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**LA THÈSE A ÉTÉ
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Column Parameters for Gas Chromatography of s-Triazines

André John Albert Müller

A Thesis
in
The Department
of
Chemistry

Presented in Partial Fulfillment of the Requirements
for the Degree of Master of Science at
Concordia University
Montréal, Québec, Canada

December 1985

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ABSTRACT

Column Parameters for GC of s-Triazines

André John Albert Müller

An investigation was carried out of the effect that concentration, support material and temperature have on the GC response of s-triazines. Depending on the concentration of s-triazine used as sample, suitable detectors, flame ionization and electron capture, were used. Column temperature studies ranged from 140 - 240 C. The investigation included analyses on 3.5% (w/w) OV-225 coated on Chromosorb P, W, G columns, as well as uncoated Chromosorb 103 and CSP-20M. Also, an attempt was made to establish the effect of column bleed on detector response. Gas chromatography - mass spectrometry was used to study the bleeding patterns determined by using the electron capture detector. Possible ways of extending column life were investigated. Heats of adsorption and entropy values were calculated from the GC data. A correlation was drawn between heats of adsorption and relative retention time and detector response.

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To My Dear Mother And Father

Thank You For Everything

"And further, by these, my son, be admonished; of making
many books there is no end; and much study is a weariness
of the flesh."

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GLOSSARY OF SYMBOLS

AFD	- Alkali Flame Detector
AW	- Acid Washed
AW-DMCS	- Acid Washed Dimethyldichlorosilane Treated
C-750	- Chromosorb 750
C-103	- Chromosorb 103
CASP	- Cyanoalkyl Substituted Polysiloxanes
CG	- Chromosorb G
CP	- Chromosorb P
CW	- Chromosorb W
ECD	- Electron Capture Detector
FID	- Flame Ionization Detector
FPD	- Flame Photometric Detector
GC	- Gas Chromatography
GC/MS	- Gas Chromatography - Mass Spectrometry
GLC	- Gas Liquid Chromatography
GSC	- Gas Solid Chromatography
H	- Plate Height
HP	- High Performance
HPLC	- High Pressure Liquid Chromatography
HP-TLC	- High Pressure Thin Layer Chromatography
i-Pr	- Isopropyl
k'	- Capacity Factor
m.p.	- Melting Point
n	- Number of Theoretical Plates
OMe	- Methoxy

R - Gas Constant
R - Resolution
SMe - Thiomethyl
T - Temperature
TCD - Thermal Conductivity Detector
TLC - Thin Layer Chromatography
(w/w) - Weight by Weight

CHAPTER

INTRODUCTION.

1.0 PESTICIDES

Since the early days of mankind, he has been plagued continuously with "pests". Four out of the seven plagues which were brought onto the Egyptians were plagues of "pests" [Exodus 9 and 10]. As man and his quest for a "better life" has progressed, so has the manufacture and synthesis of many new materials and chemicals. With experimentation it was found that some of these chemicals could actually kill some of the animals and plants that "pest" us so much.

Today there are two points of view as far as the use of pesticides is concerned. The first is summed up by the phrase, "uncontrolled pests or adequate food"! In his defence of the use of pesticides, William Furtick [1] argues that civilisation as it is known today could not have evolved, nor can it survive, without adequate food supply. In a rapidly expanding world there are two factors which could transform today's "adequate food supply" into tomorrow's inadequate food supply; these are: 1. pests and 2. expansion of the human population. It has been stated by Furtick that the magnitude of crop losses from pests is estimated to be in the region of 30 per cent or more of potential crop production. These losses are caused by diverse species of anthropod and vertebrate animals such as insects and rodents; weedy terrestrial and aquatic plants; plant diseases caused by bacteria, fungi, viruses, and

microplasm; and plant nematodes. All these crop losses have encouraged leading plant protection experts to use more and more pesticides to combat crop losses from "pests". Today millions of dollars are spent on the production of pesticides to "effectively" combat "pests".

The second point of view is expressed, with concern, by Rachel Carson [2], as follows: "Since the mid-1940's over 200 basic chemicals have been created for use in killing insects, weeds, rodents, and other organisms described in the modern vernacular as "pests". These sprays, dusts, and aerosols are now applied almost universally to farms, gardens, forests, and home-nonspecific chemicals that have the power to kill every insect, the "good" and the "bad", to still the song of birds and the leaping of fish in the streams, to coat the leaves with a deadly film, and to linger on in the soil - all this though the intended target may be only a few weeds or insects. Can anyone believe it is possible to lay down such a barrage of poisons on the surface of the earth without making it unfit for all life? They should not be called "insecticides" but "biocides".

1.1 PURPOSE OF THESIS

The reality today is that we have these chemicals dispersed in our environment, and the only possible hope is that there will be a reduction in the use of these chemicals.

This means that we will have to carry out studies of the effects that these chemicals have on the environment and in general on the ecosystem. It is therefore important that we optimise our methods of analysis to determine accurately and precisely the amounts of these chemicals that are still prevailing in our environment. This thesis is such a study of optimisation of an analytical method, gas liquid chromatography (GLC) for the determination of s-triazines. Similar studies were done by Setiawan [3], Haniff and Zienius [4,5], and Kouloulis [6]. Haniff and Zienius investigated the role of column support and temperature on the gas liquid chromatographic analysis of organophosphorus (phorate, disyston and malathion). Kouloulis and Setiawan investigated the suitability of different diatomaceous supports in the analysis of typical chlorinated pesticides, such as dieldrin and methoxychlor. The results obtained by these authors have shown the importance of optimization of a chromatographic system for the analysis of a particular group of pesticides, herbicides or fungicides.

Based on the above discussion, an attempt was made in this thesis to address the following issues in the analysis of s-triazines:

1. the effect of temperature on the overall column performance, i.e., column efficiency;
2. the supports which are the best based on column

- efficiency, resolution or the limit of detection;
- 3. the effect of increasing column temperature on the response of s-triazines using the flame ionization and electron capture detectors;
- 4. possible ways of extending column life;
- 5. bleeding and possible reasons for certain bleeding patterns;

1.2 CHEMISTRY OF S-TRIAZINES

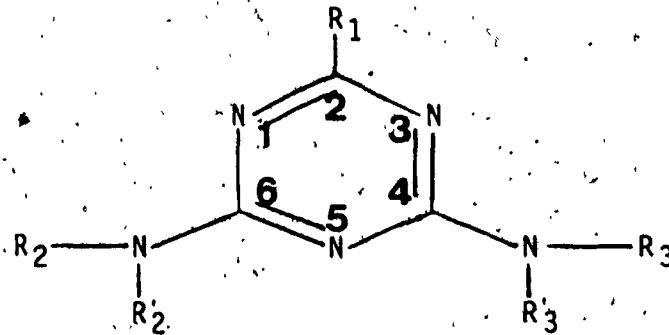
The herbicidal properties of the s-triazines were discovered in 1952 by a research group of J.R. Geigy Ltd., in Basel, Switzerland [7]. Today s-triazine derivatives are important compounds in agriculture and industry. s-Triazines are among the most widely used herbicides, and contaminate the environment with undesirable residues. These are 1,3,5 triazines substituted in positions 2, 4 and 6. (See Table 1).

Most properties of the s-triazine derivatives are determined by the substituents; the ring itself is not involved except for its effect on the charge distribution.

1.3 HERBICIDAL ACTIVITY OF S-TRIAZINES

The herbicidal activity of s-triazines is determined by the substituent in position 2, commonly chlorine (in which case the commercial name ends with -azine), methoxy (name ending

Table 1. Structure of 1,3,5 triazines



Di(monoalkylamino) derivatives ($R_2 = R_3 = H$)

Trivial name	R_1	R_2	R_3
Prometone	OMe	i-Pr	i-Pr
Atrazine	Cl	Et	i-Pr
Ametryne	SMe	Et	i-Pr

in -tone) or thiomethyl (name ending in -tryne). A change in the substituent in position 2 will cause a change in the selective effect of the compound. Positions 4 and 6 are usually substituted by various alkylamino groups. The herbicidal efficiency of the compound is also determined by the total number of carbon atoms in the aminoalkyl groups in positions 4 and 6.

Low doses of s-triazine herbicides affect the roots of plants; higher doses may have stimulating affects and may cause soil sterility [8]. Substances that enhance the production of agricultural plants adversely affect the environment by leaving undesirable residues, which may exert pathogenic (and sometimes also mutagenic) effects on

7
living organisms.

Acute toxicity is a method of assessing the effects of a single dosage of the pesticide. Acute toxicity is expressed as LD₅₀, which is the dosage necessary to produce death or reproducible effects in 50% of the animal population tested [9].

1.4 S-TRIAZINES STUDIED IN THIS THESIS

1.4.1 PROMETONE

Prometone (2-methoxy-4,6-bis-isopropyl amino-s-triazine) has the structural formula shown in Table 1. Prometone is a pre- and post-emergence s-triazine for nonselective use. It has been applied selectively in sugar cane fields [10]. As a nonselective pre- and post-emergence s-triazine, prometone has been used to control most annual and perennial broadleaf and grassy weeds on non-cropland [11].

Prometone has a very low toxicity to wildlife and fish.

Acute toxicity: oral LD₅₀ - mice: 2160 mg/kg

- rats: 2980 mg/kg

The residual activity of prometone in soil depends mainly upon soil type, moisture and dosage used. It can persist for several years [11].

1.4.2 ATRAZINE

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) has the structural formula shown in Table 1. Atrazine is a widely used selective s-triazine for broadleaf and grassy weeds in corn, sorghum, millet, vine, asparagus, sugar cane, macadamia orchards, pineapple and turf sod [12]. Atrazine is also used widely as a nonselective s-triazine for vegetation control in non-cropland.

Atrazine like prometone has a very low toxicity to wildlife and fish. Acute toxicity: oral LD₅₀ - mice: 1750 mg/kg
- rats: 3080 mg/kg

The residual activity of atrazine in soil at selective rates for specific soil types is such that most rotational crops can be planted one year after application, except under an arid or semiarid climate [13].

1.4.3. AMETRYNE

Ametryne (2-methylthio-4-ethylamino-6-isopropylamino-s-triazine) has the structural formula shown in Table 1. Ametryne is a selective s-triazine for control of broadleaf and grass weeds in pineapple, sugar cane, small grains, peanuts soybeans and bananas [14]. It can also be used as a post-directed spray in corn and in citrus. It is also used

Ametryne has a very low toxicity to wildlife and fish.

Acute toxicity: oral LD₅₀ - mice: 965 mg/kg

- rats: 1110 mg/kg

The residual activity of ametryne in soil at selective rates for specific soil types is from 1 to 3 months under most normal conditions. Under more tropical conditions, however, ametryne not only gives better post- and pre-emergence control of a wider range of weeds, but its residual life in the soil is often extended to several months and it may persist as long as atrazine [15].

The physical properties of the three s-triazine derivatives studied appear in Table 2.

Table 2. Physical Properties of s-Triazine Herbicides [16].

<u>Chemical name</u>	<u>Color</u>	<u>m.p (°C)</u>	<u>Vapour pressure</u> <u>at 20 °C (mm Hg)</u>	<u>Density</u> <u>(g/cm³)</u>
Prometonè	Colorless solid	91 - 92	2.3×10^{-6}	1.088
Atrazine	Colorless solid	175-177	3.0×10^{-6}	1.187
Ametryne	Colorless	84 - 86	8.4×10^{-7}	1.190

1.5 GAS LIQUID CHROMATOGRAPHY

1.5.1 INTRODUCTION

The term chromatography embraces a family of closely related separation methods based on experiments described by Runge (1834 - 1850) [17], Day [18] and Tswett [19] during the period 1897 - 1906. Keulemans [20] gave the following definition for the various chromatographic methods:

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

The first work done on "classical GLC" was published by James and Martin in 1952 [21]. Since then GLC has played a major role in separation techniques. GLC can be defined as a separation method in which the stationary phase is a liquid distributed on an inert solid support or coated on the column wall and the mobile phase is a gas. The separation occurs by the partitioning of the sample components between two phases. Applications of GLC are numerous and include the field of pesticides and have been well documented by Grob [22]. A schematic diagram of a typical gas liquid chromatograph is shown in Figure 1.

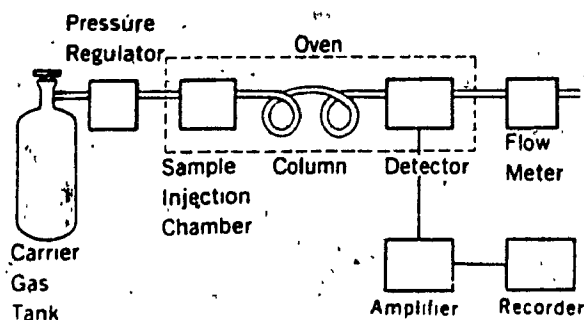


FIGURE 1. Essential Features of a Gas Chromatograph.

1.5.2 RETENTION BEHAVIOUR OF SOLUTES IN GAS CHROMATOGRAPHY.

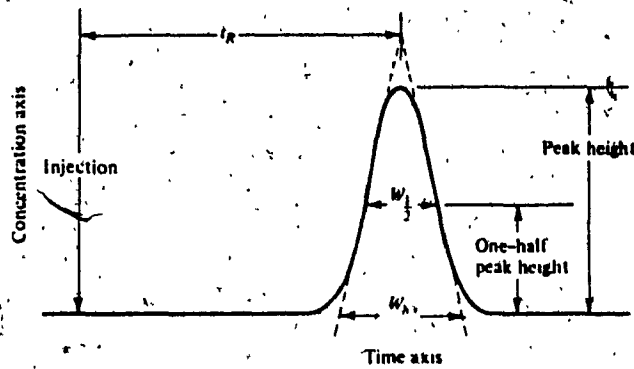
The terminology used to describe the behaviour of a solute that is well behaved in a chromatographic sense (i.e., gives a symmetrical peak) is illustrated in Table 3. The gas hold up volume, V_M , is the retention volume of a non-adsorbed sample and it includes contributions due to the interstitial volume of the column and the effective volumes of the sample injector and the detector. In order to achieve solute separation, there must be solute retention. The capacity factor, k' , is a measure of the degree of retention of the solute.

1.5.3. COLUMN EFFICIENCY AND RESOLUTION

1.5.3.a. PLATE HEIGHT AND PLATE NUMBER.

