-DMCS	228
26	Chromosorb G HP	229
27	Chromosorb P NAW	230
28	Chromosorb P AW	231
29	Chromosorb P AW-DMCS	232

**Figure 18** Chromosorb W NAW

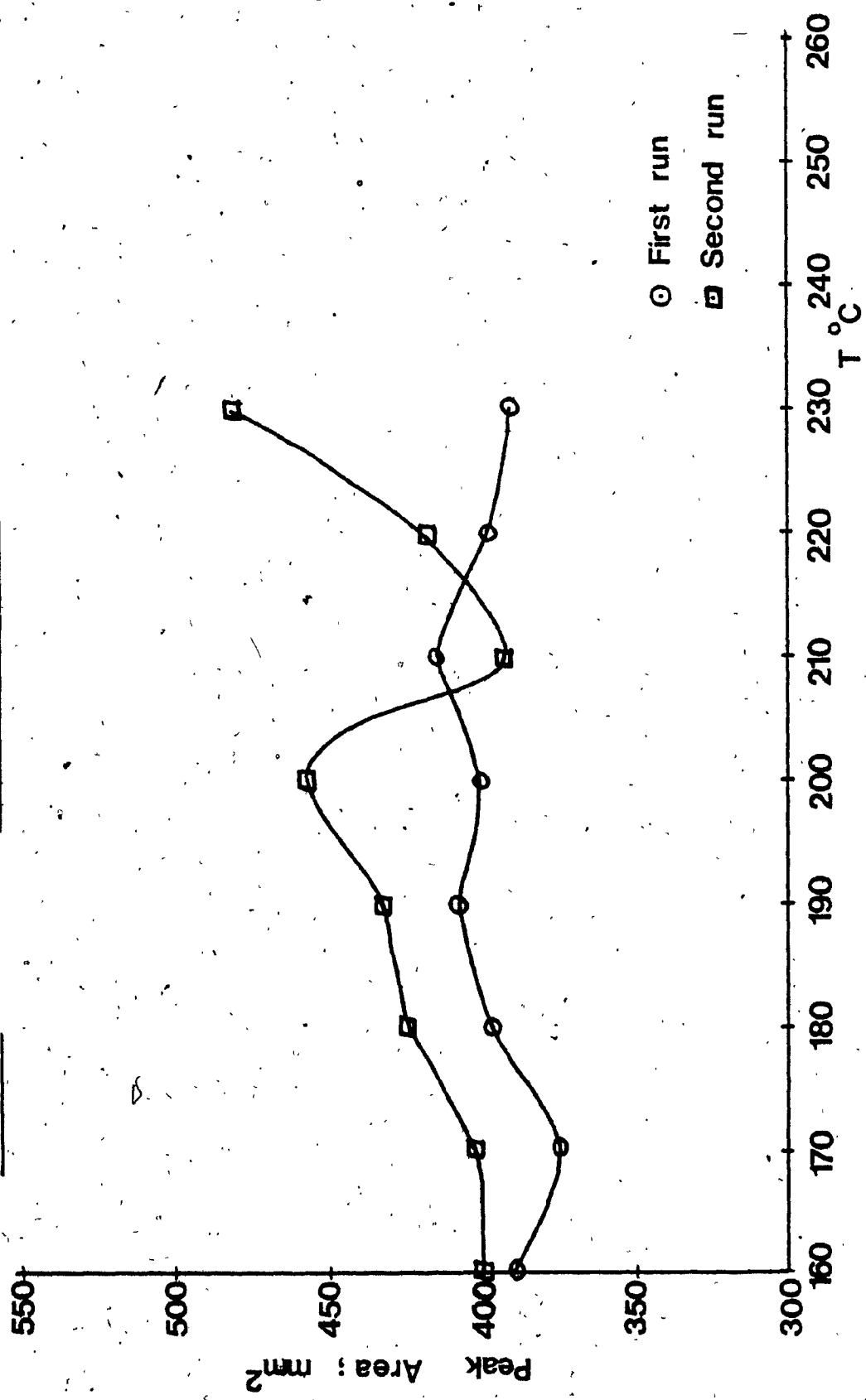


Figure 19 Chromosorb W AW

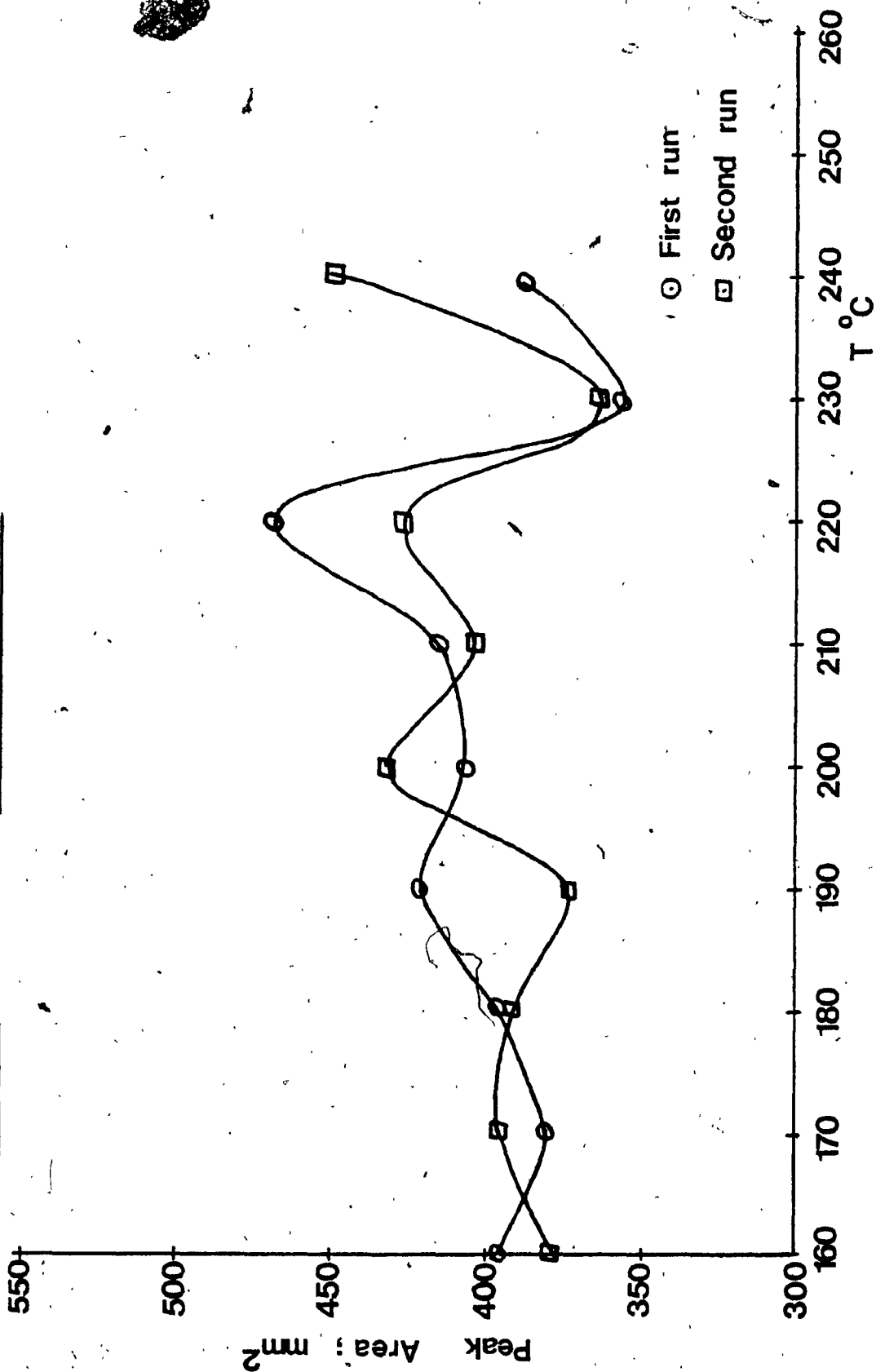


Figure 20 Chromosorb W AW-DMCS

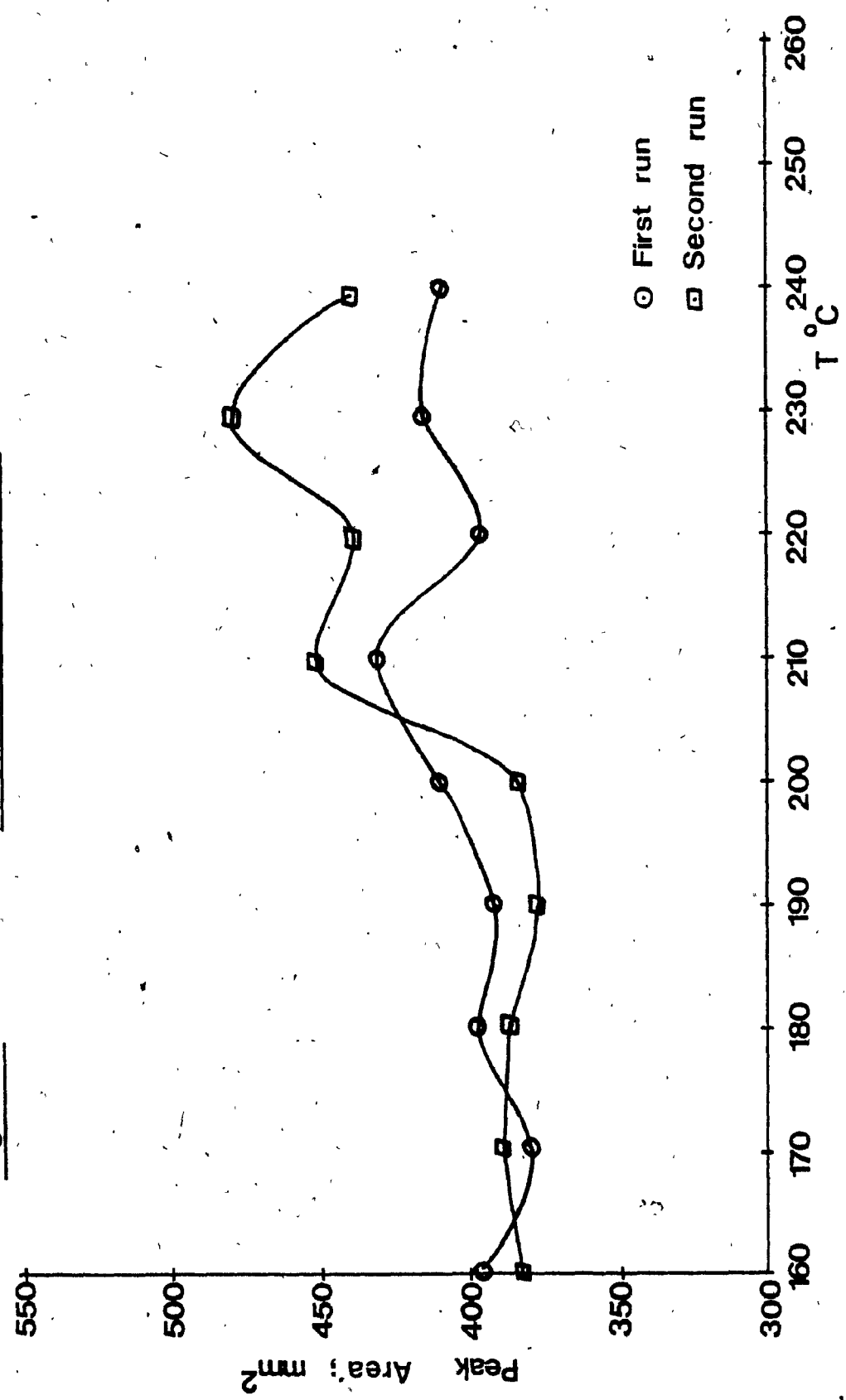