The quantity that measures column efficiency and is related to the peak width is called the plate height, also sometimes referred to as the height equivalent of a

Table 3. Equations for Retention Behaviour



t_R = retention time, minutes

F_C = carrier gas flow rate, ml/min

$V_R = t_R F_C$ = retention volume

$V_R = V_R - V_M$ = adjusted retention volume

V_M = gas hold up volume

$V_N = j V_R$ = net retention volume

$$\text{where } j = \frac{3[(P_i/P_o)^2 - 1]}{2[(P_i/P_o)^3 - 1]}$$

j = compressibility factor

where P_i and P_o are the inlet and outlet pressures of the column

$V_g = 273 V_N / T W_L$ = specific retention volume

where W_L = weight of the stationary phase, g

T = temperature, °K

$k' = \frac{\text{total moles of solute in stationary phase}}{\text{total moles of solute in mobile phase}}$

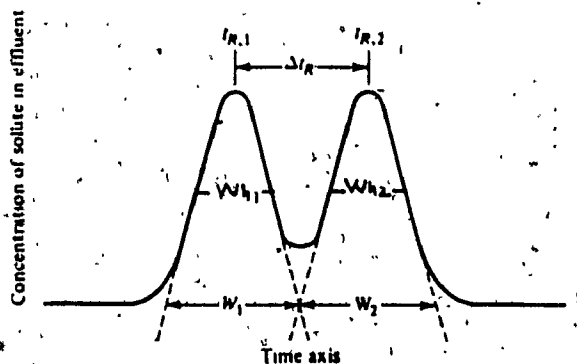
k' = capacity factor

theoretical plate. It has the dimension of distance. Plate height, H , has become a measure of dispersion in chromatography and can be determined for any solute from the elution chromatogram. (See Table 4).

Column efficiency is often stated in terms of theoretical plates, n . (See Table 4). The higher n , the more efficient the column. These factors depend on retention behaviour and peak shape. The latter, therefore, necessarily affect the column efficiency. The retention time depends upon the amount of liquid phase in the column. i.e., a high loading of liquid phase will result in longer retention times [23]. The shape of the eluted peaks is affected by the following three factors: non-linearity of response and other concentration-dependent partitioning effects, non-ideality, and extra column factors.

1.5.3.b. RESOLUTION

As the solute zones migrate through a chromatographic column they broaden. Resolution of mixtures into discrete solute bands will occur only if the bands widen to a lesser extent than their maxima separate. Resolution of adjacent peaks, if inadequate, can be improved in two independent ways: by increasing peak separation and by decreasing peak width [24]. These two approaches to improve resolution are associated, respectively, with alternating the

Table 4. Equations for Column Efficiency and Resolution.

$$H = \frac{L}{5.54} \left(\frac{W}{t_R} \right)^2$$

where H = column length, cm

$$n = 5.54 \left(\frac{t_R}{W} \right)^2$$

where n = number of theoretical plates

$$R = \frac{t_{R,2} - t_{R,1}}{0.5(W_1 + W_2)} = \text{resolution}$$

$$R_h = \frac{t_{R,2} - t_{R,1}}{0.5(W_{h1} + W_{h2})}$$

$$R = R_h / 1.699$$

thermodynamics and improving the kinetics of the chromatographic system.

A resolution greater than 1.5 is considered as a complete separation between two adjacent peaks. Ettre [23] has suggested that the resolution, R_h , can also be determined by calculation of peak widths at one-half of peak height. This resolution can be converted to R using the equation in Table 4.

1.6 QUANTITATIVE ANALYSIS

When a chromatogram is obtained with a differential detector which has a linear response, the area of each peak recorded is proportional to the amount of the component responsible for the peak. A quantitative analysis can therefore be obtained by measurement of the areas of all peaks.

Methods for peak area determination include peak height measurement, planimetry, ball-and-disk integration, electronic digital integration, computer integration, peak height times peak width at half peak height measurement and peak triangulation. Harris et al. [25] have discussed errors in manual integration techniques. Their basic conclusion was that precision depends more on peak shape than on the particular manual method used, and peak shape

is significantly affected by the apparatus parameters, by separation efficiency, by the characteristics of the detector and its ancillary devices and by the operation and characteristics of the recorder. The experience and skill of the operator are important factors.

Although peak height measurements are inherently simple, the peak height does not always remain directly proportional to size. Above some critical concentration peak broadening becomes significant and rate of increase in peak height diminishes [24]. Planimetry is less precise than peak height times half width measurement for peaks of small area, but is comparable or somewhat better in precision for large or irregular areas [25].

Digital integrators are used when budgets allow and give excellent results. Measurement of peak height times width at half-height is the most commonly used method for measuring peak areas manually. It was the method of choice in this thesis.

1.7 HEATS OF ADSORPTION

Structural changes in the stationary phase can be detected from thermodynamic data obtained from GC data. If $\log V_g$ is plotted as a function of the reciprocal of the absolute temperature, the resultant curve can be linear [26] or have

discontinuities [27]. This behaviour arises from the thermodynamic properties of the solute-solvent system as described by the equation:

$$\log V_g = \frac{\Delta H_a}{2.3RT} + \text{constant} \quad (1)$$

where ΔH_a is the molar heat of adsorption of the solute and R is the gas constant.

This equation will be used to study the thermodynamic behaviour of the columns prepared in this project.

1.8 THE GAS CHROMATOGRAPHIC COLUMN.

A typical gas liquid chromatographic column is packed with an inert support which is coated with a thin film of liquid phase. The solid support must comply with two requirements:

1. it should provide a surface that can hold tenaciously a uniform thin liquid film, i.e., the support should have a great surface activity and a strong affinity towards the liquid;

2. it should be inert towards the components of the sample.

To meet the above requirements, the ideal support should satisfy the following requirements:

- a. mechanically firm to avoid dust formation;
- b. particles with regular, preferably spherical, shape to reduce pressure drop;
- c. particles with almost identical dimensions to ensure highest efficiency;

- d. pore structure should be open and uniform;
- e. good wetting ability;
- f. a homogeneous, chemically inert surface towards polar substances [28].

Such ideal supports have been approached, but not yet obtained.

1.8.1. DIATOMACEOUS EARTH SUPPORTS.

The first researchers to use diatomaceous earth were James and Martin [21]. They used Celite 545, a filter-aid, in their original work in GLC of fatty acids. In 1955, Keulemans and Kwantes [29] reported the use of Sterchamol, a German diatomite (also known as diatomaceous earth), diatomaceous silica, or the German kieselguhr. The composition and properties of diatomite are well described in the literature [30,31]. It is sufficient to note here that two basic types of supports are made from diatomite. One is a pink material derived from "brick" and the second is a white material derived from filter-aid. The "brick", or pink material (e.g., Chromosorb P (CP)) consists of diatomite that has been crushed, blended and pressed into brick, then calcined or burned above 900°C. The filter-aid, or white material (e.g., Chromosorb W (CW)) is prepared by mixing diatomite with a small amount of flux, sodium carbonate, and calcining it at temperatures above 900°C. The colour of this support is white, because of the flux.

which converts the iron originally present as an oxide to a colourless sodium iron silicate complex.

Chromosorbs W and P have considerably different properties (Table 5) primarily because of the different calcination processes used in their manufacture. Pink particles are relatively hard compared to the friable white particles. Baker et al. [32] were the first to examine the physical properties of the pink and white supports. They showed that properties differed considerably with respect to surface area, pore distribution, pore volume, and packing density (Table 6).

Another support, Chromosorb G (CG), developed after CP and CW, is claimed to combine the high column efficiency and good handling characteristics of CP with the comparatively non-adsorptive surface of CW [35]. The CG has been designed for the separation of polar compounds where surface interaction is frequently a problem. CG will accept a maximum liquid phase loading of 5%; however, since CG is about 2.4 times as heavy as CW, a 5% loading on CG is equivalent to 12% liquid phase on CW.

Table 5. Typical Chemical Analysis, Weight % [34].

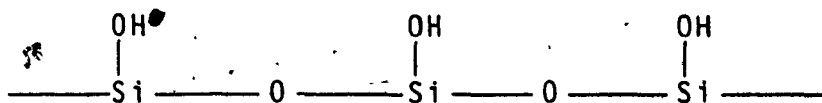
	CP	CW
H ₂ O and ignition loss	0.3	0.3
SiO ₂	90.6	88.9
Al ₂ O ₃	4.4	4.0
Fe ₂ O ₃	1.6	1.6
TiO ₂	0.3	0.2
P ₂ O ₅	0.2	0.2
CaO	0.8	0.6
MgO	0.7	0.6
Na ₂ O + K ₂ O	0.5	3.6

Table 6. Typical Properties of Chromosorb Supports [32, 33, 34].

	CP	CW	CG	C-750
Colour	light pink	white	oyster white	off white
Type	calcined	flux	flux	flux
Handling character.	good	slightly friable	good	calcined
Max. liq. phase load	30%	15%	5%	-
Surface Area m^2/g	4.00	1.00	0.50	0.5 - 1
Surface Area m^2/ml	1.88	0.29	0.29	-
Specific Gravity	6 - 7	8 - 10	8.5	-
pH	6.5	8.5	8.5	-
Density, g/ml				
(i) Loose Weight	0.38	0.18	0.47	0.32 - 0.35
(ii) Packed	0.47	0.24	0.58	-
Pore Size,	1u	9u	-	-

1.8.2. CLASSIFICATION OF DIATOMITES ACCORDING TO THE CHEMICAL TREATMENT [31].

Diatomite support surfaces contain a number of different types of active sites such as silanol and siloxane groups and up to 10% mineral impurities. Chemically, the surfaces can be represented as follows:



The major type of active site on the surface is the silanol and its interaction with various solutes is probably one of hydrogen bonding [34], which leads to excessive tailing of peaks. Iler's [36] study of the surface of silica showed that surface silanol groups will complex with polar organic compounds. Such compounds contain electron-donor atoms, and it was inferred that hydrogen bonds between the electron-donor and the silanol groups were probably involved.

Elder and Springer [37] accounted for the sorption of organic acids on silica gel from various solvents in terms of hydrogen bonding formed between the carbonyl group and the surface silanol group. Other types of active sites on diatomite surfaces include (1) basic sites causing the tailing of acidic compounds such as aliphatic and aromatic carboxylic acids, phenols, barbiturates, etc.; and (2) acidic sites causing the tailing of basic compounds such as amines. There are three major methods of

deactivating the support surfaces. These are:

1. removal of mineral impurities by acid or base washing of the support;
2. elimination of surface silanol groups by reaction with a silanizing agent to form a silyl ether;
3. saturation of the active sites with an active agent.

Application of various deactivation techniques leads to a number of products as follows.

1.8.2.a. NONACID WASHED (NAW).

This support has received no treatment.

1.8.2.b. ACID WASHED (AW).

This support is washed with with HCl to remove soluble iron [30,31]. Such treatment is generally insufficient to reduce tailing.

1.8.2.c. ACID WASHED DIMETHYLDICHLOROSILANE TREATED SUPPORTS (AW-DMCS).

After acid washing, the supports are further deactivated by DMCS treatment. Horning et.al. [38] were the first to prepare a DMCS treated support and used it successfully to separate methyl ester fatty acids and reported good results. The DMCS treatment was based on the method of

Howard and Martin [39], who prepared a hydrophobic support for reverse-phase chromatography by treating Hyflo Super-Cel with DMCS vapour and then washing the support until neutral with methanol to remove HCl formed during treatment. Other silanizing agents that have been used successfully include hexamethyldisilazane [40,41] and trimethylchlorosilane (TMCS) [38,39].

Kirkland [42] compared the three silanation agents and by careful measurements of the asymmetry of the test peaks on chromatograms showed that DMCS was the most effective and TMCS the least effective of the three. This observation was confirmed in a similar study done by Ottenstein [43]. Ottenstein also found that the AW-DMCS-treated supports were more effective in reducing tailing than the NAW-DMCS-treated materials. The real benefits of acid washing were therefore seen only after the support was further silane treated.

1.8.2.d. CHROMOSORB HIGH PERFORMANCE (HP).

The "HP" grade has been developed for use with steroids, bile acids, alkaloids and for the analysis of pharmaceuticals, medical and toxicological compounds [44]. Chromosorb HP is carefully acid washed and silanized. Its features include superior inertness and column efficiency.

no catalytic surface activity, and short column conditioning time. Although the column performances of CG-HP and CW-HP are very similar, the hardness and better handling characteristics of CG represent real advantages over CW and other supports derived from filter-aids.

1.8.2.e. CHROMOSORB 750 (C-750).

C-750 is described as the most inert, non-friable, free flowing and highly efficient support designed specifically for biomedical and pesticide analysis. It is prepared from high purity diatomite and with exhaustive acid washing and effective silane treatment. Some of the features of C-750 include:

1. high degree of chemical inertness;
2. hard particles and, hence, minimum fines generated during coating and packing procedures;
3. provides uniform distribution of the liquid film on the particle surface;
4. minimum adsorption of polar compounds;
5. short column conditioning.

1.8.3. POROUS POLYMERS.

In recent years, macroporous copolymers have been used frequently as packings for gas chromatographic columns. Hollis [45] first described the use of the macroporous

copolymers of the styrene-divinyl benzene type in GC. At present various porous polymer beads are available for chromatography and are designated by different trade marks, such as Porapak (Waters Associates, Inc.), Polypak (F & M Scientific), and the Chromosorb 100 series (Johns-Manville).

It is considered that the separation processes on these sorbents are different from those encountered in GLC or GSC [46]. Adsorption and absorption take place simultaneously. The adsorption effect can be distinguished quite easily in the shape of the peaks especially of solutes which, because of their polarity do not diffuse into the skeleton, and are separated primarily by adsorption. The slight asymmetry in their peaks is an indication of a non-linear separation isotherm [47].

In this thesis Chromosorb 103 (C-103) was used to investigate the separation of s-triazines and hence is described here in some detail. C-103 is a polyaromatic porous polymer packing material developed specifically for amines and for basic compounds [48]. Table 7 gives the physical properties of C-103.

Supina and Rose [49] found that C-103 is not suitable for compounds such as acids, nitriles, glycols, nitro-alkanes, but it is recommended by Johns-Manville [48] for the

Table 7. Typical Physical Properties of C-103 [48]

<u>Physical Property</u>	
Type	Cross linked polystyrene
Free fall density (g/cc)	0.32
Surface area (m ² /g)	15 - 25
Average pore diameter μ	0.3 - 0.4
Water affinity	hydrophobic
Colour	white
Temp. limit (isothermal) C	275
Temp. limit (programmed) C	300

analysis of amines, amides, aldehydes and ketones. This observation was confirmed by Supina and Rose.

1.8.4. CSP-20M

CSP-20M is a new general purpose gas chromatographic packing prepared by bonding a thin film of Carbowax 20M to diatomaceous earth support [50]. It is claimed by the manufacturer that the inert surface of the CSP-20M packing produces sharp symmetrical peaks. It is also claimed that CSP-20M has low bleed characteristics and hence increased thermal stability which makes it superior to Carbowax 20M or KOH treated Carbowax 20M. The bleed test, however, was carried using a flame ionization detector (FID) which is less sensitive to bleed than the electron capture

detector (ECD).

1.9. THE STATIONARY LIQUID PHASE.

For the great majority of analytical separations, GLC has proved to be a very efficient technique. The use of liquid phases has the following advantages [51]:

1. the adsorption isotherm is linear under usual operating conditions so that symmetrical peaks are obtained;
2. liquid phases are available in great variety and of adequate selectivity to satisfy most separation requirements;
3. the amount of liquid phase in a column can be varied easily, therefore both preparative and high-efficiency columns can be made with the same liquid phase;
4. liquid phases are available in great purity and in well defined quality; thus retention time values are reproducible.

The greatest disadvantage of liquid phases is their volatility. Any liquid phase in a column has a vapour pressure, the magnitude of which depends primarily on the nature of the phase and on the working temperature. It is exposed to the continuously streaming carrier gas which removes a certain amount of the liquid phase per unit gas volume. This process is known as bleeding. Bleeding is

undesirable because: it can disturb the proper functioning of the detector; it causes baseline shift in programmed column temperature operation; it contaminates the trapped solutes; and because of the loss of the stationary phase, it gradually changes the separation characteristics of the column to the point where unacceptable deterioration occurs. The vapour pressure of the liquid phase in the column might be influenced by the support material and also by the loading. Hawkes and Mooney [52] have reported that propylene sebacate and adipate are catalytically dehydrated on the column at 150 °C. They found the sebacate to be stable, however, at 150 °C under reflux in the absence of the support. Some liquid phases are not homogeneous materials [46], e.g., commercial polyglycols or silicone greases are composed of homologues, and may also contain some chemically different materials. Column conditioning, which results in the removal of the volatile constituents, can extend the upper temperature limit of these liquid phases [51].

1.9.1. CYANOALKYL SUBSTITUTED POLYSILOXANES (CASP).

This group of liquid phases falls under the category of dilute stationary phases [53]. These are liquid phases in which the majority of the molar volume is occupied by non-polar groups but in which there are some polar groupings. The retention characteristics of this type of liquid phase

are determined by these polar groups with which polar solutes can interact. The retention of polar solutes is therefore determined in part by volatility as in the case of a non-polar liquid phase, but in addition, there is the effect of the specific interaction between solutes and the polar group of the liquid phase.

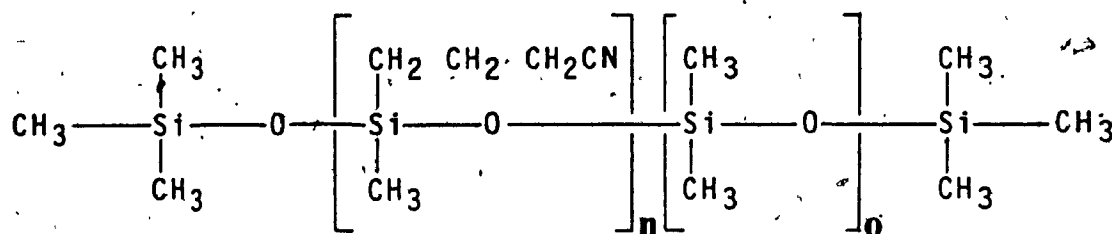
Cyanoethyl siloxanes produced by General Electric appear to have been first described in detail by Litchfield et.al. [54]. Using either an experimental polymer 238-149-99 (i.e., equivalent to XF-1150) with 50% cyanoethyl substitution, or XE-60 with 25% cyanoethyl substitution and/or a 1:1 mixture of the two, the separation of some geometric isomers of C₁₈ fatty esters was achieved.

Bayer et.al. [55] found nitrile liquid phases to be effective in the resolution of aliphatic, olefinic and aromatic hydrocarbons of similar boiling points and suggested the selectivity to be due to the formation of a π -complex between the nitrile groups and the π -electrons of the olefins and aromatic compounds.

Silicone gums and oils are known for their thermal stability and low bleed. CASP are polar in nature and in comparison with other polar liquid phases e.g., polyglycols, their thermal stability is better. The maximum operating temperature of CASP is very much higher than that

of other polar phases.

In this thesis we have used OV-225 (25% cyanopropyl; 25% phenyl; 50% methyl) as the liquid phase. OV-225 falls in the category of methyl cyanopropyl phenyl silicones; it has the following configuration.



OV-225 has been offered as a substitute for XE-60 although it cannot be considered as an equivalent [56].

The position of substitution of the cyano group is of considerable importance. A cyano group on the α -carbon atom leads to much reduced thermal stability as compared with substitution on the β or γ -carbon atoms [57]. With a γ -cyanopropyl methyl polysiloxane, the liquid phase has an oxidative stability which is equivalent to that of dimethyl polysiloxane [58].

Thermal stability of liquid phases has been examined by McKinney et. al. [59]. In their investigation of the thermal behaviour of stationary phases, they made use of thermogravimetry. They found high volatility for XE-60 (10% weight loss at 298°C). Although no such data are available for OV-225, a similar assumption can be made, i.e., high volatility at elevated temperatures.

1.10. DETECTORS:

Detectors have the task to sense continually, rapidly, and with high sensitivity, the solutes which are contained in the carrier gas as it emerges from the column. Detectors sense a change in some physical or chemical property of the effluent gas stream upon elution of the components. This change is converted into an electrical signal which is amplified and recorded.

For detecting the s-triazines studied in this thesis. The FID and the ECD were used. The linear ranges of these GC detectors are shown in Fig. 2.

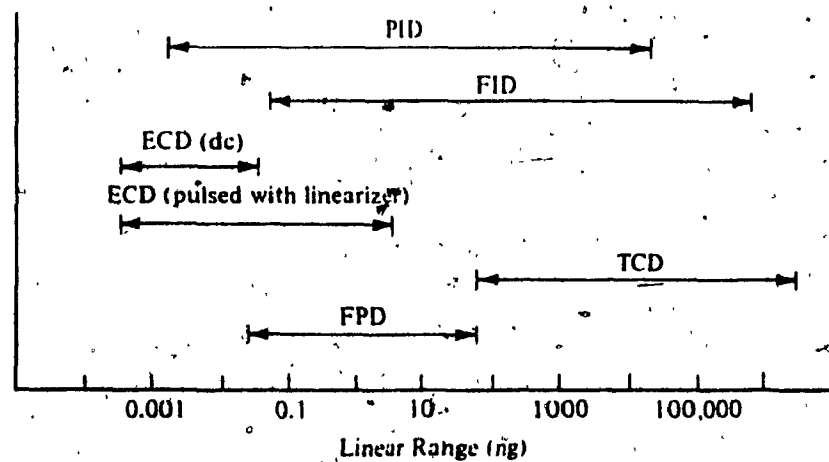


FIGURE 2. Linear Dynamic Ranges of Gas Chromatographic Detectors: PID; FID; ECD; TCD; and FPD.

1.10.1 FLAME IONIZATION DETECTOR (FID).

The FID is the most commonly used detector in GC. Some of the features that make the FID attractive include:

1. high sensitivity;
2. almost uniform response for almost all components;
3. wide dynamic range (good response linearity);
4. and invulnerability to temperature fluctuation and to the presence of impurities in the carrier gas.

The only disadvantage is that the FID is sensitive only to organic compounds. A schematic diagram of an FID is shown in Fig. 3.

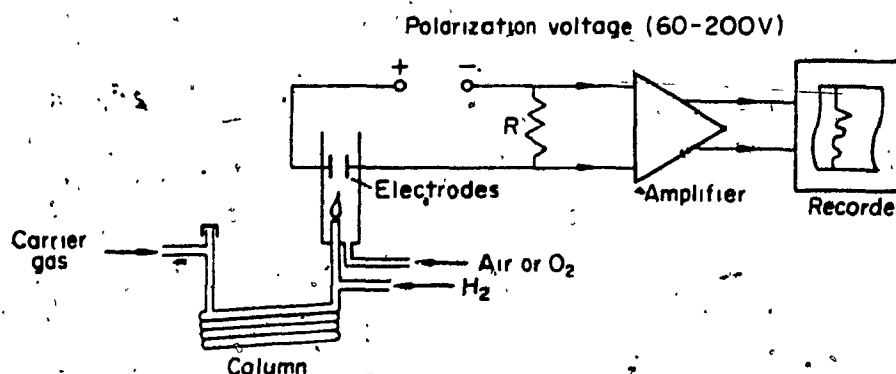
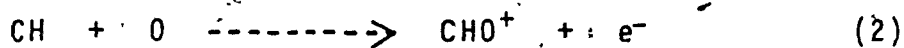


FIGURE 3. Principle Diagram of the FID.

The detector consists of a diffusion type hydrogen burner. The effluent gas from the column is mixed with hydrogen, and air or oxygen, and led into the combustion region between two electrodes (60 - 200 V applied potential). At the temperature of the hydrogen flame (2000 - 2200 °C) hydrogen is somewhat ionized (10^7 ions/cm) producing a constant background current. When the column effluent

contains organic substances, these will burn in the hydrogen flame (see reaction 2) and produce ions (up to 10^{11} ions/cm) increasing the conductivity of the flame and consequently the intensity of the ion current. The ion current between the two electrodes is recorded after appropriate amplification. The basic process taking place in the hydrogen flame is described by equation 2 [60].

The thermal energy released from the flame splits organic molecules and it is assumed that a chemionization reaction occurs:



The use of the FID in the analysis of pesticides has been reported [61] although it is not very common. Compounds giving certain flame products, e.g., benzene and chlorinated solvents, should be avoided [62]. These flame products may cause deposits to form on the insulator resulting in high background currents and high noise levels.

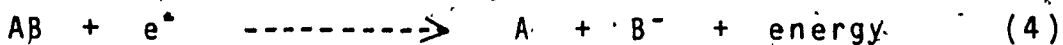
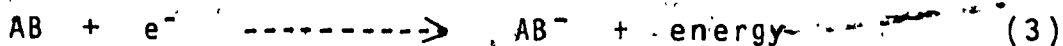
1.10.2 ELECTRON CAPTURE DETECTOR (ECD) (Figure 4).

The ionization of eluted substances by electron capture was first utilized in GC by Lovelock and Lipsky in 1960 [63]. In an ECD two basic processes are involved in the detection

of eluted substances:

1. production of thermal electrons, and
2. electron capture of thermal electrons.

The current produced in an ECD arises from secondary electron production through inelastic collisions between primary electrons, e.g., β particles, and molecules of nitrogen. The detector used for work done in this thesis, was fitted with a ^{63}Ni source for the production of beta particles and subsequently electrons and nitrogen ions. The probability of recombination of electrons and positive nitrogen ions is low because of their very different velocities (the velocity of an electron is approximately 104 times higher than that of positive ions)[63]. If the ionized inert gas contains compounds having high electron affinities, however, some free electrons may be captured by the molecules of these compounds with the formation of negative ions according to reactions 3 and 4 [62].



The velocity of the anions produced is much lower than that of free electrons, and the probability of recombination between negative and positive ions is therefore, $10^5 - 10^7$ times higher than that between electrons and positive ions [64]. The presence of a compound able to capture electrons

will be indicated by a decrease in the ionization current in the detector.

Pellizzari [65] gave an extensive review in which the operating parameters of the ECD are discussed. Because there are numerous parameters involved in achieving optimum performance of the ECD, the application of this device is fairly difficult. Pellizzari stated that the temperature of the detector should be constant, since fluctuations in temperature affect the electron capture coefficient, which in turn affects quantization of solute molecules.

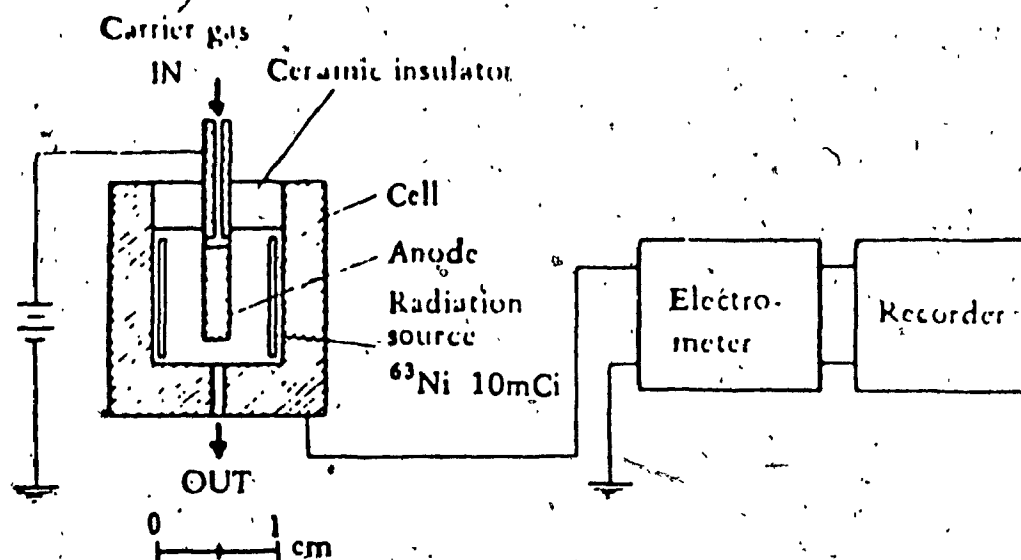


FIGURE 4. Principle Diagram of a d.c. ECD.

The potential to the electrodes can be applied in several ways:

1. at constant voltage;

2. under pulsed-constant frequency; and
3. under pulsed-variable frequency.

The pulse mode was used in this thesis work since higher sensitivity by a factor of about four is obtained.

A major problem in the use of the ECD is that the surface of the radioactive source can acquire a film coating due to column bleed and/or sample contamination. In penetrating this film, the beta emission is weakened progressively decreasing the electron gradient and thereby the sensitivity of the detector. The points on a response vs. voltage curve (Fig. 5) will gradually shift to the right as the film builds up [66]. Response will either decrease or increase depending on the voltage range selected.

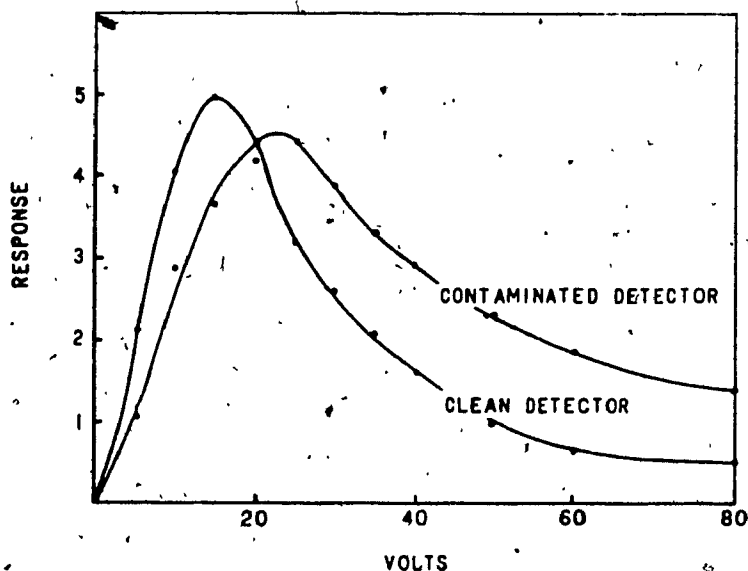


FIGURE 5. Response vs. Voltage Relation for the ECD Illustrating the Effect of Film Buildup on the Radioactive Source.

Bleed consists of the vapour or the decomposition products of the stationary phase. Since all liquid phases have a vapour pressure, bleeding is bound to happen at higher temperatures. The decomposition of the liquid phase may be catalyzed by the support on which the liquid phase is coated [67].