Figure 21 Chromosorb W HP

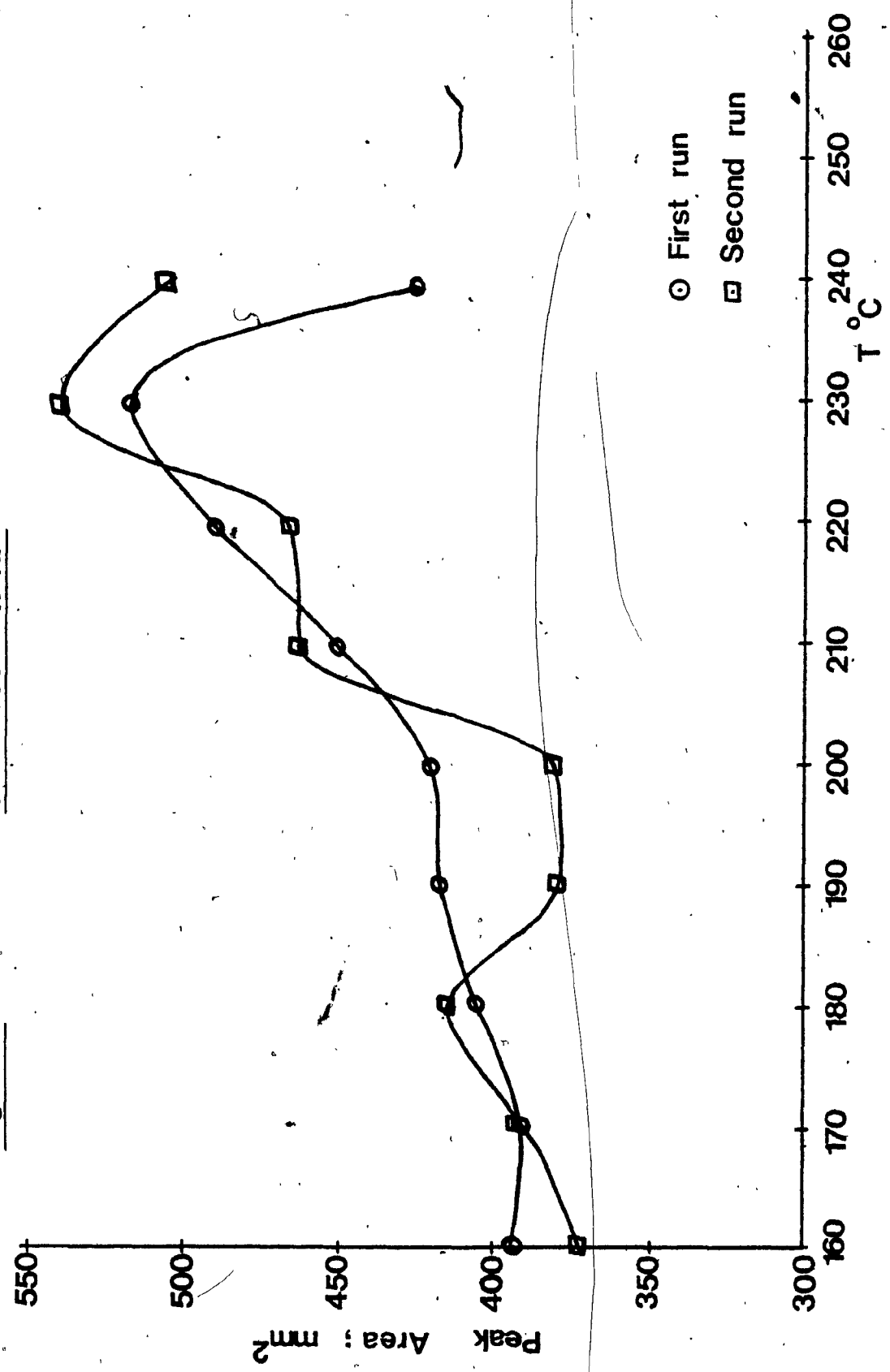
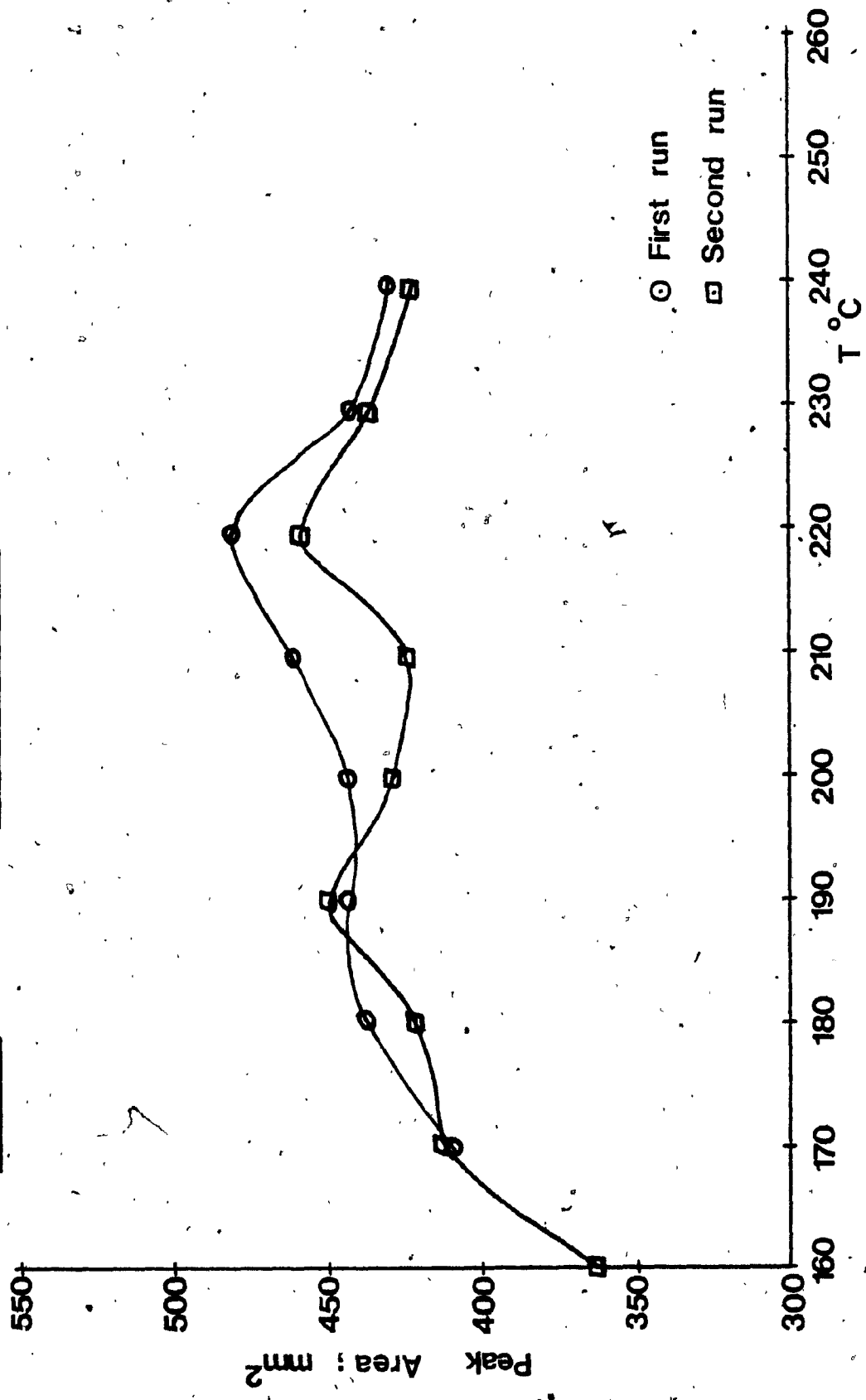


Figure 22 Chromosorb 750



Chromosorb G NAW

Figure 23

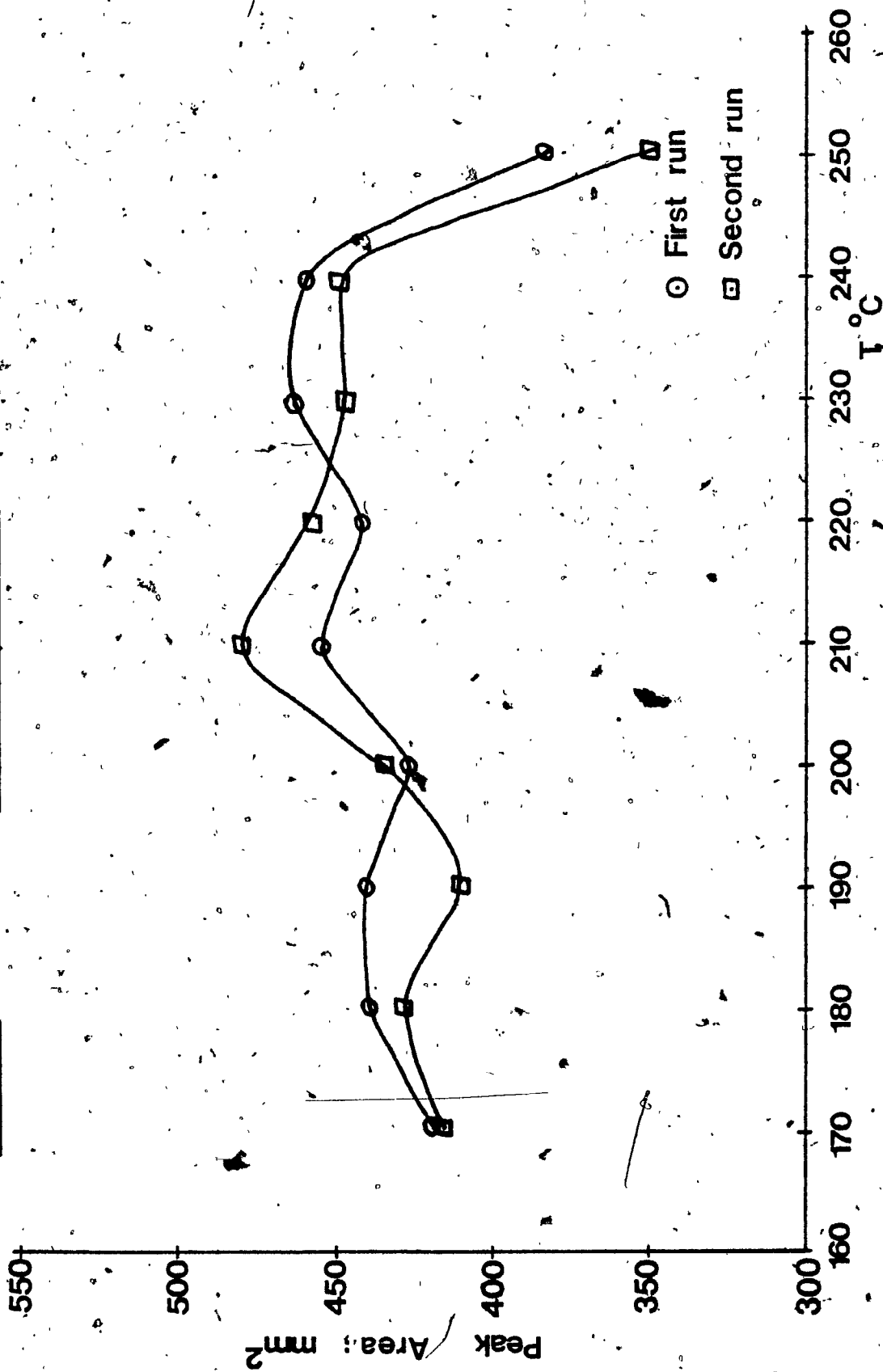
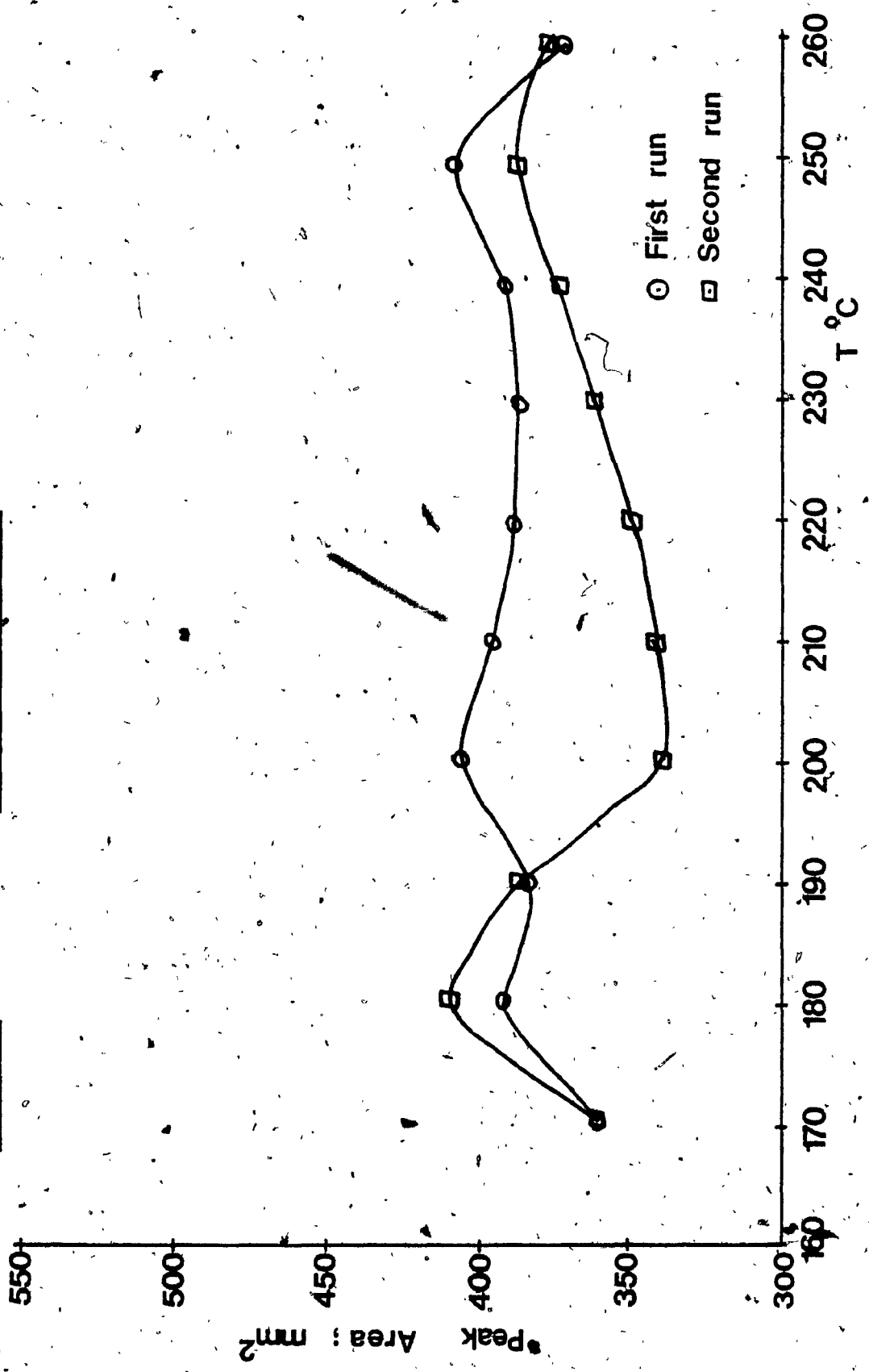
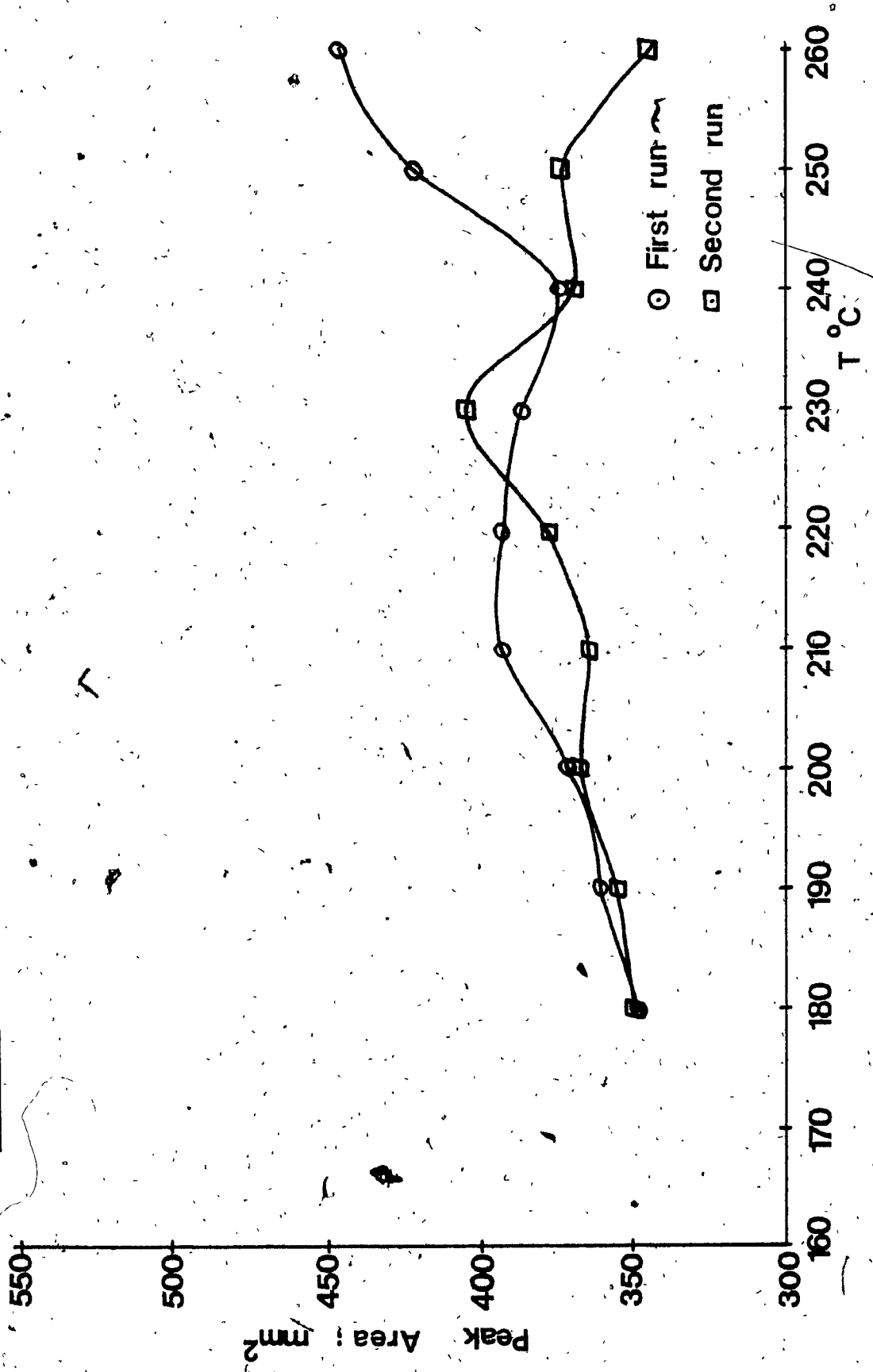


Figure 24 Chromosorb G AW



Chromosorb/G AW-DMCS

Figure 25



Chromosorb G HP

Figure 26

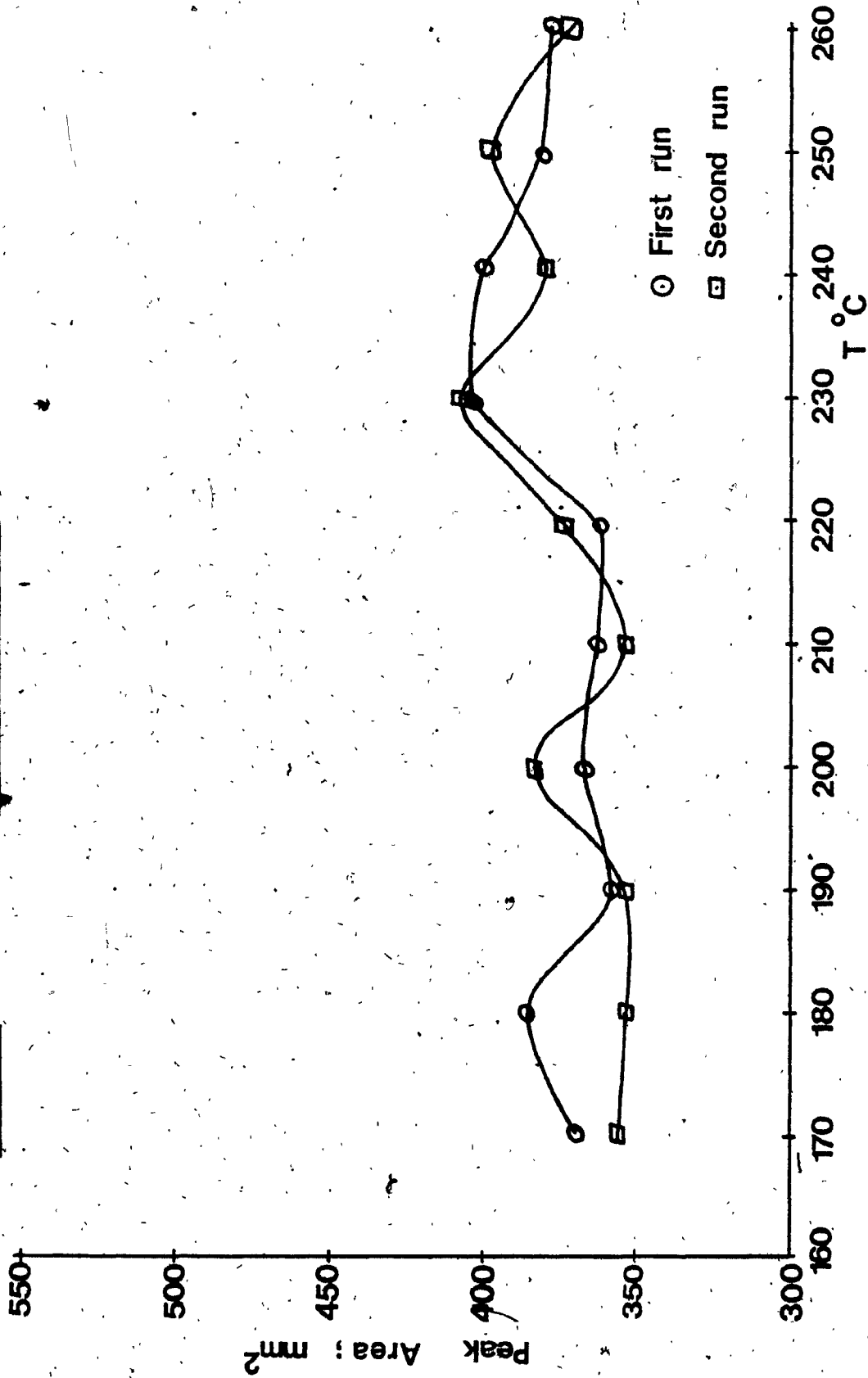


Figure 27 : Chromosorb P NAW

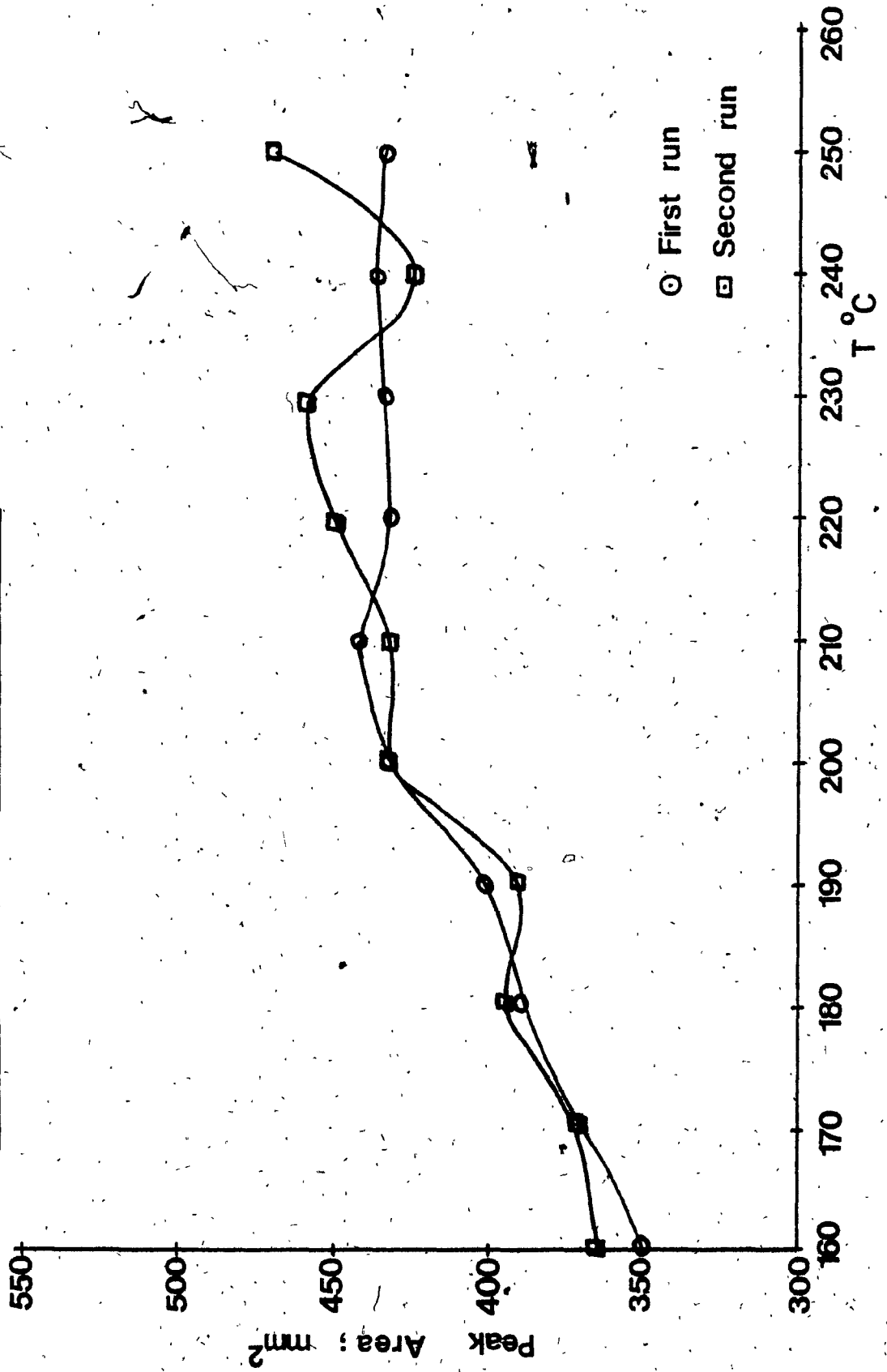
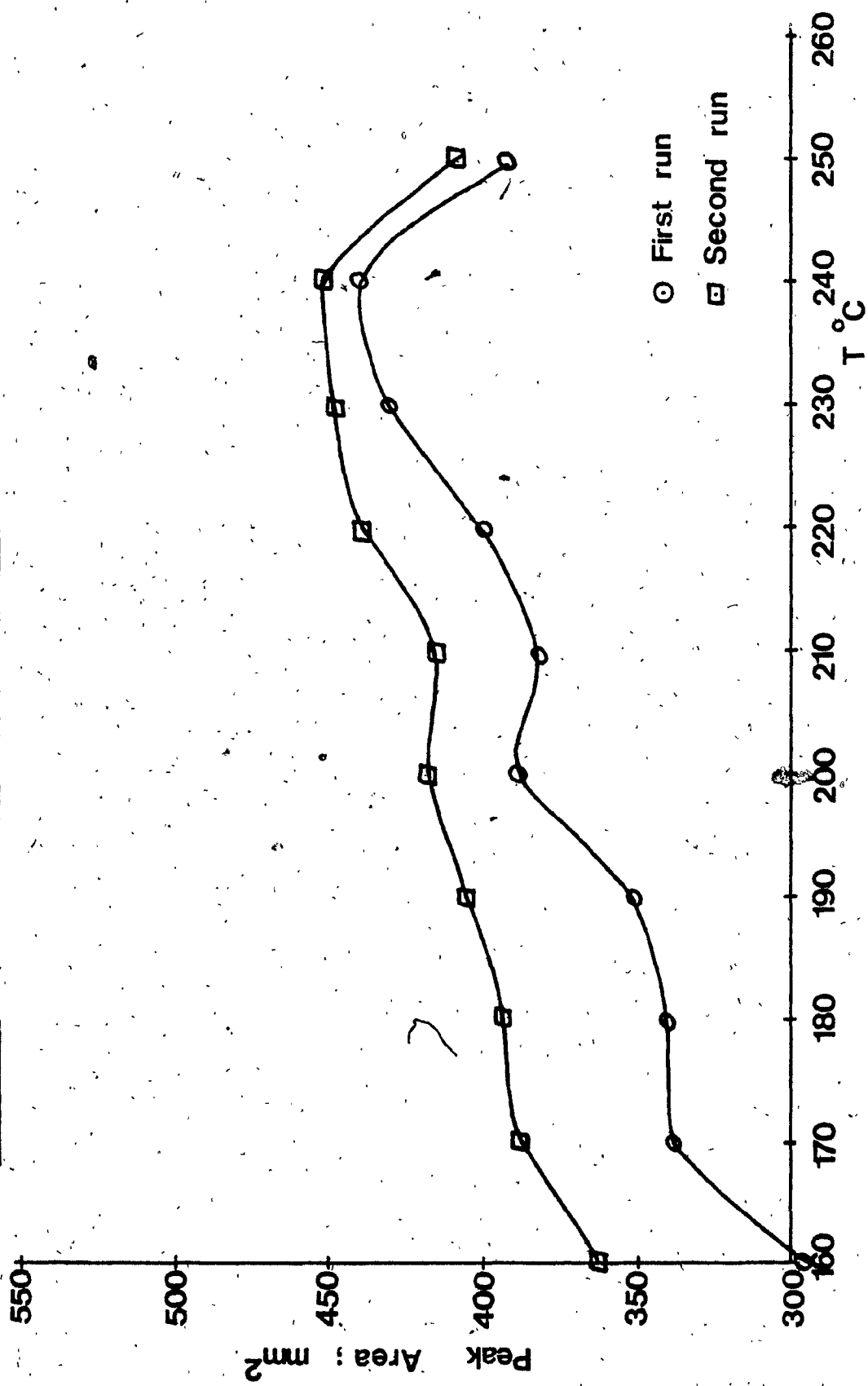
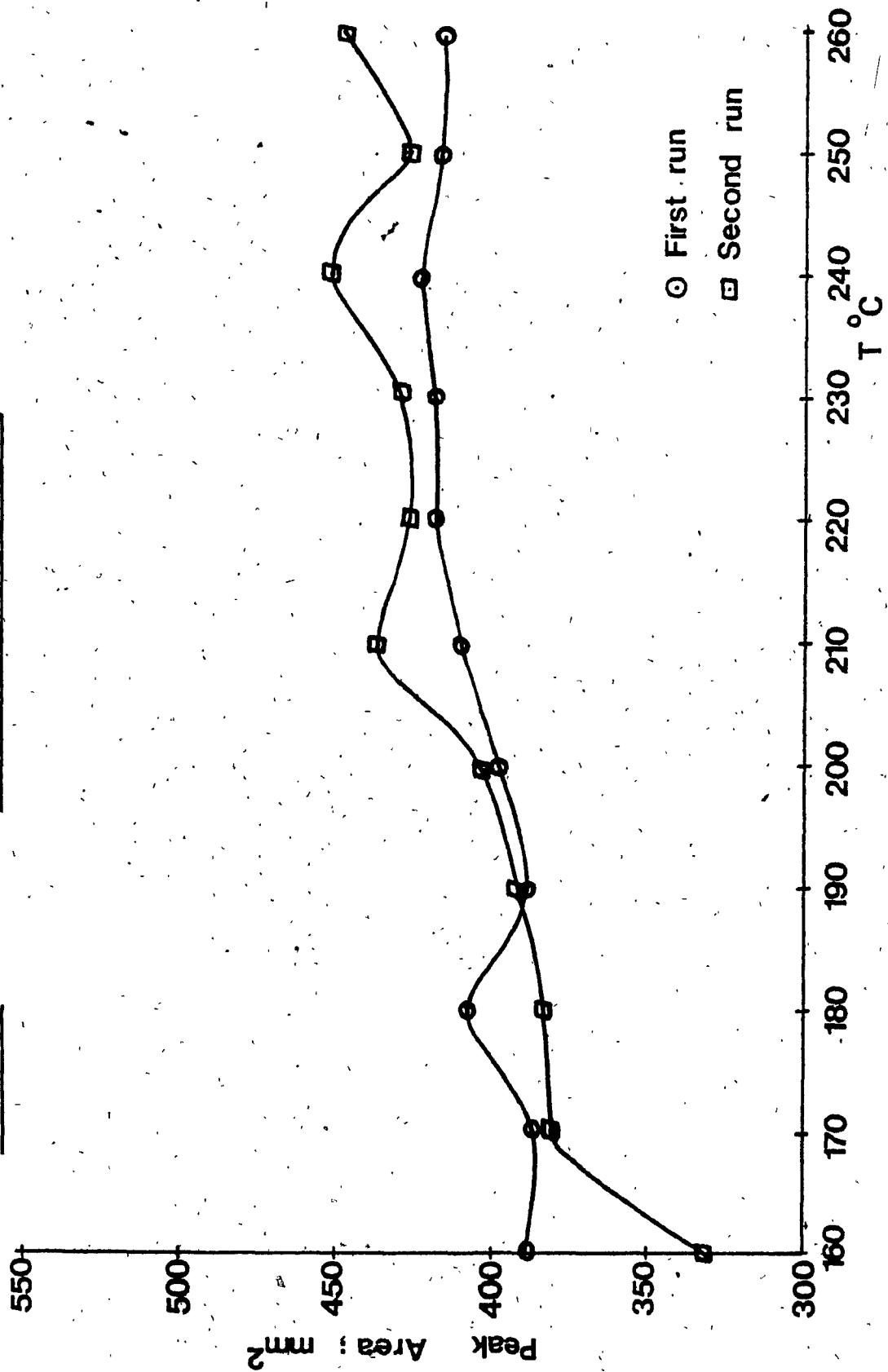


Figure 28 Chromosorb P AW



**Figure 29** Chromosorb P AW-DMCS



APPENDIX DTHERMOGRAMS FOR METHOXYCHLOR ON CHROMOSORBS W,P, G AND 750 COATED WITH  
3.5% W/W OV-17 USING THE FID

<u>Figure</u>		<u>Page</u>
30	Chromosorb W NAW	234
31	Chromosorb W AW	235
32	Chromosorb W AW-DMCS	236
33	Chromosorb W HP	237
34	Chromosorb 750	238
35	Chromosorb G NAW	239
36	Chromosorb G AW	240
37	Chromosorb G AW-DMCS	241
38	Chromosorb G HP	242