Devaux and Guiochon [68] studied the influence of the bleeding of the liquid phase on the detector response. The base current, I_0 , is observed under all experimental conditions when a flow of pure carrier gas is passed through the detector. When there is a concentration C of a compound with some electron affinity passing through, the detector gives a current or signal I , smaller than I_0 . The difference $I_0 - I$ is the detector response. Lovelock [69] has shown that the signal is given by:

$$I = I_0 e^{-kC} \quad (5)$$

where k is the coefficient of electronic absorption. The response

$$I_0 - I = I_0(1 - e^{-kC}) \quad (6)$$

does not vary linearly with C , except for very small values of current where

$$1 - e^{-kC} \approx kC$$

and therefore

$$I_0 - I = kI_0 C \quad (7)$$

kI_0 is the response factor of the detector in the linear

range. When bleeding occurs Equation 6 becomes:

$$I_0 - I = I_0(1 - e^{-[k_1C_1 + k_2C_2]}) \quad (8)$$

where k_1 and C_1 , k_2 and C_2 are the coefficients of electronic absorption and the concentrations of the bleeding compounds and of the solute, respectively. If both concentrations are small, Equation 7 is still valid and

$$I_0 - I = (k_1C_1 + k_2C_2)I_0 \quad (9)$$

the response factor can be derived from peak height or area after due correction for baseline displacement.

Devaux and Guiochon have also shown that polar phases are much more prone to have a high electron affinity than non-polar phases. In their comparison between the effect of liquid phase bleed on the FID and ECD, they found that when working with an ECD the use of a liquid phase will have to be restricted to much lower temperatures than with an FID. The ECD has its greatest utilization in the field of pesticide analysis [70].

1.11 GLC OF S-TRIAZINES.

Various methods, colorimetric [71], UV spectrophotometric [72] and electrochemical [73] have been used in the analysis of s-triazines. These methods, however, allow the

determination of only one individual s-triazine at a time, and are therefore cumbersome and inadequate for multi-residue analysis. For several years chromatographic procedures [72], paper chromatography, TLC, GLC, and recently even HPLC [74,75] and HP-TLC [75] have been applied for the separation, identification and determination of s-triazines and their metabolic and degradation products in environmental residue sources.

GLC with packed columns has played a major role in the analysis of s-triazine residues, especially since a number of detectors are available. Use has been made of the FID [73,76,77], ECD [78,79,80], microcoulometric detector [81], AFD [82], FPD [83], and electrolytic conductivity detectors [79,82]. Bailey et.al. [84] have reported that the nitrogen selective electrolytic conductivity detector is the most sensitive one towards s-triazines.

Various researchers have used a variety of supports, including Diatoports [85], Anachrom ABS [81], glass Ballotini [86], Gas Chrom Q [84], CW-HP [84], etc. The number of liquid phases used to coat supports are too numerous to list here. Fishbein [87] reports in a review a variety of liquid phases that had been used. Since that report the use of many more liquid phases have been described. A careful study of the literature has shown that the preferred liquid phase which appears to give the best

resolution of s-triazines, is Carbowax 20M [81,88,89,].
Gas Chrom Q has been the most commonly used support.

CHAPTER

2

EXPERIMENTAL

2.1. INSTRUMENTATION.

The effect of column temperature and nature of the support on peak area response of the three s-triazines (prometone, atrazine, and ametryne) were studied using a Shimadzu Gas Chromatograph GC-6AM fitted with an FID and ECD.

The dual column FID system was used to study "high" concentrations of s-triazines. The ECD was operated only in the single column mode. "Moderate" and "low" concentrations of s-triazines were studied with the ECD.

In order to compare responses on different supports all the parameters on the instrument were kept constant except for the one investigated. For example, in the case of column temperature studies, only the column temperature was varied, all other parameters were kept constant. Chromatograms were plotted with a Fisher Recordall Series 5000 recorder.

All the cylinder gases used were manufactured by Union Carbide. High purity nitrogen gas (less than 10 ppm oxygen) was used as carrier gas throughout this thesis. The carrier gas was filtered through oxygen and moisture traps before it entered the column. A flow rate of 30 ml/min was found to give maximum sensitivity with both FID and ECD. With this flow rate relatively short retention times were

obtained. Maximum sensitivity of the FID was found with air and hydrogen flow rates of 611 and 44 ml/min, respectively.

2.2 COLUMN PARAMETERS.

All the experiments were carried out making use of glass tubing columns. All glass tubing was silanized prior to use (see section 2.5). The tubing material was of the standard borosilicate glass type (pyrex). Column dimensions were 122cm X 3mm i.d. The columns were generally packed with diatomaceous supports coated with 3.5% (w/w) OV-225 liquid phase. This low load of liquid phase was sufficient to give a good separation of the three s-triazines. Columns were also packed with CSP-20M and uncoated C-103 porous polymer beads.

Columns were used only after conditioning at 250°C for 24 hours. Columns containing coated diatomaceous supports were conditioned under a stream of nitrogen gas at a flow rate of 30 ml/min. Columns packed with CSP-20M were conditioned as follows: they were heated at 100°C for 30 minutes with carrier gas (nitrogen) flowing through. The column was then heated to 270°C at a rate of 4°C/min and it was held at this temperature under nitrogen carrier gas flow for 20 minutes after which the column was ready for use. Columns packed with C-103 were conditioned at 250°C under helium flow. Tables 8 and 9 summarize the GLC operating conditions

Table 8. GLC Operating Conditions for Analyzing s-Triazines Using the FID.

Column	Dual 122cm X 3mm i.d. glass columns with 3.5% OV-225 on 80/100 mesh support
Temperature	
Column	140 - 240 °C at 10 deg. intervals
Injector/detector	285 °C
Flow rates	
Carrier gas (N ₂)	30 ml/min
Air	611 ml/min
Hydrogen	44 ml/min
Sensitivity and range	10 ³ and 4
Recorder	
Voltage	0.1 V
Chartspeed	1.25 cm/min
Sample size	
"High" concentration	1 ul containing a mixture of 1.3 ug prometone, 2.2 ug atrazine, and 3.0 ug ametryne.

Table 9. GLC Operating Conditions for Analyzing s-Triazines Using the ECD.

Column	Single 122cm X 3mm i.d. glass column with 3.5% OV-225 on 80/100 mesh support
Temperature	
Column	160 - 240 °C at 10 deg. intervals
Injector/detector	285 °C
Flow rate	
Carrier gas (N ₂)	30 ml/min
Sensitivity	10 ²
Range: "moderate" conc.	4
"low" conc.	2
Recorder	
Voltage	0.001 V
Chart speed	2.5 cm/min
Sample size	
"moderate" conc.	2 ul containing a mixture of 50.6 ng prometone, 6.2 ng atrazine, and 50.0 ng ametryne
"low" conc.	2 ul containing a mixture of 25.3 ng prometone, 3.1 ng atrazine, and 25.0 ng ametryne.

used for analyzing s-triazines.

2.3 MATERIALS USED.

Diatomaceous earth supports used were manufactured by Johns-Manville (purchased from Chromatographic Specialities, Brockville, Ont.). This was the source of all our supplies, except where otherwise noted. For the three grades of supports (CP, CW and CG), all types, NAW, AW, AW-DMCS and HP, were coated with 3.5% OV-225 liquid phase. C-750 was also coated with OV-225. All the supports were of the same particle size, 80/100 mesh.

The CSP-20M packing a modified Carbowax 20M liquid phase coated on a support. The nature of the support is not specified by the manufacturer. C-103 80/100 mesh was manufactured by Johns-Manville. The liquid phase, OV-225, was manufactured by Pierce Chemical Co., Rockford, IL., USA. Solvents (benzene and methanol) used for making up solutions were both of the pesticide grade type, purchased from Anachemia Chemical Co. (Montreal, Que.). The three s-triazines, of 99%+ purity, were manufactured by Chem Service Chem. Co. and supplied by Caledon Laboratories Ltd., Georgetown, Ont.

2.4 COATING OF THE SUPPORT WITH THE LIQUID PHASE.

All diatomaceous earth supports were coated with 3.5% (w/w) of OV-225 liquid phase. 10.0 g of support and 0.35g of OV-225 were weighed out with an analytical balance. The liquid phase was dissolved in 140 ml chloroform (analytical grade, Anachemia Chemical Co.). The support was then slowly poured into the solution while the beaker was swirled lightly so as to avoid the formation of agglomerates. The beaker was subsequently placed on a hotplate and the solvent evaporated off at 60 °C. The beaker was swirled intermittently to assure a uniform coating of liquid phase on the support. Heating was continued until the support particles were free flowing. The beaker was then removed from the hotplate and the support was further dried under a constant stream of high purity nitrogen gas. This process was continued until the support was free from solvent. Recovery of coated support was 98% plus.

2.5 PACKING OF THE COLUMN.

In packing of columns two conditions have to be kept in mind:

1. the need for uniform packing of the support in the column;
2. the need to avoid crushing of support particles during the packing process.

The column tubing used was precoiled and silanized before being packed. Silanization was carried out as outlined by Supina [90]. Tubing was filled with a silane agent (a Sylon CT solution of 5% DMCS in toluene, supplied by Supelco, Inc. Oakville, Ont.) and deactivation of silanol groups allowed to proceed for 5 minutes. The tubing was then emptied and washed with analytical grade reagent toluene (Fisher Scientific Co., Montreal, Que.). This washing step was repeated. Following the toluene washing, the column was washed three times with pesticide grade methanol. After this washing the column was dried with a stream of nitrogen gas.

Packing the precoiled tubing was done by the suction technique [90]. One end of the tubing was plugged with silanized glass wool. Support was introduced through the other end while the plugged end was connected to a source of vacuum. After the column was filled with support it was vibrated for a few minutes to secure a tight packing. If necessary the column was then further filled with support. After completely filling the column the open end was plugged with silanized glass wool.

2.6 SOLUTIONS.

All the experiments done using the FID, were with s-triazines in the microgram concentration (1 - 5 ug) range.

The solution (mixture of three s-triazines) was made up as follows: 0.065g of prometone, 0.110g of atrazine, and 0.150g of ametryne were weighed out and transferred to a 50.0 ml volumetric flask and made up to volume with methanol. This solution had concentrations of 1.30ug/ul of prometone, 2.20ug/ul of atrazine, and 3.00ug/ul of ametryne. Of this solution 1ul volumes were injected into the GC for analysis.

Solutions for experiments with the ECD were made up in benzene as a solvent. Benzene was used as a solvent instead of methanol, because the methanol available had an impurity which interfered with the prometone peak in GLC. The "moderate" concentration solution was prepared as follows: 0.084g of prometone, 0.010g of atrazine, and 0.083g of ametryne were weighed out, dissolved and made up to volume in a 100.0ml volumetric flask with benzene as solvent. This solution was then further volumetrically diluted to give concentrations of 25.3ng/ul of prometone, 3.1ng/ul of atrazine, and 25.0ng/ul of ametryne. Of this solution 2ul portions were injected into the GC.

For experiments with "low" s-triazine concentrations, the above solution was diluted with benzene by a factor of two to give concentrations of 12.6ng/ul of prometone, 1.5ng/ul of atrazine, and 12.5ng/ul of ametryne. Of this solution 2ul portions were injected into the GC.

2.7. INTRODUCTION OF SAMPLE INTO THE GC.

Injection technique is important in quantitative GLC, since it has an effect on the reproducibility of peak areas. Injections were made with a 10ul Hamilton glass micro syringe. Injection volumes of 1 and 2ul were used with the FID and ECD, respectively.

The technique used was as follows: a large volume (5ul) of the sample is pulled into the syringe. The plunger is then pushed forward to the appropriate volume mark; the needle is then wiped clean with tissue paper; the plunger is pulled back to create an air pocket between the sample and the needle. Care must be taken not to introduce an air pocket between the plunger and the sample. The needle is used to pierce the septum of the injector port, the plunger is pushed down with a quick thrust and after a count of three the needle is pulled out from the injector port. This injection technique gave excellent reproducibility (better than 99%) of peak areas.

2.8 A TYPICAL GLC RUN.

In this thesis a typical GLC run represented a temperature study of a column, starting at a column temperature of 140°C, which was increased at intervals of 10 degrees up to 240 °C. The exception to this was that using "low"

s-triazine concentrations, the detector response was measured only at 170 and 210 °C. To ensure consistency of responses within a given run it was considered advantageous to complete a run on the same day that it was started. On the average a run took 18 hours to complete. During a run all the GC parameters were kept constant except for the column temperature.

At each specific column temperature injections of test solution were repeated until three successive injections gave the same peak heights. When the column temperature was increased to the next higher temperature to be studied, approximately 5 - 10 minutes were required for the column temperature and baseline to stabilize when a dual column system was used. During the period that column temperature is increased (for any 10 deg. increment), any column effect on the detector is hidden when a dual column system is used. With single column tests and the ECD, bleeding of the liquid phase caused a significant shift in the recorder base line. The recorder pen was re-zeroed as required.

2.9 GAS CHROMATOGRAPHY - MASS SPECTROMETRY STUDIES (GC/MS).

Independent experiments were done on the bleeding of the OV-225 liquid phase using a GC/MS. Since bleeding of the liquid phase in a chromatographic column is a well known phenomenon, the GC/MS experiments were merely used to

determine the extent of bleeding over the temperature range studied.

For these experiments an LKB 9000 Shimadzu GC/MS was used. The mass spectrometer is fitted with a magnetic sector. With the GC/MS, experiments were done from a column temperature of 140°C up to 220°C at 20 deg. intervals. Mass spectra of the liquid phase were obtained only after the column temperature had stabilized at the required specific value. When column temperature was increased to the next temperature level tested about 30 minutes was required for the instrument to restabilize.

2.10. PRELIMINARY EXPERIMENTS.

Experiments were first carried out to determine the optimum GC conditions at which the analysis of s-triazines could be carried out. This was done with both the FID and ECD. This work led to the use of operating parameters listed in Tables 8 and 9. Experiments were also carried out to determine the optimum concentrations ("high", "moderate", and "low") of the three s-triazines that were studied.

As this work was part of a long term, systematic study of effects of sample concentration, column temperature, and column support material on the gas chromatographic analysis of a variety of pesticides, it was desirable that the

liquid phase selected be of the general type previously used. In their study of organophosphorus pesticides, Haniff and Zienius [4], used OV-1 as the liquid phase, while Kouloulis [6] used OV-17 for the study of organochlorine pesticides. Of all the common silicone liquid phases only OV-225 gave a good separation of the three s-triazines under investigation. OV-225 has the additional advantage of having a higher maximum temperature limit than Carbowax 20M, which was not suitable for the temperature range (140 - 240 °C) studied. Hence experimentation was carried out with OV-225.

CHAPTER

3

COLUMN PERFORMANCE USING DIFFERENT SUPPORT MATERIALS

3.1. INTRODUCTION.

This comparative study was done by processing results obtained studying "high" concentrations of s-triazines using the FID and "moderate" concentrations using the ECD. The column performance parameters (n, R and H) were calculated from gas chromatograms obtained at 170 and 210 °C. Calculations for n, R and H were done using the equations in Table 4. In calculating the relative retention time (RRT), the shortest retention time was assigned a value of unity and the other retention times were expressed as a ratio to unity.