Figure 30

Chromosorb W NAW

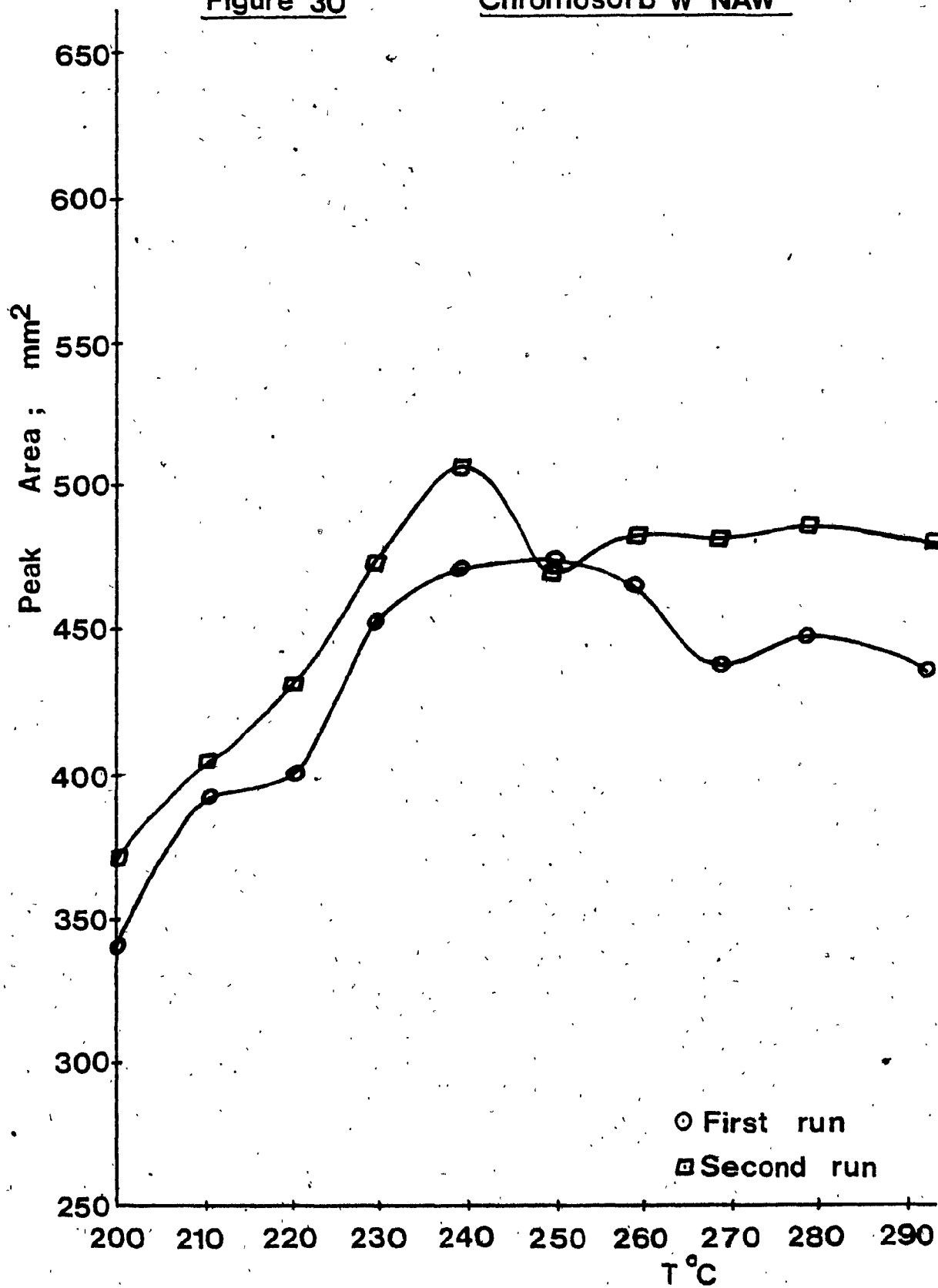


Figure 31

Chromosorb W AW

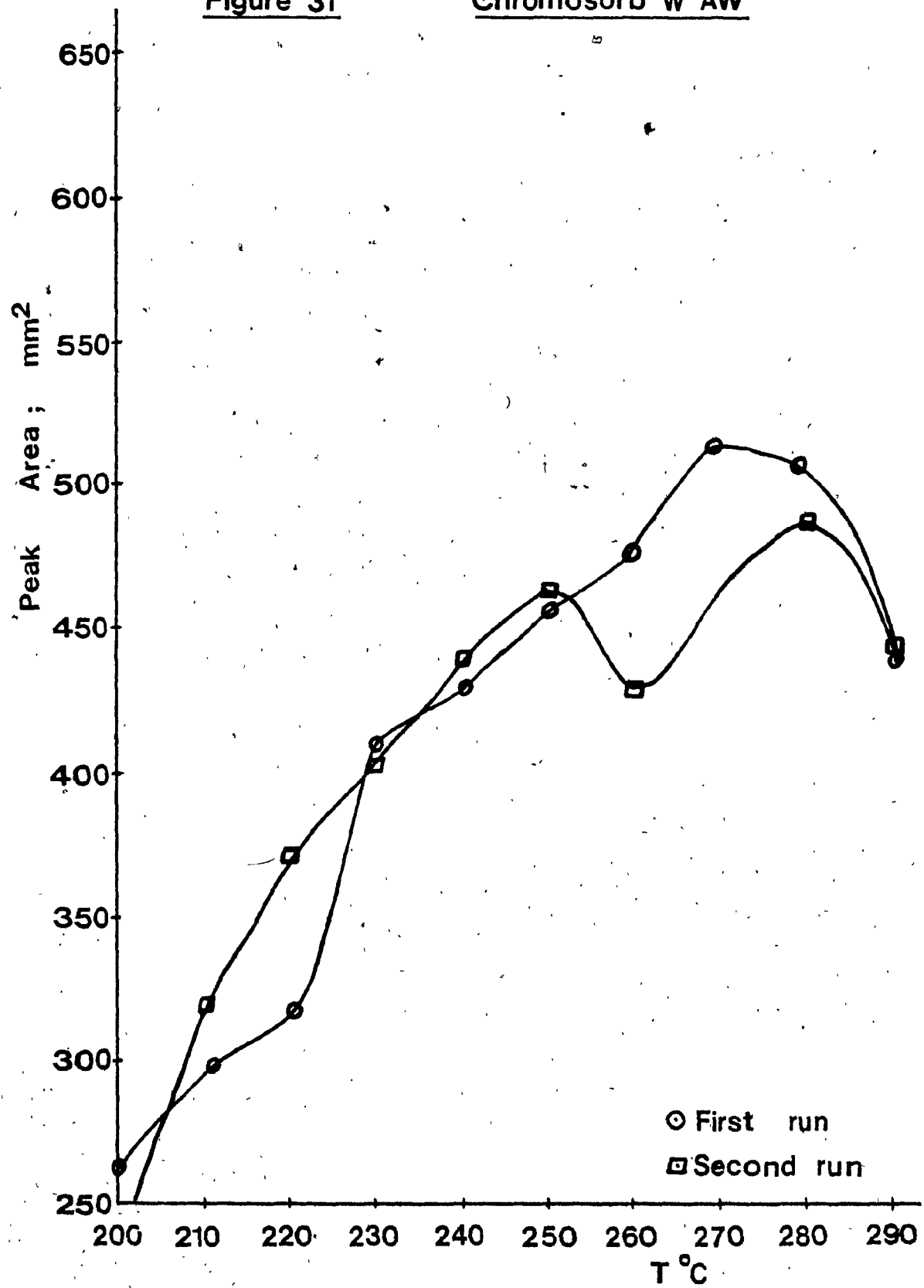


Figure 32

Chromosorb W AW-DMCS

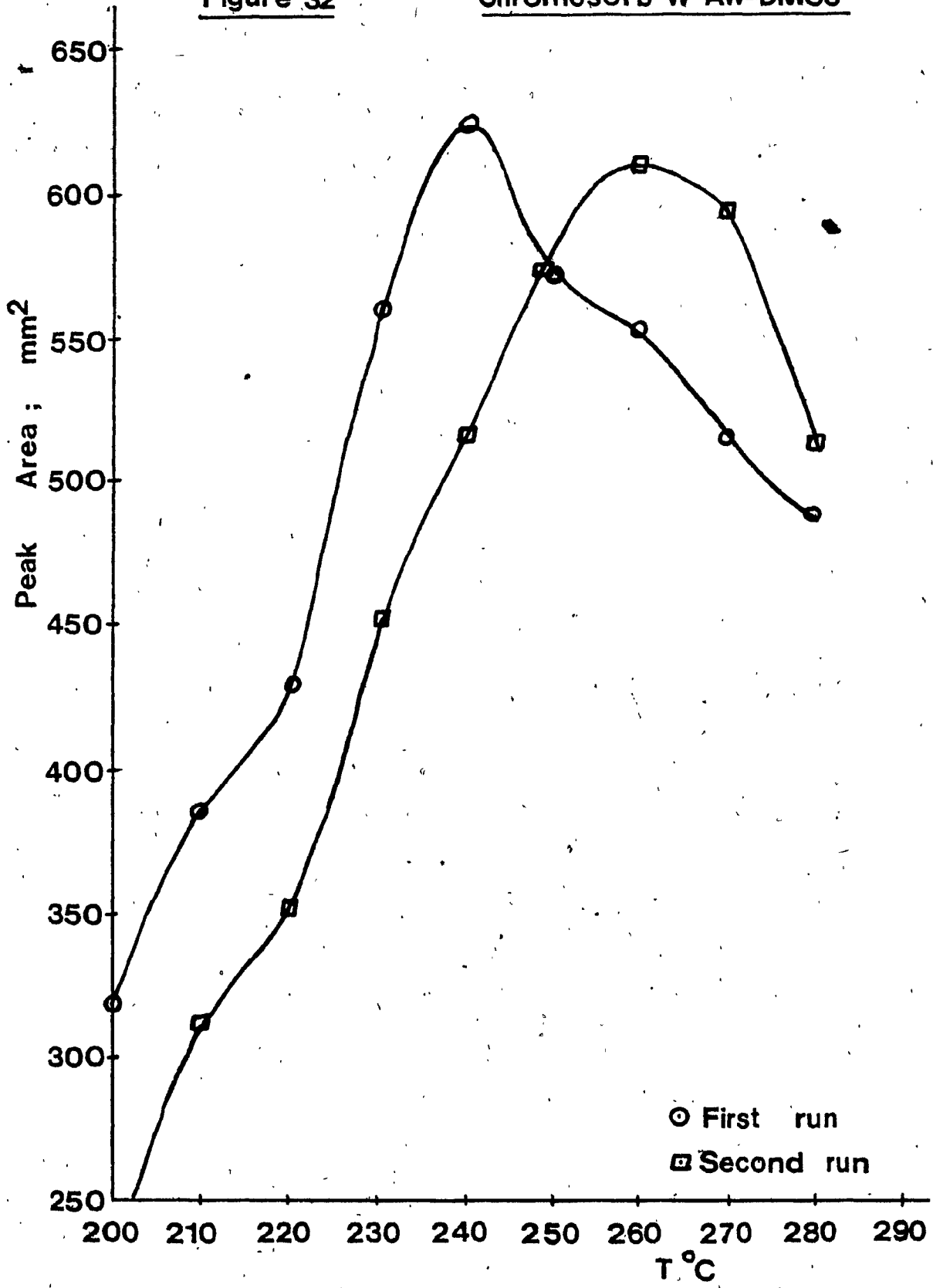


Figure 33

Chromosorb W HP

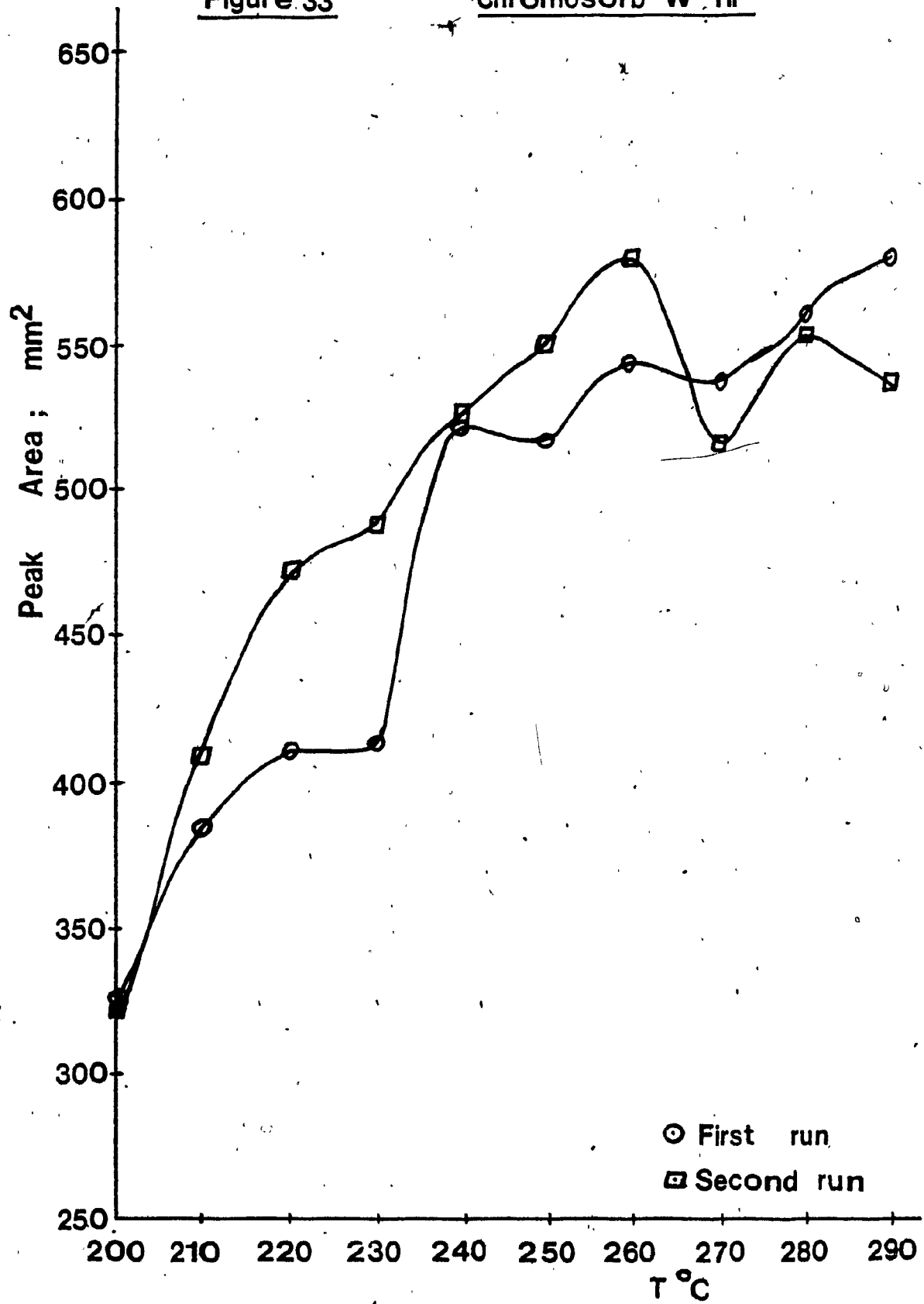


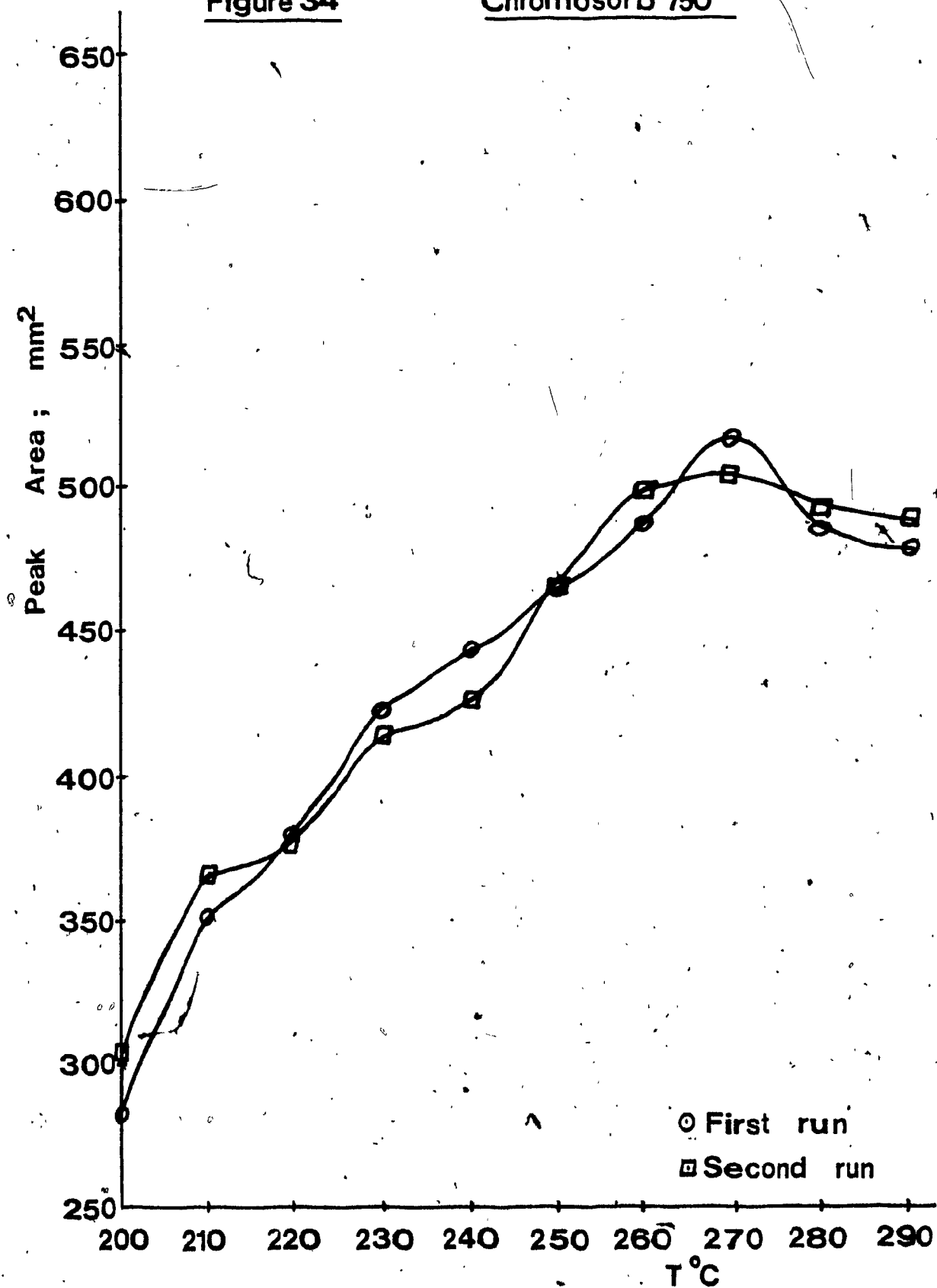
Figure 34Chromosorb 750

Figure 35                      Chromosorb G NAW