3.2. ORDER OF ELUTION.

The order of elution of the three s-triazines is shown in Fig.6. The elution order was consistent with that expected based on literature references. It depends primarily on the nature of the substituent in position 2 (see Table 1). The order of elution is methoxy, chloro, and finally thiomethyl derivatives. Within the chloro-s-triazine series, the order of elution depends chiefly on the spatial shielding of the -NH groups in the 4- and 6- positions by alkyl groups and on their number. The weakest shielding, causing the longest retention, is exerted by the ethyl group, the strongest by the tert.-butyl group, and isopropyl lies in between [73]. A similar dependence can be observed in the series of methoxy-

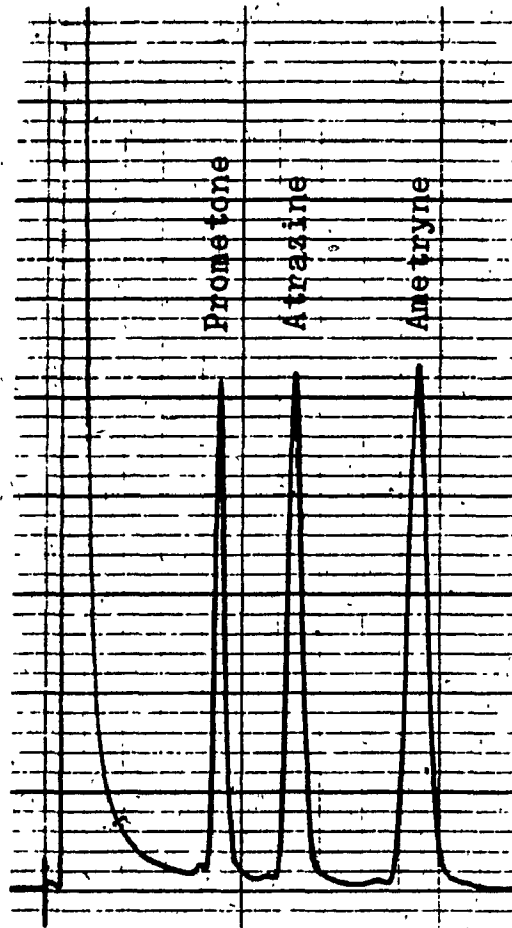


FIGURE 6. Elution Order of s-Triazines at 200°C on a CW-HP Support Using the FID.

and thiomethyl-s-triazines. Pacakova and Nemeč [73] also found that retention data for the s-triazines are influenced by their basic character. The dissociation constant of the s-triazine compound is most strongly affected by the substituent in the 2-position.

3.3. COLUMN PERFORMANCE.

3.3.1. MEASUREMENTS OF EFFICIENCY USING "HIGH" CONCENTRATIONS OF S-TRIAZINES.

Table 10 shows the RRT for atrazine at two temperatures on various columns. The temperature did not affect the RRT. It can be seen that the s-triazine has a longer residence time in the OV-225 when it is coated onto the CG than when it is coated onto the CW supports. This is due to the fact that the CW have a larger surface area than the CG supports. Thus, given a constant weight of liquid phase it will have to spread into a thinner layer to coat the surface of the CW compared to CG supports. Because of the thinner layer of liquid phase, the s-triazines spend less time in the liquid phase on the CW supports. CW-NAW and CG-NAW show the shortest retention times of all CW and CG supports, respectively, probably due to inefficient coating of the liquid phase upon these supports.

By consideration of the other column efficiency parameters, n and H (Table 11), it is clear that the CW supports show

Table 10: Relative Retention Times for "High" Concentration of Atrazine .

<u>Support</u>	<u>170 °C</u>	<u>Rank</u>	<u>210 °C</u>	<u>Rank</u>
CW-NAW	1.00	1	1.00	1
CW-AW	1.88	4	1.75	4
CW-AW-DMCS	2.46	5	2.25	5
CW-HP	1.55	3	1.46	2
C-750	1.50	2	1.46	2
CG-NAW	2.80	6	2.53	6
CG-AW	6.05	8	5.25	9
CG-AW-DMCS	5.29	7	4.66	7
CG-HP	6.05	8	5.11	8

Table 11. Column Efficiencies at 200 °C for "High"
Concentrations of Atrazine Using the FID.

<u>Support</u>	<u>n⁺</u>	<u>H (mm)</u>	<u>R[*]</u>
CW-NAW	6733	0.18	5.60
CW-AW	6054	0.20	7.50
CW-AW-DMCS	9406	0.13	9.32
CW-HP	6228	0.20	6.80
C-750	3851	0.32	5.30
CG-NAW	6193	0.20	7.20
CG-AW	4137	0.30	6.52
CG-AW-DMCS	6512	0.19	8.10
CG-HP	6312	0.19	8.00

* - resolution of prometone and atrazine

+ - number of theoretical plates per 122 cm of column

better column efficiency. This agreed with findings by Giddings and Saha [91] that in terms of the overall efficiency, CP was the best followed by CW and then CG. CW-AW-DMCS has the highest number of theoretical plates ($n = 9406$; $H = 0.13\text{mm}$). Although C-750 has a short RRT it shows rather poor column efficiency ($n = 3851$; $H = 0.32$) compared to the other supports. Short retention time is therefore no guarantee of high efficiency. Neither is the extent of surface pretreatment that the support has been given. For the CW supports, overall the order of n was:

$$\text{CW-AW-DMCS} > \text{CW-NAW} > \text{CW-HP} > \text{CW-AW}$$

and for the CG supports:

$$\text{CG-AW-DMCS} > \text{CG-HP} > \text{CG-NAW} > \text{CG-AW}$$

It is clear that there is a general pattern in column efficiency for these supports. This must be a reflection of the chemical deactivation treatment these supports received.

3.3.2. RESOLUTION.

Although resolution (R) can also be used as an indicator of column efficiency, it really only indicates the degree of separation. From Table 11, it can be seen that, overall, the CG supports gave better resolution, even though the support which gave the best resolution was a CW, i.e., CW-

AW-DMCS. The CG supports give better resolution since the s-triazines are retained longer in the liquid phase, thus enhancing separation.

The order of resolution for CW supports was:

CW-AW-DMCS > CW-AW > CW-HP > CW-NAW

and for the CG supports:

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

Although all the columns tested gave good resolution ($R > 1.5$), it was advantageous to identify the column on which resolution was best since it should be the most useful one for separation of a large number of s-triazines.

3.3.3. MEASUREMENTS OF EFFICIENCY USING "MODERATE" CONCENTRATIONS OF S-TRIAZINES.

With "high" concentrations of s-triazines, some support surface activity effects may be masked. With a decrease in sample concentration such effects may be amplified, showing up as changes in retention time, the peak shape and subsequently the column efficiency. Low sample concentrations have a tendency to give tailing peaks due to adsorption of the solute on the support. A study of the peak symmetry would highlight concentration effects, but in experiments carried out with low concentrations of the s-

triazines, baseline irregularities made impossible the determination of degree (if any) of peak tailing that occurred (see Fig. 7).

Column efficiencies measured for atrazine at 200 °C using "moderate" concentrations of s-triazines are reported in Table 12.

Table 12. Column Efficiencies at 200 °C for "Moderate" Concentration of Atrazine Using the ECD.

<u>Support</u>	<u>n⁺⁺</u>	<u>H (mm)</u>	<u>R⁺</u>
CW-NAW	1539	0.79	1.18
CW-AW	1588	0.76	1.74
CW-AW-DMCS	1712	0.71	1.77
CW-HP	1957	0.63	1.95
C-750	858	1.43	1.96
CG-NAW	1480	0.83	1.82
CG-AW	1638	0.75	1.93
CG-AW-DMCS	1278	0.95	1.69
CG-HP	902	1.35	1.73

*+ - resolution of prometone and atrazine

++ - number of theoretical plates per 122 cm of column

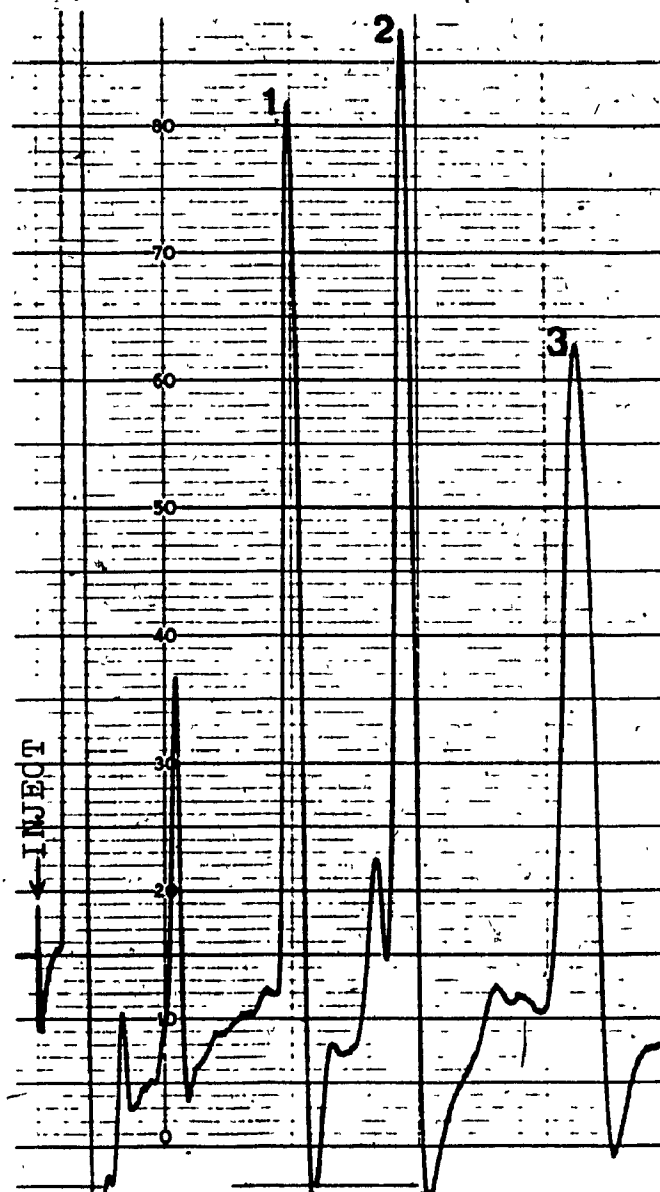


FIGURE 7. Typical Chromatogram of s-Triazines at 200 °C on a CW-HP Support Using the ECD. 1. Prometone. 2. Atrazine; 3. Ametryne

It can be seen that, overall, the column efficiency significantly decreased compared to results with "high" concentrations. This drastic decrease in column efficiency can be ascribed to adsorption of the s-triazines on the support. Adsorption of s-triazine causes broadening and tailing of peaks which in the extreme results in overlapping of peaks, i.e., poor resolution. Such adsorption is masked using "high" concentration of s-triazines. In addition, the FID is not as sensitive to liquid phase bleed as the ECD. Decreased efficiency was also reflected in decreased resolution (Table 12). With the exception of CW-NAW, however, all supports still showed resolution better than 1.5.

CHAPTER

4

RESPONSES FOR "HIGH", "MODERATE" AND "LOW" CONCENTRATIONS
OF S-TRIAZINES

When analyzing "high" concentrations of s-triazines (1.3ug prometone; 2.2ug atrazine; 3.0ug ametryne) the FID was used since it is less sensitive than the ECD. One microliter samples were injected. For "moderate" concentrations (50.5ng prometone; 6.0ng atrazine; 50.0ng ametryne) the ECD was used and two microliter volumes were injected. Responses obtained at the peak maxima of the thermograms for both "high" and "moderate" concentrations of s-triazines, were recorded in addition to responses at 10 degree intervals. For "low" concentrations (25.3ng prometone; 3.0ng atrazine; 25.0ng ametryne) the sensitivity of the ECD was decreased to 2×10^2 . At this sensitivity a fairly noise-free baseline was recorded.

4.1. RESULTS AND DISCUSSION.

Initial results showed that there was no decomposition of the s-triazines in the temperature range covered, since all peaks were symmetrical and no extraneous peaks showed up (Figs. 7 and 8). Relative peak area calculations on different chromatograms could, therefore, be carried out readily. Classification of the supports based on peak areas measured for "high", "moderate", and "low" concentrations of s-triazines are listed in Appendix I. For comparison purposes, results at 170 and 210 °C only are presented. Data at other temperatures substantiated these results as can be deduced from the figures in Appendices II and III.

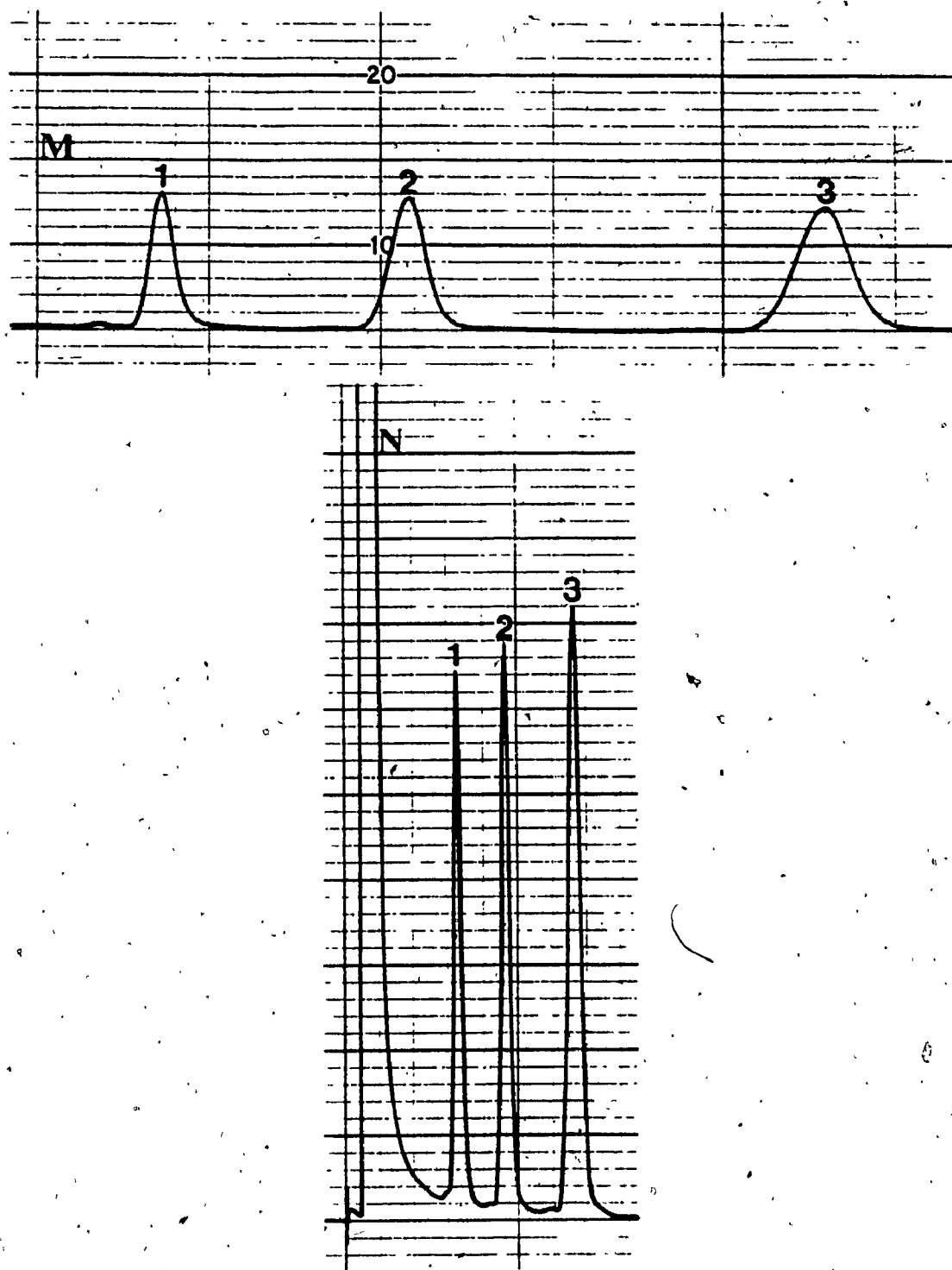


FIGURE 8. Typical Chromatograms for s-Triazines at (M) 170°C and (N) 210°C Using the FID. 1. Prometone; 2. Atrazine; 3. Ametryne.

4.1.1. CHROMOSORB W SUPPORTS (Tables 16 - 18, Appendix I).

For "high" concentrations of s-triazines W-NAW and W-AW showed more or less the same responses, higher than what was observed for W-AW-DMCS and W-HP. Responses were higher with C-750 than with any W support. Temperature variation had negligible effect.

For "moderate" and "low" concentrations of s-triazines, responses at 210 °C were significantly lower than at 170 °C. This was at least partly due to liquid phase bleeding leading to decreased ECD response at higher column temperatures.

Silanized W supports showed markedly improved responses towards "moderate" and "low" concentrations of s-triazines. The possibility existed that this was related to non-reproducibility in filling column tubing with packing since different columns were packed for tests with "high" and "low" concentrations. The same batch of coated packing, however, was used in both cases.

For "moderate" and "low" concentrations of s-triazines W-NAW gave the poorest response of any W support. This indicated that acid washing and silanization were beneficial in obtaining enhanced responses, probably because of subsequently decreased adsorption of solute

molecules on the supports.

For "high" and "low" concentrations of s-triazines the W-AW support was the best W support. Responses were lower on W-HP at all s-triazine concentrations, an indication of adsorption of s-triazines onto the surface of the W-HP support. This was inconsistent with manufacturer's specifications that W-HP is an extremely efficiently surface deactivated support. C-750 gave a very good response for "high" concentrations of s-triazines and very poor response with "moderate" and "low" concentrations.

In summary: the responses of W supports towards "high" concentrations of s-triazines followed the order:

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

towards "moderate" concentrations:

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

and towards "low" concentrations:

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

Where conclusions regarding relative responses differ for "high" and "moderate/low" concentrations of s-triazines the temptation is to place more faith in the lower concentration results. High sample concentrations can frequently mask support adsorption effects.

4.1.2. CHROMOSORB G SUPPORTS (Tables 20 - 22, Appendix I).

For high concentrations of s-triazines G-AW and G-AW-DMCS gave equal responses. For "moderate" and "low" concentrations G-AW gave better responses than G-AW-DMCS, the difference in response being magnified as sample concentrations decreased (maximum 40% difference in response at lowest concentration tested). G-NAW gave the lowest response of all G supports for all concentrations of s-triazines. The observation that responses of G-AW-DMCS decreased with concentration of s-triazine is quite significant. The poor behaviour on G-AW-DMCS indicates that this silanized support surface is more adsorptive than the un-silanized W-AW, most unlikely, or that the silanized surface is more difficult to coat effectively with a liquid phase. A support further chemically treated to decrease surface adsorption, i.e., G-HP, behave even more poorly than G-AW-DMCS. The poor response on G-NAW was anticipated, since it was not chemically deactivated in any way.

Temperature did not affect the ranking of G supports at any concentrations of s-triazines. This is a reflection of the nature of the CG particle. It is hard, less prone to fracture than CW. Its surface area is less than that of CW supports, and on top of that is covered with more liquid phase. Hence fewer active sites will be exposed at any

column temperature. This explains the consistent behaviour of the G supports in terms of response ranking at different temperatures.

In summary, towards all concentrations of s-triazines the order of responses was:

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

4.1.3. RESPONSES OF CW AND CG SUPPORTS AT PEAK MAXIMUM TEMPERATURE (Tables 19 and 23, Appendix I).

At the thermogram maxima, i.e., those column temperatures at which responses were a maxima, the order of response with both CW and CG supports was the same; i.e.,

AW > AW-DMCS > HP > NAW > 750

This observation was more or less in agreement with that at the other temperatures reported. The only factors that play a role in determining the response at the peak maxima temperature are the type of chemical deactivation the support received and the type of support, i.e., CW, CG or C-750. It should be noted that although the peak maxima did not occur at the same temperature for every support, the order of responses was not changed. This suggests that G and W-AW supports should be the most advantageous for s-triazine analysis regardless of column temperature used.

4.1.4. FURTHER OBSERVATIONS.

The FID sensitivity was similar towards all three s-triazines. Since the FID is sensitive to CH groupings and the three s-triazines have approximately equal numbers of carbon atoms, this result was not un-expected.

The ECD, however, showed higher sensitivity towards atrazine than towards prometone and ametryne. This is expected since atrazine has a chlorine atom in position 2 of its ring and the ECD is very sensitive to chlorine atoms, much more so than to the less electron affinitive groups such as methoxy and thiomethyl. The latter two groups have the same electron affinity and their responses to the ECD are accordingly equal.

4.2 THERMOGRAMS FOR S-TRIAZINES USING THE FID (Figs. 33 - 41, Appendix II).

Thermograms were obtained on CW, CG, and C-750 supports by plotting peak area responses measured at particular temperatures versus those temperatures in the 150 to 230 C range. Where a response value is not reported at some particular temperature, then either the s-triazine was totally adsorbed or it gave so flat a peak that its area could not be measured without large error (low temperature range) or else the peaks were so sharp and narrow as to be

impractical to measure manually (high temperature). This was the case, for example, for W-NAW support (Fig. 32). All the thermograms given in Appendix II represent first run results. There were basically two types of patterns observed in the thermograms; one type where there was more than one maximum in the thermogram; and a second type where there was a continuous increase in peak area response with increase in column temperature. Results on W-AW and G-NAW (Figs. 9 and 10) illustrate these patterns. It was thought that these thermogram shapes could be attributed either to instrument idiosyncracies on a day to day basis or represented real column variations. If due to instrument faults, these thermograms should not have been reproducible from run to run since the instrument could not be expected to respond in an identical manner every time. In tests carried out on two different days, however, the shapes of the thermograms were almost identical (Figs. 9 and 10).

No more than two maxima were observed in any one thermogram. Haniff and Zienius [4,5] and Kouloulis [6] observed the same trends in thermograms when using the FID for detection of pesticides. Haniff and Zienius proposed that the maxima are the consequence of bleeding of the liquid phase followed by priming of the exposed adsorption sites. An increase in detector response was attributed to the decrease in adsorptivity of pesticides due to the

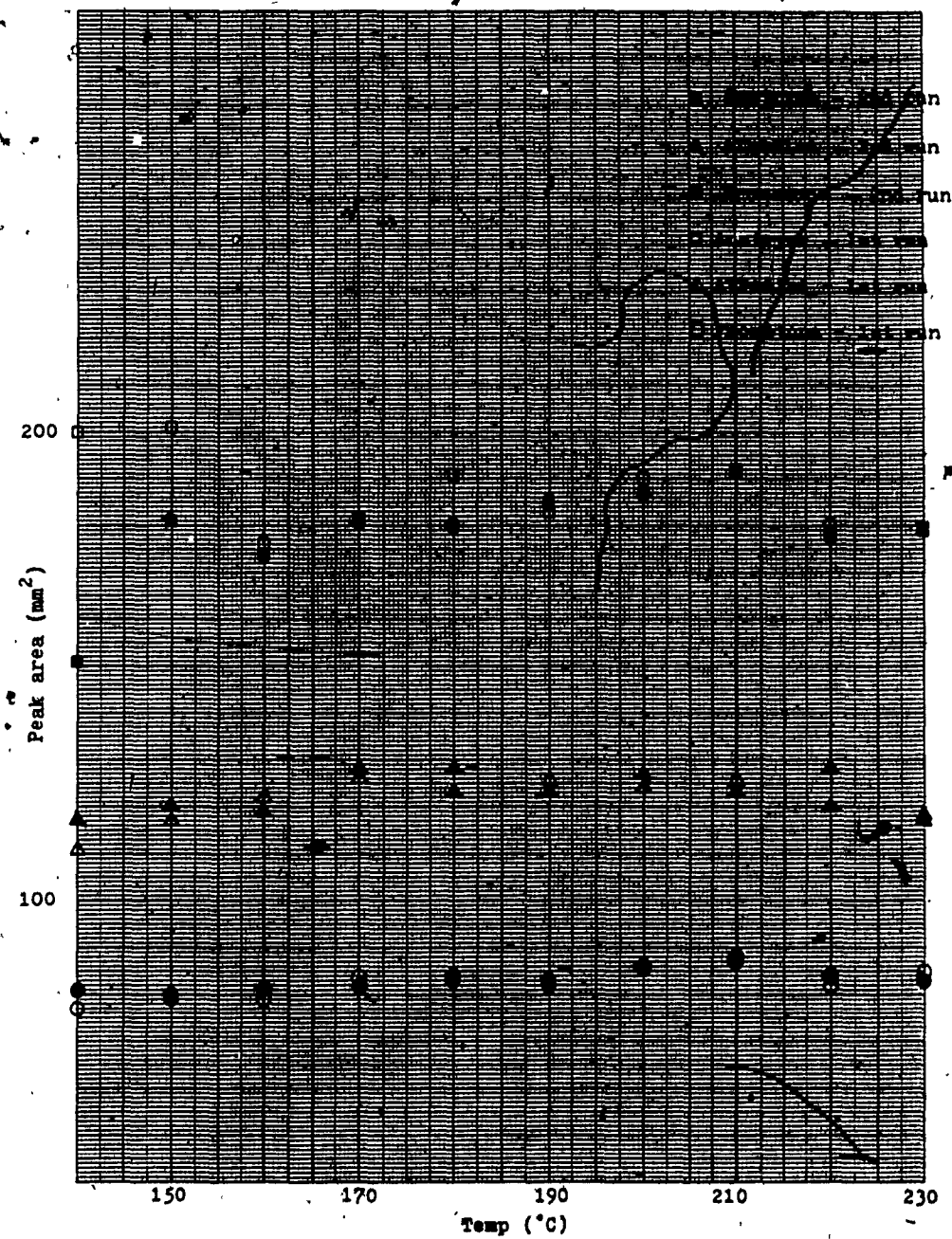


FIGURE 9. Thermograms of 1st and 2nd Runs of s-Triazines on a CW-AW support (FID).

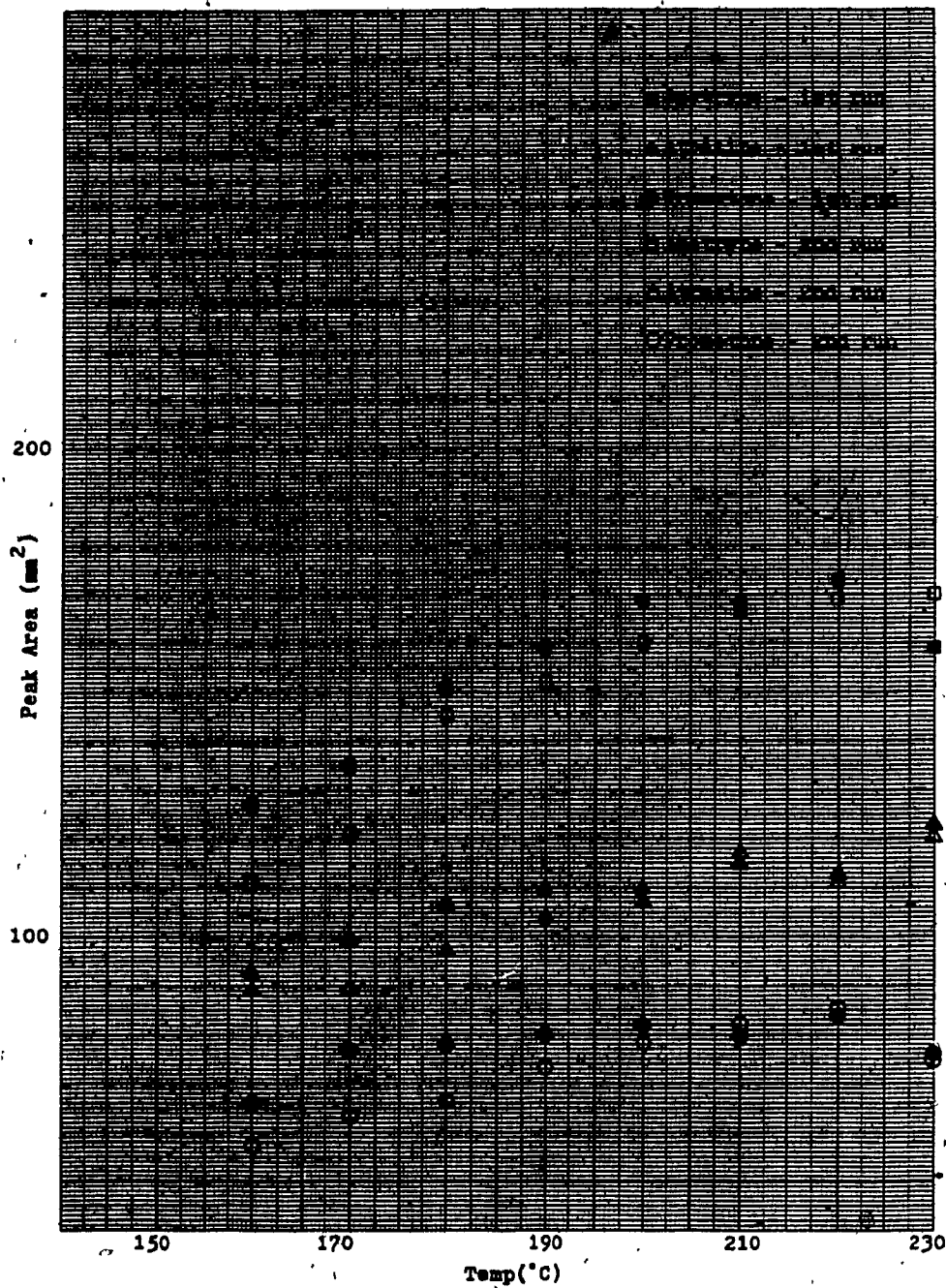


FIGURE 10. Thermograms of 1st and 2nd Runs of s-Triazines on a CW-NAW Support (FID).

increase in column temperature. A decrease on the thermogram was explained in terms of excessive bleeding leading to exposure of adsorption sites, and these sites adsorbed solute molecules to undergo priming which resulted in a decreased detector response. There are basic weaknesses in Haniff and Zienius' hypothesis. It cannot account for the fact that in the course of a single run with three s-triazines, the thermogram of one may give a distinct maximum while the other two show less pronounced maxima or even no maxima (Fig. 33). An alternative explanation for this phenomenon of multi-maxima can be proposed on the basis of an unidentified interaction between the solutes and the liquid phase. Such interaction between solutes and liquid phase will be greater for increased amounts of liquid phase and will change with factors such as bleeding which acts to decrease the amount of liquid phase. Also the longer the retention of the solute in the liquid phase the greater the degree of interaction that is likely. Experimental evidence in fact confirmed this prediction. For example, it can be noted in Fig. 33 that ametryne, which is eluted last does give a thermogram with more maxima than appear in the thermograms of atrazine and prometone on the same support.