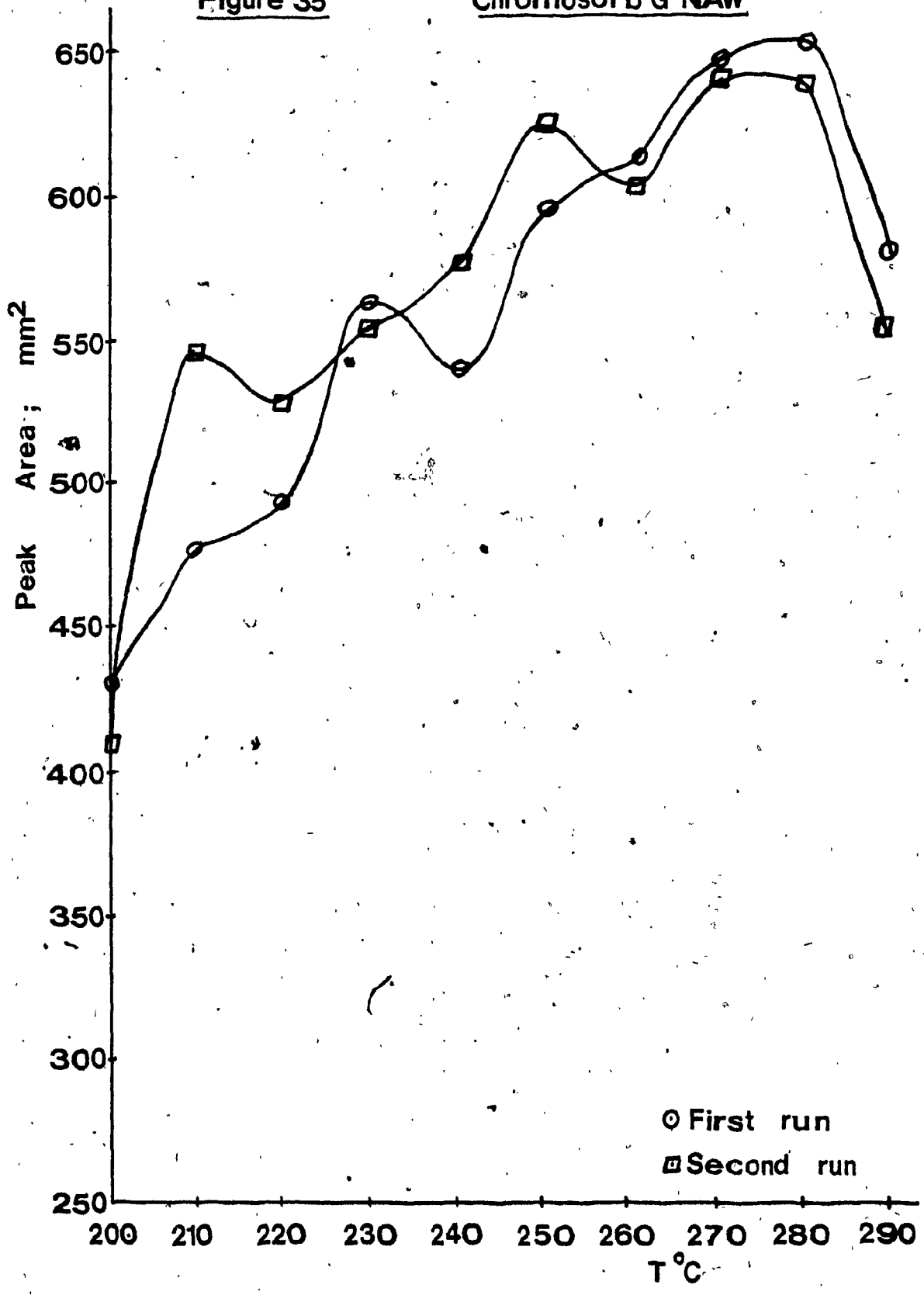




Figure 36

Chromosorb G AW

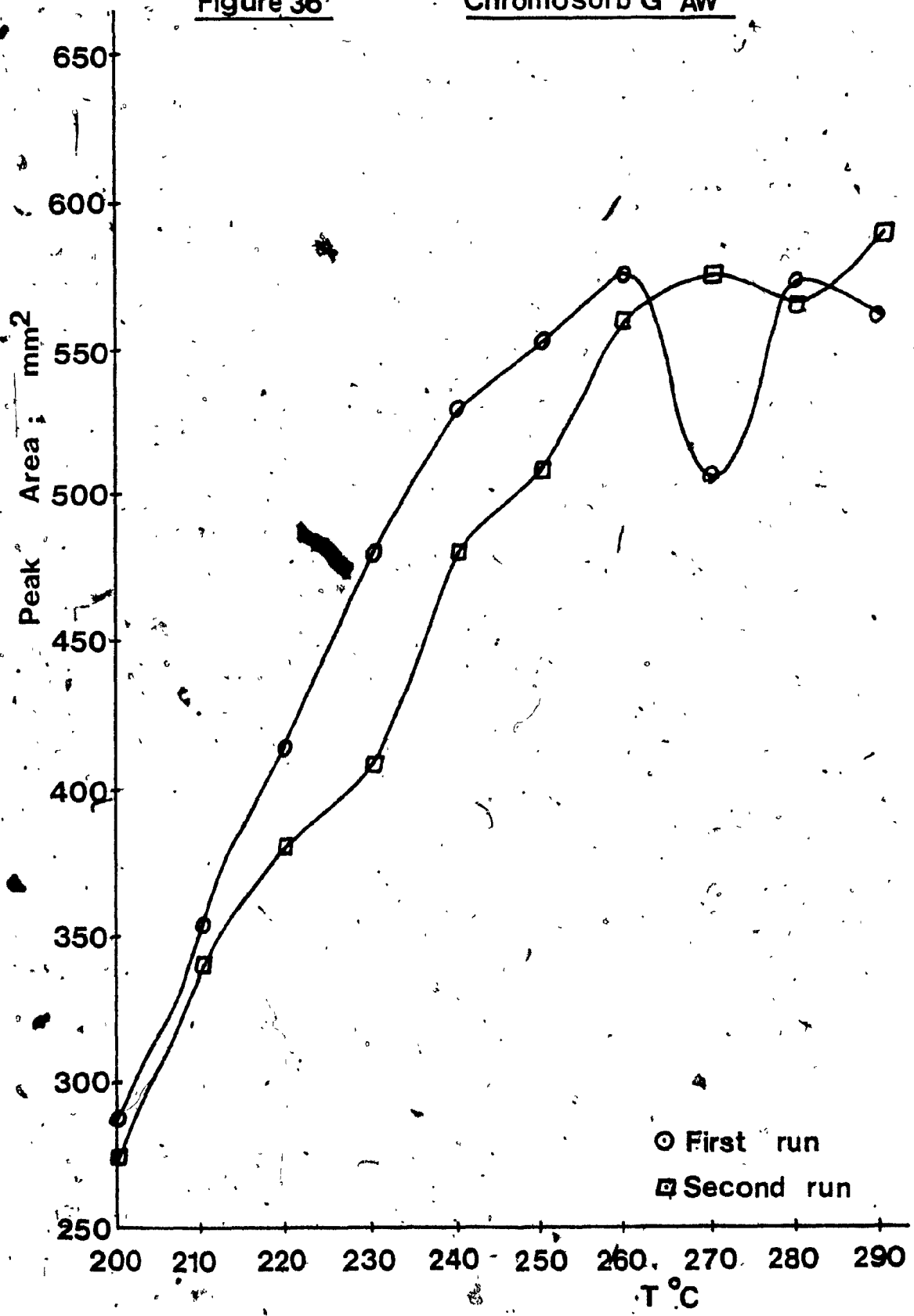


Figure 37

Chromosorb G AW-DMCS

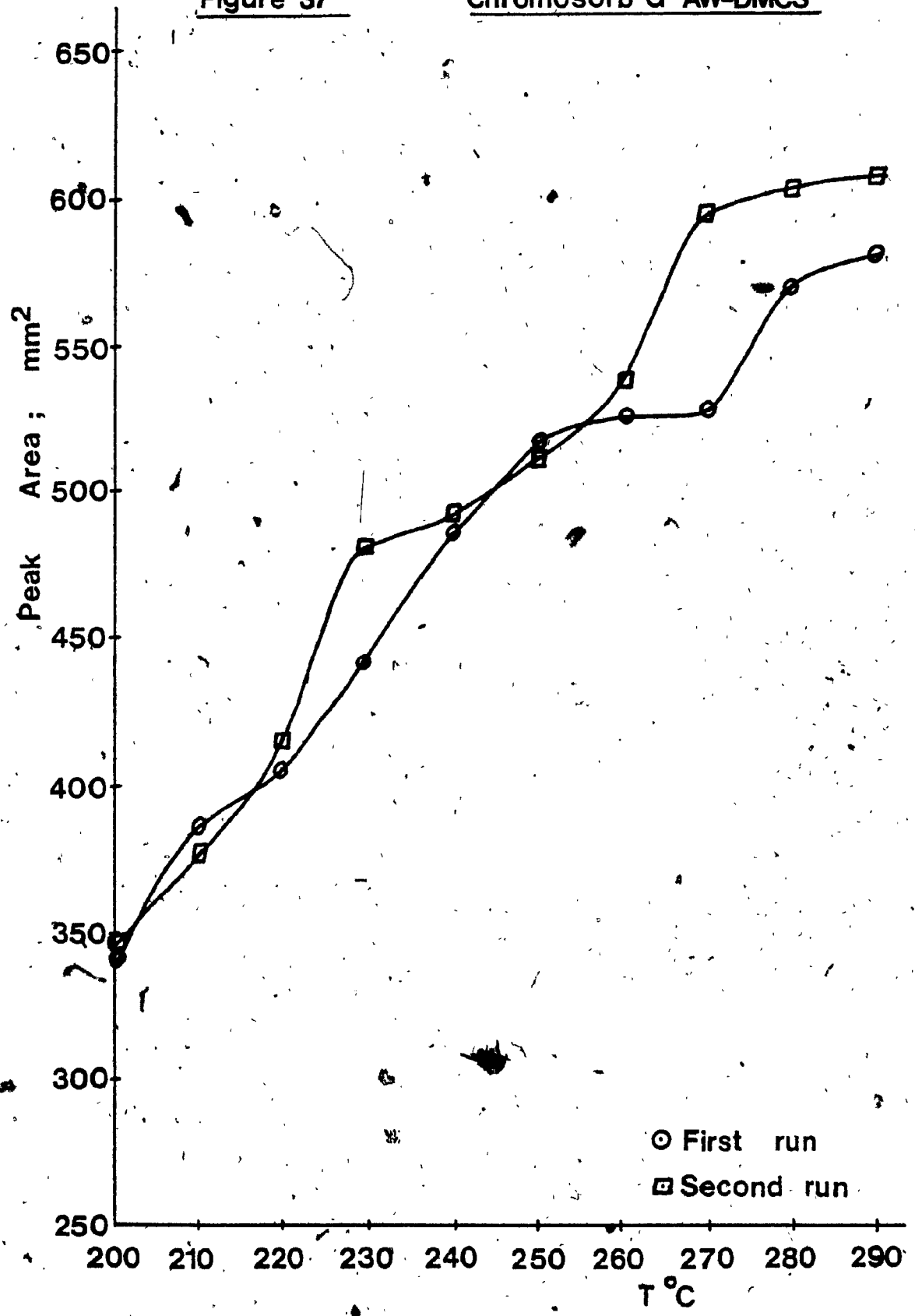
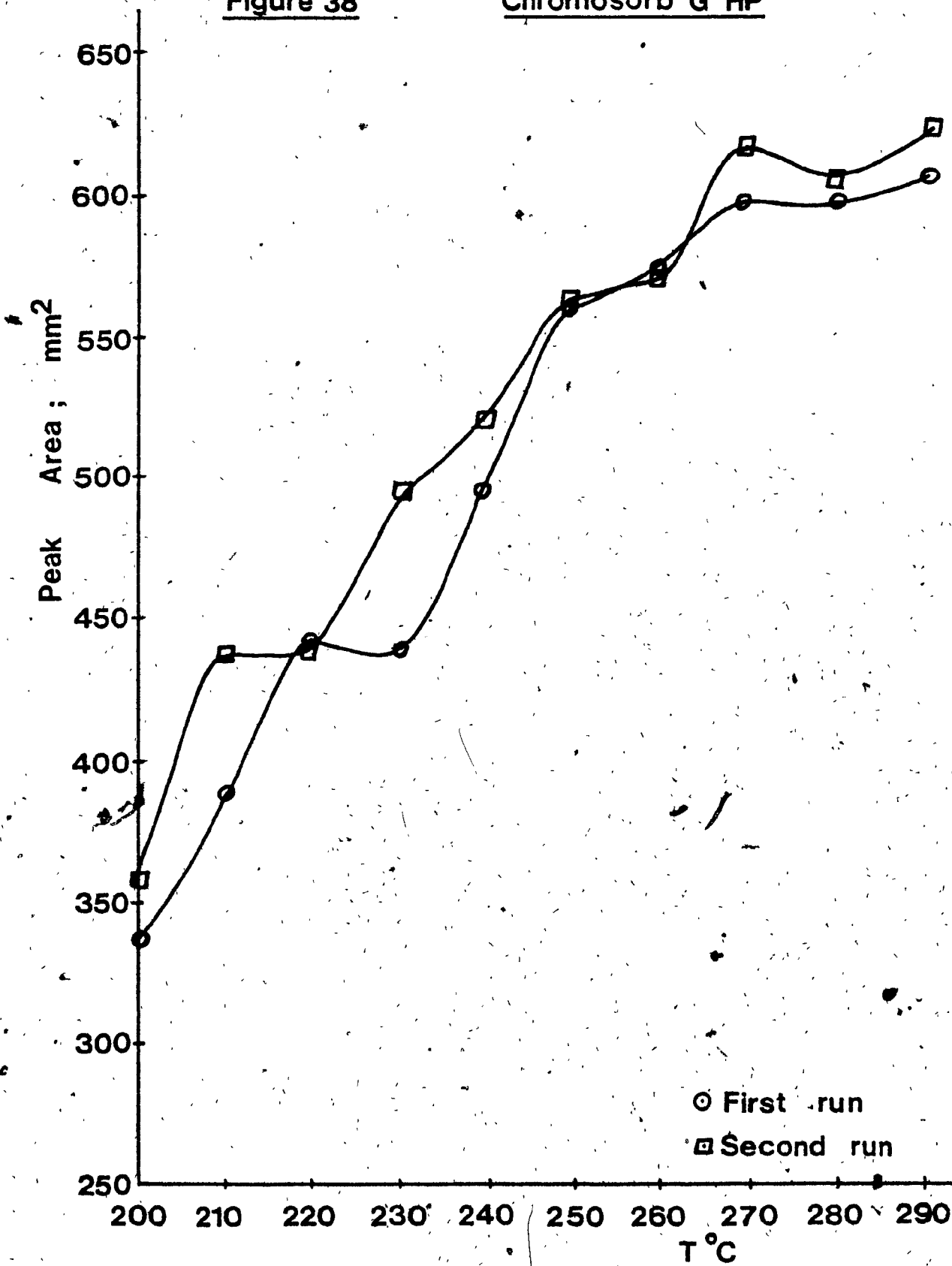


Figure 38

Chromosorb G HP



APPENDIX ETHERMOGRAMS FOR DIELDRIN ON COLUMNS CONSISTING OF VARIOUS TUBINGS  
PACKED WITH 3.5% W/W OV-17 ON CHROMOSORB W AW-DMCS

<u>Figure</u>		<u>Page</u>
68	Copper	244
69	Aluminum	245
70	Glass	246
71	Nickel	247

Figure 68      Copper Tubing Column

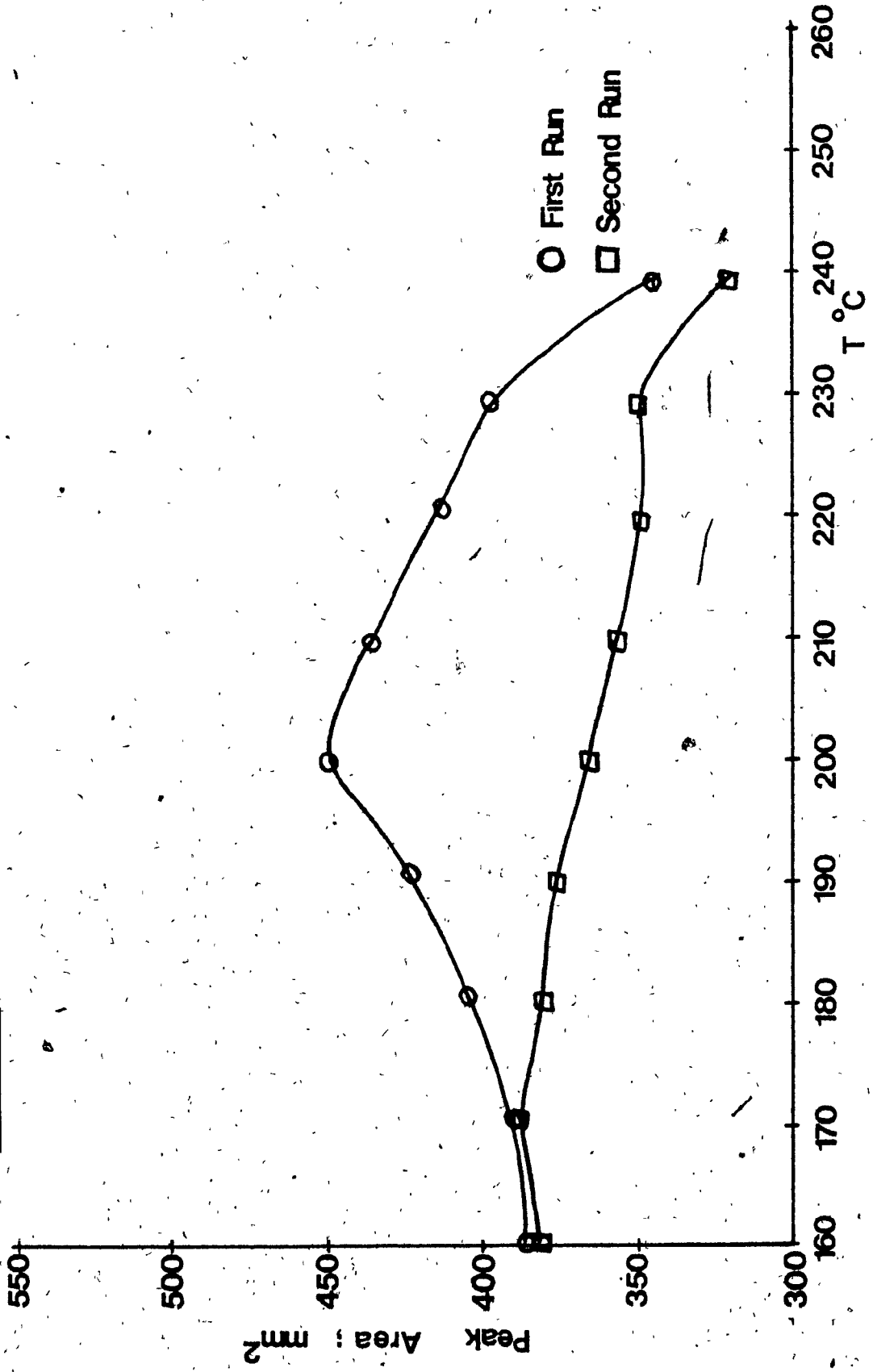
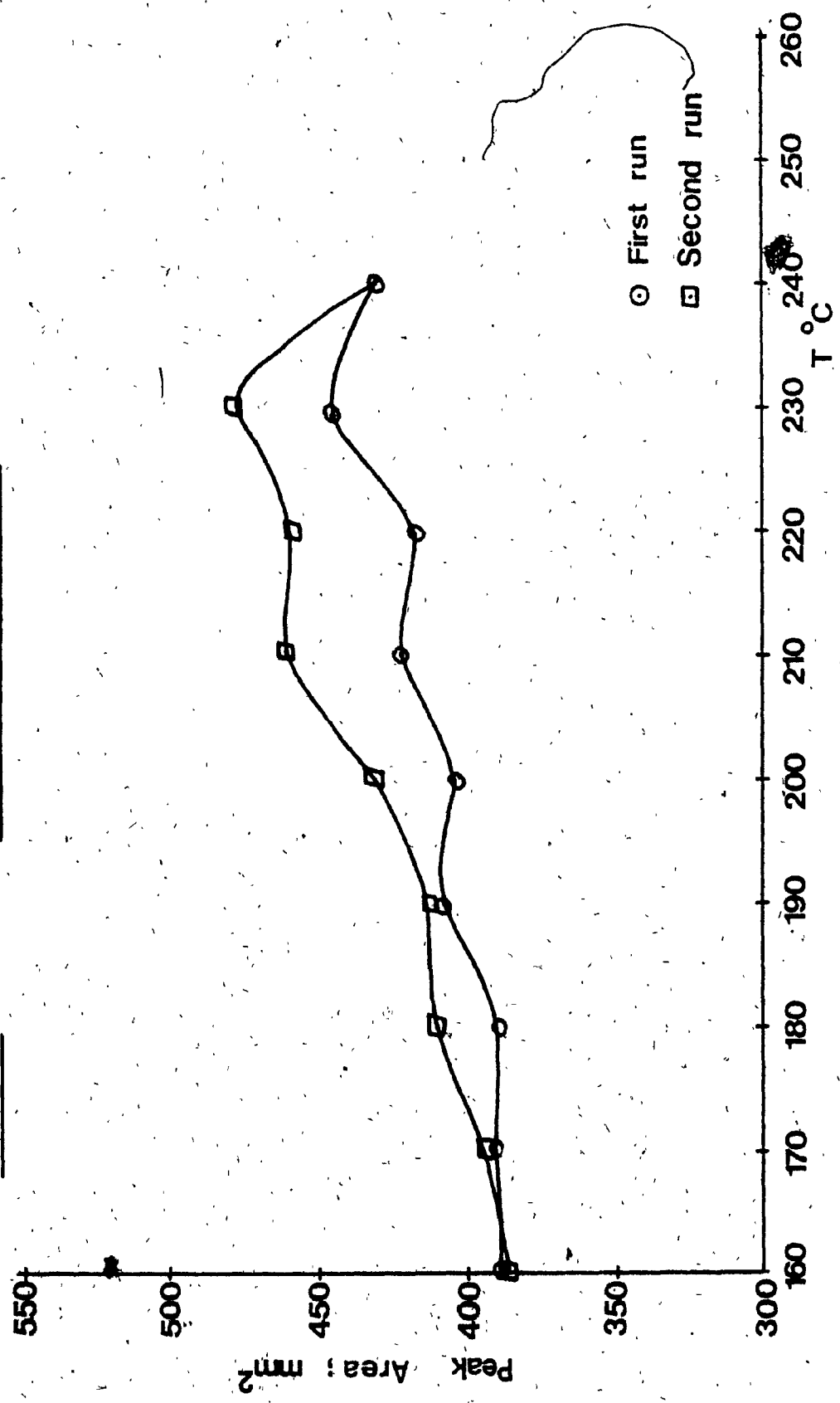