The behaviour on supports such as CW-AW-DMCS, CG-NAW and CG-HP which showed a gradual increase in detector response up to 230 °C can be explained as follows. This gradual

increase indicates that liquid phase bleeding was not drastic between 160 and 230°C. As would be predicted from normal adsorptivity behaviour adsorption decreases with increase in temperature and consequently the response increases. Later tests with the ECD confirmed that bleeding of these three supports was not very drastic, appreciably less than that for supports whose thermograms did not show a continuous increase in response with temperature.

4.3 THERMOGRAMS USING THE ECD (FIGS. 41 - 49, Appendix III).

Thermograms were obtained using "moderate" s-triazine concentrations (50.5ng prometone; 6.0ng atrazine; 50.0ng ametryne) and the ECD by methods similar to those using the FID described above. Runs with the ECD took longer since this detector responded to bleeding of the OV-225 liquid phase and at least 15 minutes were required for the recorder baseline to restabilize whenever column temperature was raised. At higher temperatures, above 200 C, restabilization was not complete even after 15 minutes and the recorder had to be mechanically re-zeroed to permit experimentation to proceed. Fig. 11 shows extent of bleeding at high temperatures. Thermograms obtained using CW, CG, and C-750 supports are shown in Figs. 41 - 49; some are first runs, others second.

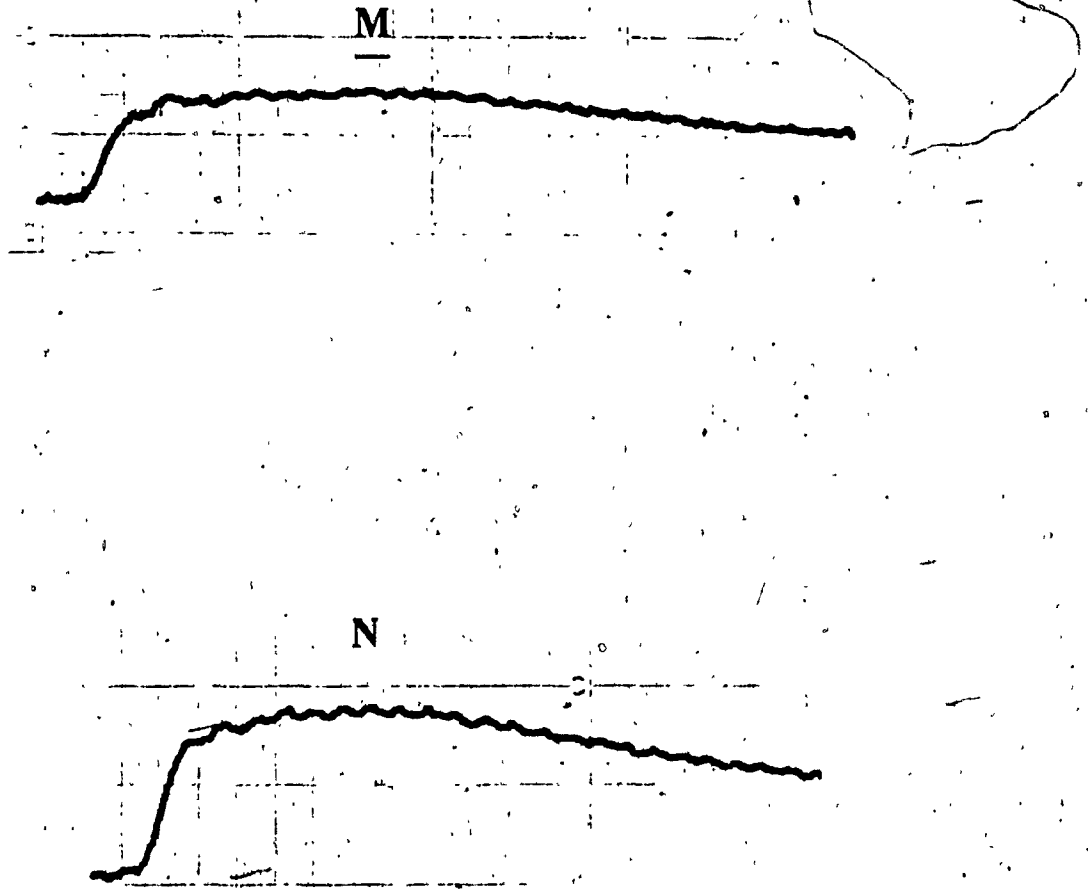


FIGURE 11. (M) Bleeding of the Liquid Phase from a CG-AW Support (220 - 230 °C).
(N) Bleeding of the Liquid Phase from a CG-AW Support (230 - 240 °C).

The typical thermogram obtained using ECD was a bell shape type of curve as illustrated in Fig. 12. Only the thermograms for s-triazines on CW-NAW showed different patterns, in fact almost straight lines. The shape of thermograms such as those in Fig. 12 have been explained by Haniff and Zienius [5] on the following basis. At temperatures below the peak maxima bleeding of the liquid phase is low. As the temperature is increased, the adsorptivity of the s-triazine onto the support decreases. At the maxima in response, adsorptivity is relatively low and liquid phase bleed, although increasing with temperature (as shown in Sect. 5.4), has not yet seriously affected the behaviour of the ECD. The decrease in response with column temperature increase beyond the observed maxima is primarily due to liquid phase bleed which is now quite extensive and its disastrous effect on the ECD. Devaux and Guiochon [68] have reported that the rate of phase bleeding increases exponentially with column temperature. The descending half of the thermogram is on the steep ascending half of the phase/bleeding curve (see Fig. 32). Extensive bleeding of an electron affinitive phase like OV-225 will cause a reduction in available electrons in the ECD and this will decrease detector response. Furthermore, a factor not considered by Haniff and Zienius is that bleeding also causes active adsorption sites to be exposed, which in turn will adsorb s-triazines. The observed decrease in detector response is therefore the

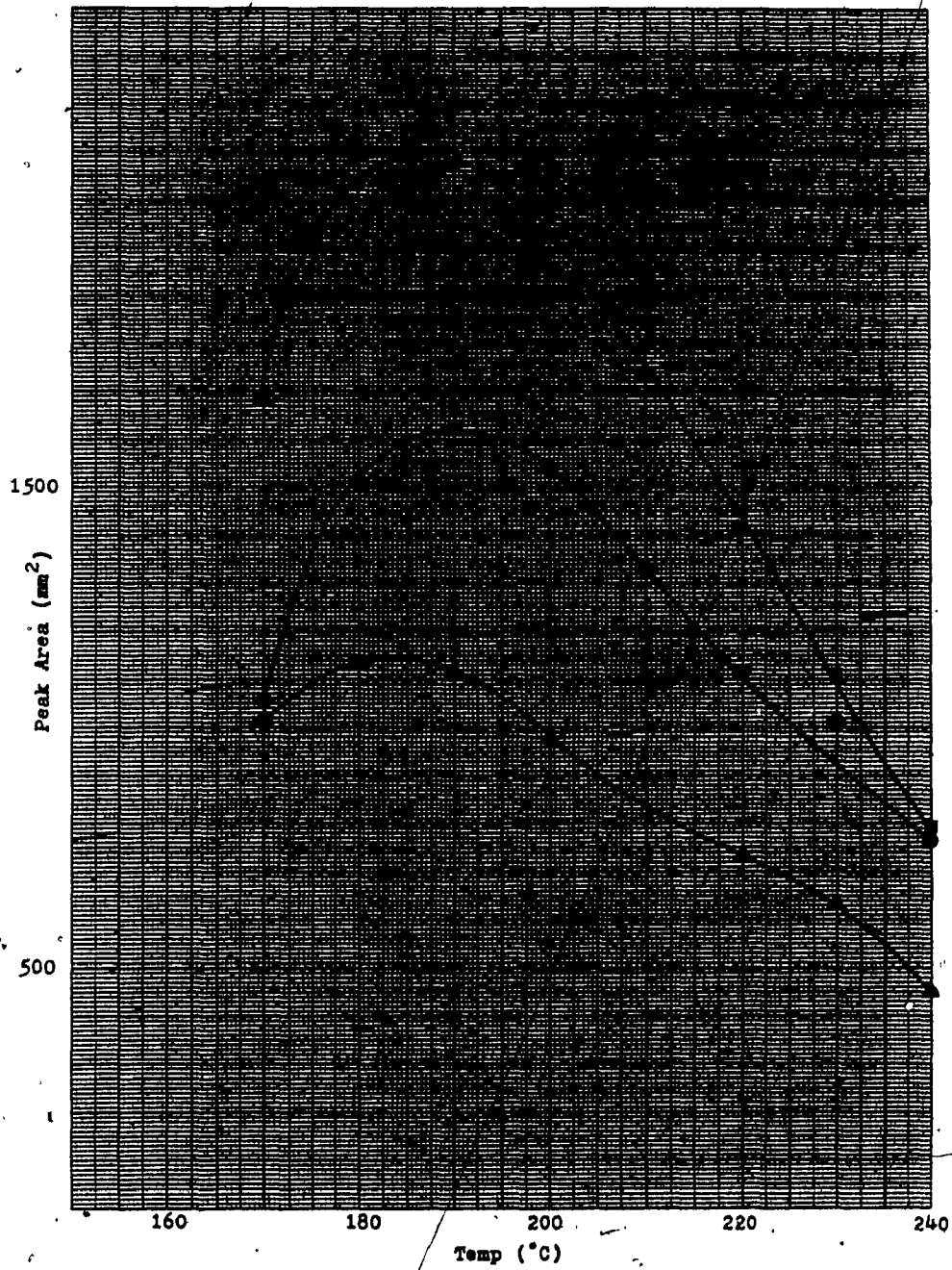


FIGURE. 12. Typical Thermogram Using CG-AW as Support (ECD).

result of both these factors at best since when the column temperature is subsequently increased the s-triazines "primed" onto the support surface will be at least partially desorbed.

The thermograms on CW-NAW did not show any distinct peak maxima (Fig.41). Between 150 and 210°C there was a modest decrease in response. This suggested that in this temperature range bleeding of liquid phase was not extensive enough to affect the ECD. This may be because the liquid phase is adsorbed more strongly to this highly adsorptive untreated surface compared to its attraction to the treated surfaces. This means that excessive bleeding would probably occur only at much higher temperatures than those used in these experiments.

On the supports CW-AW, CW-AW-DMCS and CG-HP (Figs. 42, 43, 49) the thermograms for atrazine showed peak maxima at approximately the same temperature as for prometone and ametryne. Besides this peak maximum, however, there is a second peak maximum in the atrazine thermogram at a higher column temperature. While this phenomenon may somehow be related to as yet unexplained phase bleeding effects, the fact that this behaviour is restricted to atrazine indicates that there may be occurring some particular "reaction" between atrazine and/or the liquid phase and/or

the support. This contention is supported by comparison of the temperatures at which the peak maxima occur on different supports (Table 13). The peak maxima for atrazine are frequently at lower temperatures than those for other s-triazines. This suggests the existence of some factor, as yet unaccounted for, that applies in the atrazine case only.

From Table 13 it can also be observed that for all the CG supports, the peak maxima occur at close to the same temperature. This indicates that although chemical deactivation treatment alters the surface of G supports to a certain extent, the alteration is insufficient to affect the capacity of these supports to attract the liquid phase. The various W supports, however, showed response maxima at a variety of temperatures. This indicated that the different chemical surface deactivation treatments that the W supports received did alter their surfaces significantly.

The sharpness of the bell-shaped ECD thermograms was observed to be related to the degree of liquid phase bleeding off the supports. If one compares Figs. 47 and 46, it is clear that liquid phase bleeding is more extensive for CG-AW than for CG-NAW, i.e., more rapid decrease in ECD response with column temperature rise in the case of CG-AW. This permits a means of cataloging the supports in terms of long term stability and long life of columns, i.e., a lower

Table 13. Comparison of Temperatures at Which Peak Maxima Occured on the Different Supports (ECD).

<u>Support</u>	<u>Column Temperature, °C</u>		
	<u>Prometone (50.5ng)</u>	<u>Atrazine (6.0ng)</u>	<u>Ametryne (50.0ng)</u>
CW-NAW	-	-	-
CW-AW	190	180	188
CW-AW-DMCS	205	190/220	200
CW-HP	170	170	175
C-750	180	175	180
CG-NAW	200	180	190
CG-AW	190	180	190
CG-AW-DMCS	190	175	190
CG-HP	200	170/220	190

bleed rate will give a longer column life. Predicted degrees of liquid phase bleeding as established from thermogram shapes gave the following results:

for W supports:

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

for G supports:

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

This comparison shows that liquid phase bleed is quite extensive on AW and relatively moderate on NAW supports. Bleeding from silanized supports falls between these extremes. A study of retention times showed that the s-triazines spend relatively little time in the liquid phase when it is coated onto NAW supports (see Fig. 13). This means that the film covering the support surface, is very thin and thereby strongly adsorbed. This would lead to the low bleeding as we observed.

Overall, the W supports show less bleeding than the G, probably due to the fact that G supports have a thicker film of liquid phase covering the support surface. This is confirmed in Fig. 13. The retention times for the W supports are generally shorter than those for the G supports.