Figure 69      Aluminum Tubing Column



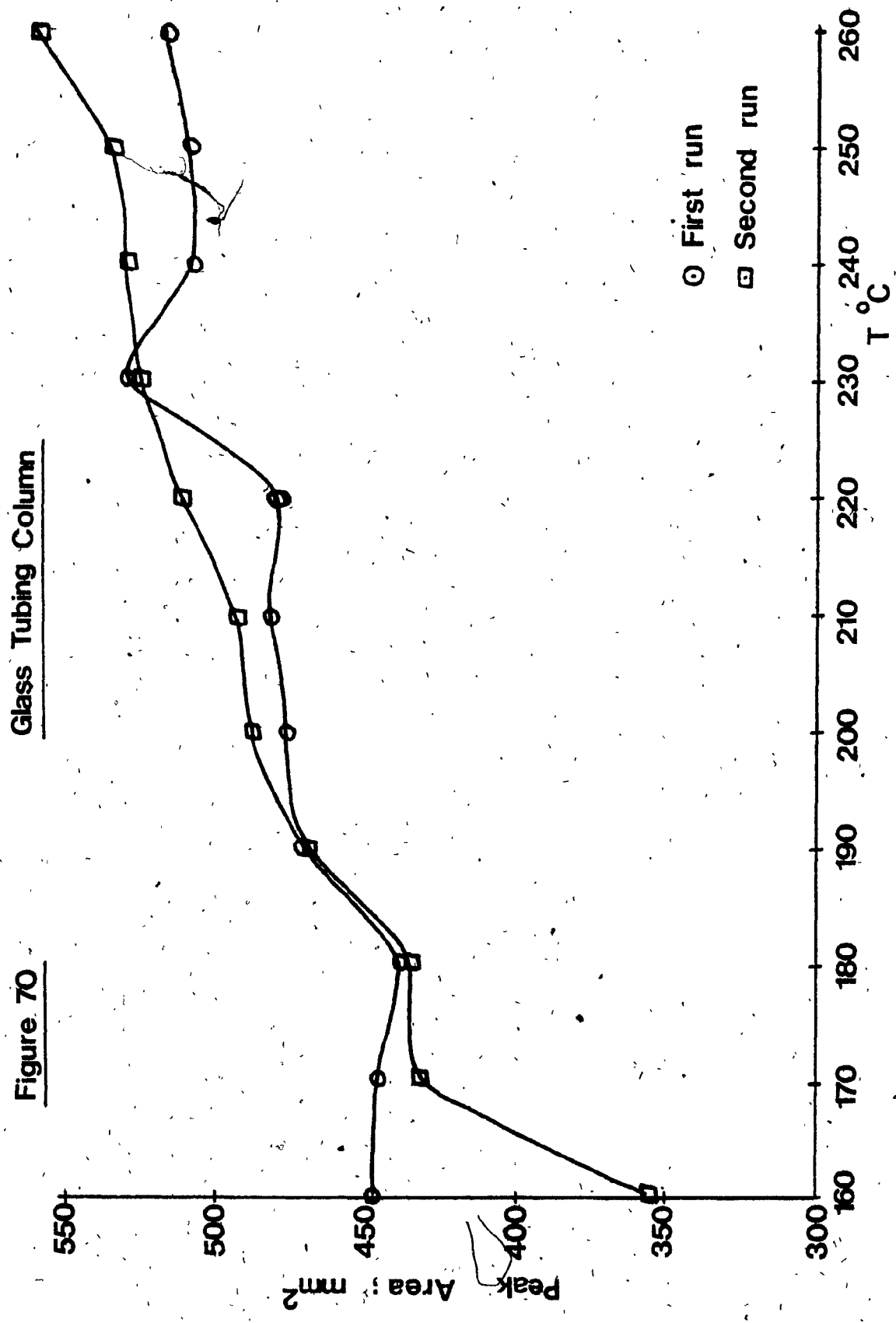
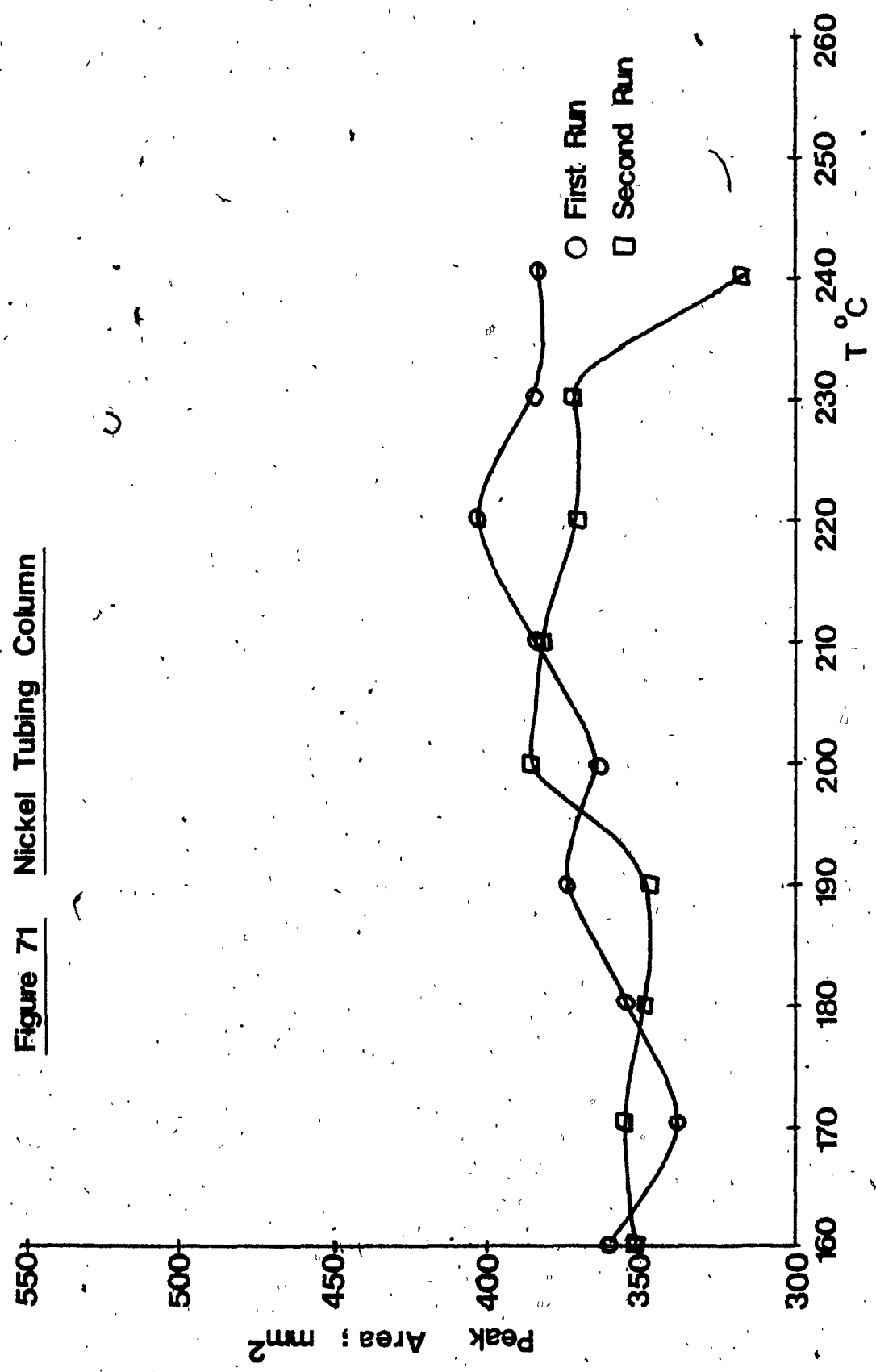


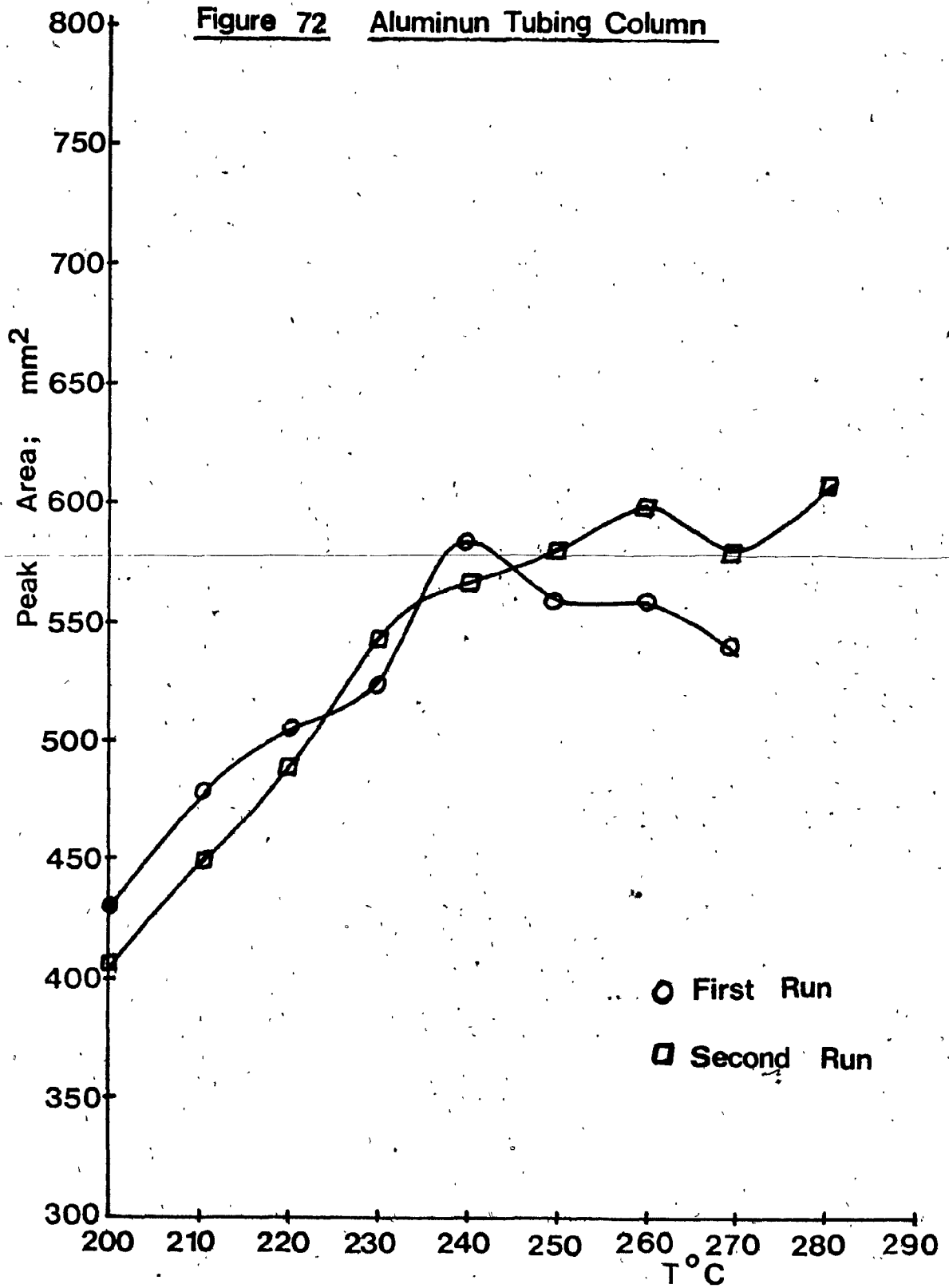
Figure 71 Nickel Tubing Column





APPENDIX FTHERMOGRAMS FOR METHOXYCHLOR ON COLUMNS CONSISTING OF VARIOUS TUBINGSPACKED WITH 3.5% W/W OV-17 ON CHROMOSORB W AW-DMCS

<u>Figure</u>		<u>Page</u>
72	Aluminum	249
73	Nickel	250
74	Glass	251



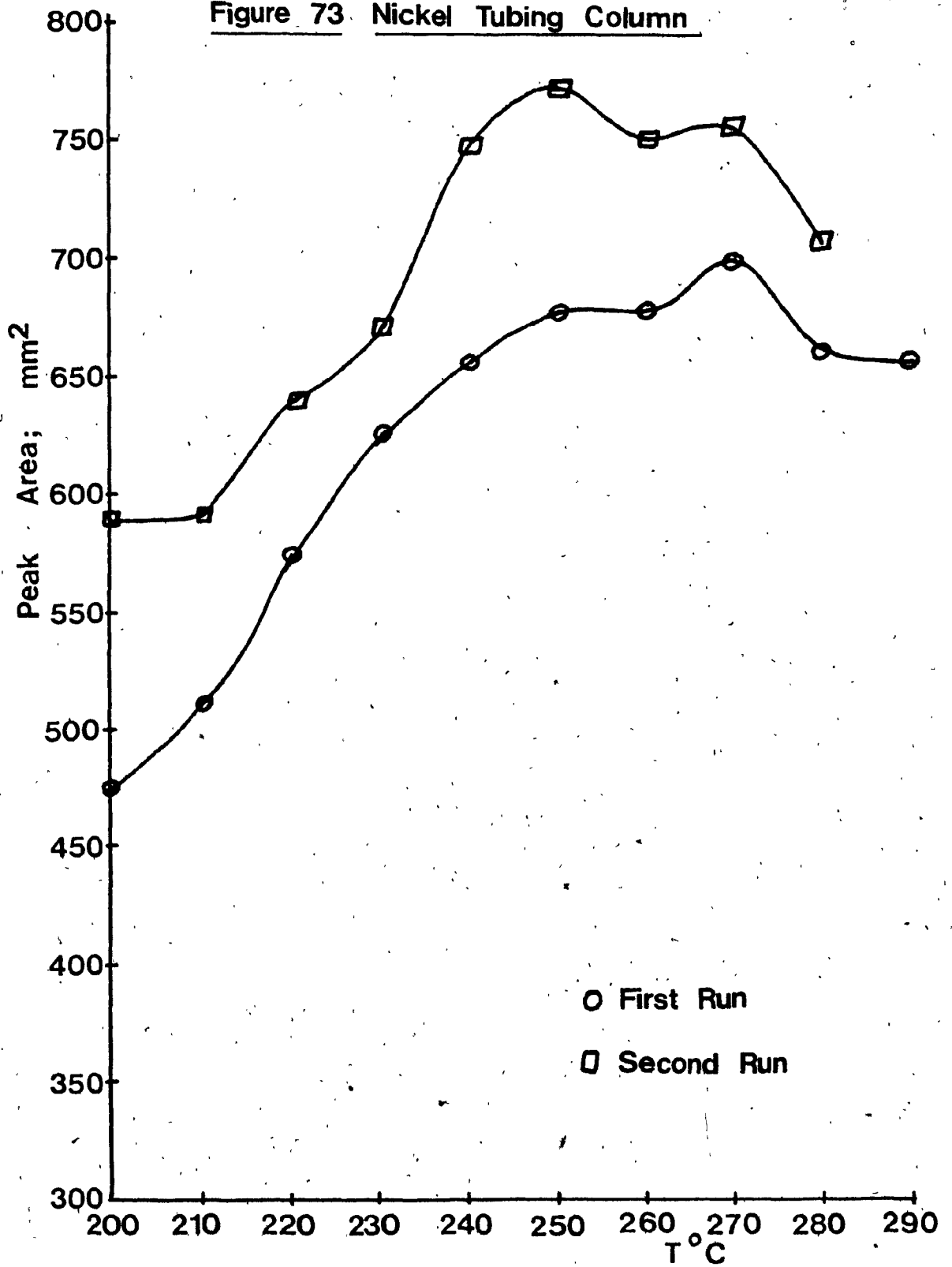
**Figure 73** Nickel Tubing Column

Figure 74. Glass Tubing Column