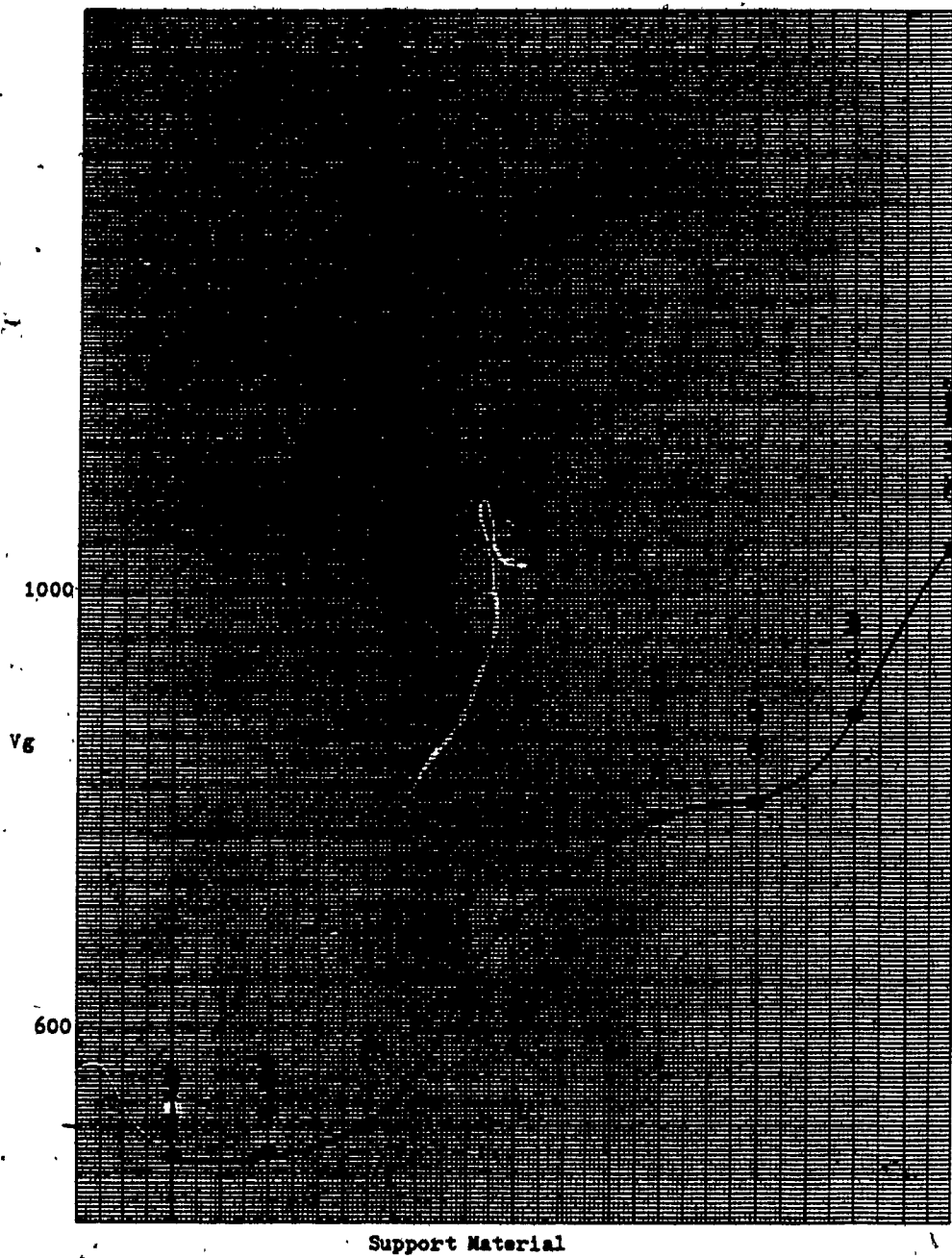


FIGURE 13. Specific Retention Volume (V_g) of Prometone Versus Support Material.

4.4 REPRODUCIBILITY OF THERMOGRAMS USING THE ECD.

The first and second runs for the s-triazines on a CW-AW support are shown in Fig. 14. These runs were performed on different days, but with all instrument parameters kept constant. From Fig. 14 it is clear that the column and detector behaved with no significant differences. Minimal differences observed did not change the shapes of the thermograms or the temperature at the peak maxima. Similar results were obtained when duplicate thermograms on other supports were compared. Overall responses may have been greater for a second run with certain supports, but others these differences were not large enough to suggest changes in column behaviour on a day to day basis.

4.5. CHROMOSORB P.

Although CP is known for its hardness, it has also been reported that CP causes greater tailing of oxygenated and amine compounds than does CW [67]. It was found in this thesis that this was also the case for s-triazines, with the exception of atrazine for which there was no tailing apparent as illustrated on a chromatogram obtained using CP-NAW and FID at 200°C (Fig. 15). On this support at 200°C atrazine and prometone were not separated, prometone showing up only as a tail on the atrazine peak. Fig. 16 shows the peak for 4µg prometone at 210°C on CP-AW support.

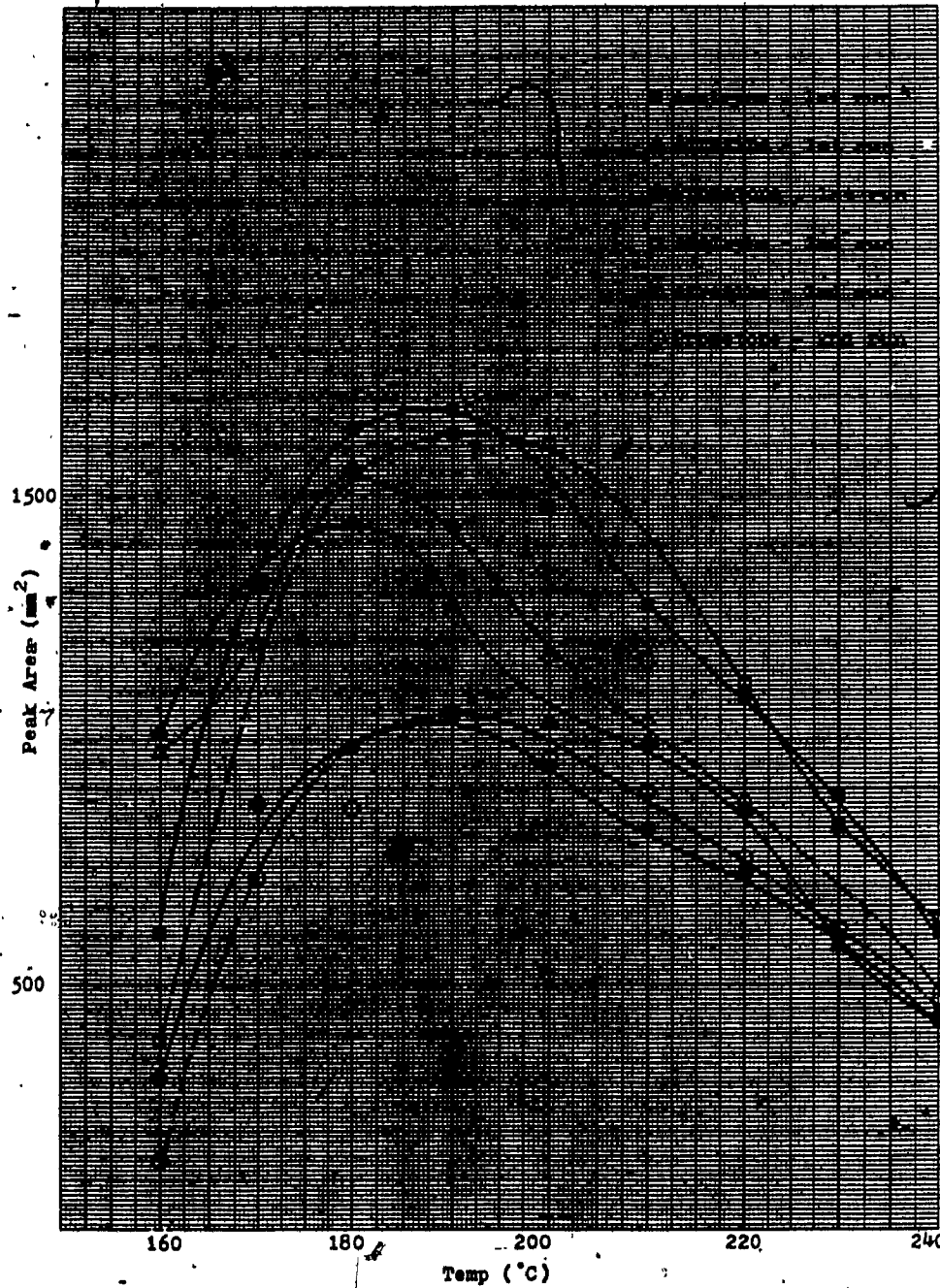


FIGURE 14. First and Second Run Thermograms on a CW-AW Support Using the ECD.

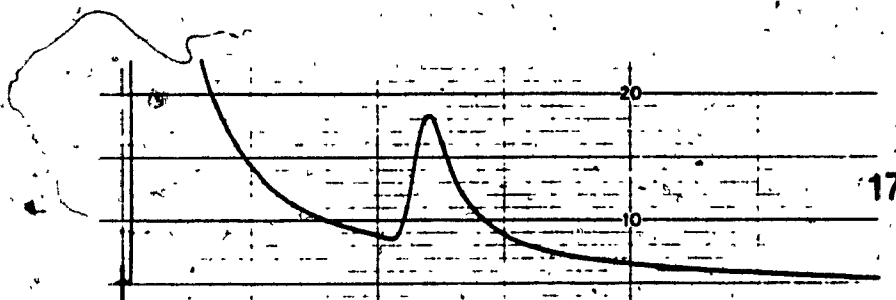
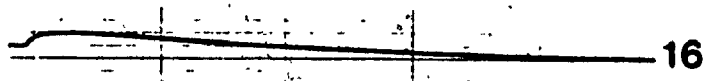
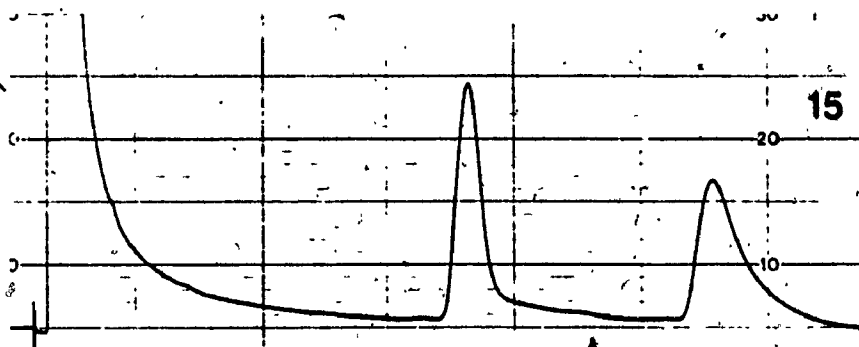


FIGURE-15. Chromatogram of a Mixture of Prometone (1.3ug), Atrazine (2.2ug) and Ametryne (3.0ug) on a CP-NAW Support at 200°C (FID).

FIGURE 16. Chromatogram of Prometone (4ug) at 210°C on a CP-AW Support (FID).

FIGURE 17. Chromatogram of a Mixture of Prometone (1.3ug), Atrazine (2.2ug) and Ametryne (3.0ug) at 210°C on CP-AW-DMCS (FID).

The severe tailing observed on this chromatogram is an indication of the high degree of adsorptivity of the support. Ametryne also showed considerable tailing, while atrazine showed little on this support. Tests with CP-AW-DMCS support showed complete adsorption of prometone and ametryne. Atrazine was the only s-triazine eluted and even its peak showed severe tailing (Fig. 17).

From the above observations it was evident that adsorption of s-triazines, especially those with either a methoxy or thiomethyl group in position 2, was quite severe on P supports, especially compared to no tailing on W and G supports. Hence there was no point to extend testing of P supports to lower concentrations of s-triazines with the ECD.

4.6. CHROMOSORB 103.

C-103 was included in this study to compare the behaviour of a porous polymer support to that of coated diatomaceous earths. The absence of a liquid phase was expected to be beneficial in reducing extraneous column effects on the detector. After preconditioning the C-103 column a mixture of the three s-triazines was injected. Only one peak was eluted (Fig. 18M). This observation led to the injection of single s-triazines at a time, with the results shown in Fig. 18N, O and R for atrazine, ametryne and prometone,

respectively. From these figures it was concluded that atrazine and ametryne eluted with the same retention time. The explanation for this similarity in behaviour lies in their structures. These two s-triazines differ only in position 2 on the ring. Prometone was either totally adsorbed or eluted with the solvent (Fig. 18R). Since the structure of prometone is not very different from that of atrazine and ametryne, it should have eluted with a similar retention time. There is in fact a very small peak in the tail of the solvent peak at a very low level of detection which could be prometone. Even though the use of C-103 for separation purposes was not promising, a thermogram was obtained for ametryne (3ug) to obtain some idea of the effect of a non-liquid coated column on the FID. The results for the first and second runs are shown in Fig. 19. The response was virtually constant over the temperature range studied. Since no liquid phase was involved, there was no "bleeding" and therefore reproducible thermograms were obtained. Also peaks were symmetrical at all temperatures, a further indication of no unusual ametryne - C-103 interactions.

An attempt was made to use lower s-triazine concentrations and the ECD. Chromatograms obtained showed multiple peaks for injection of solvent alone. Using benzene or methanol, the same peaks were observed. These peaks could be attributed to impurities in the solvent, although it was

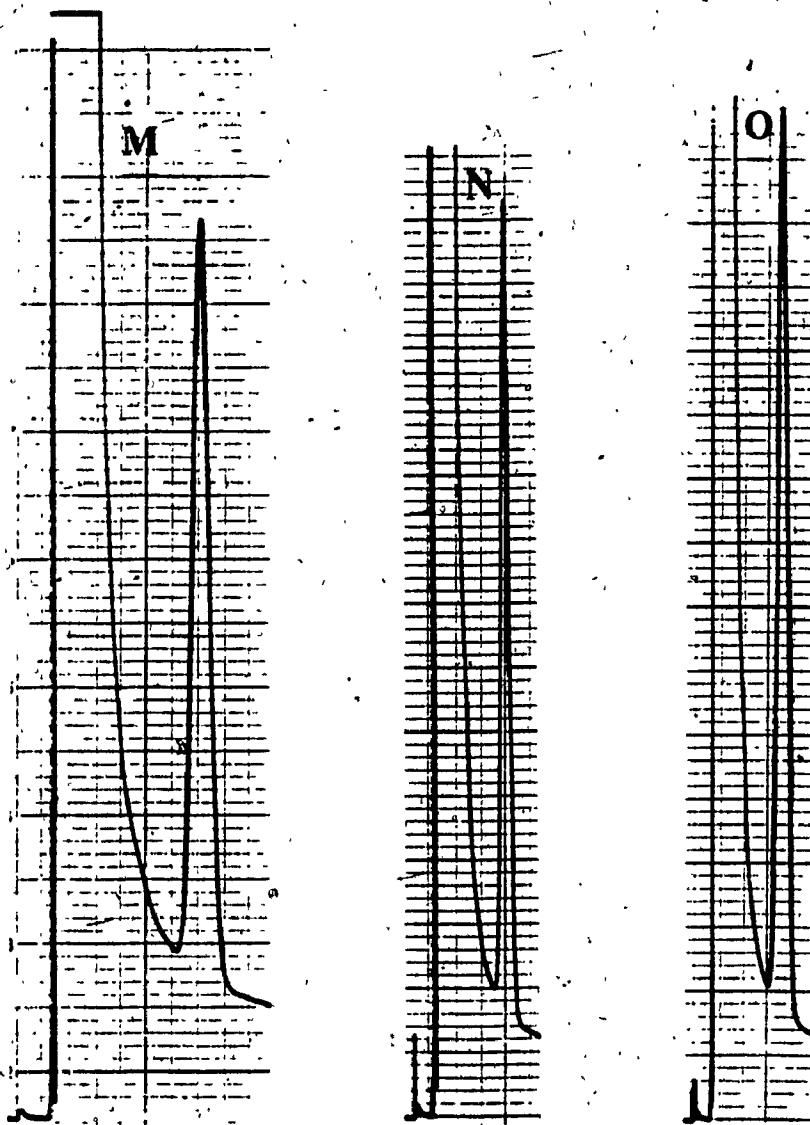


FIGURE 18. Chromatograms of (M) a Mixture of Prometone (1.3ug),
Atrazine (2.2ug) and Ametryne (3.0ug);
(N) Atrazine (3.0ug); (O) Ametryne (3.0ug) on
C-103 at 170 °C.

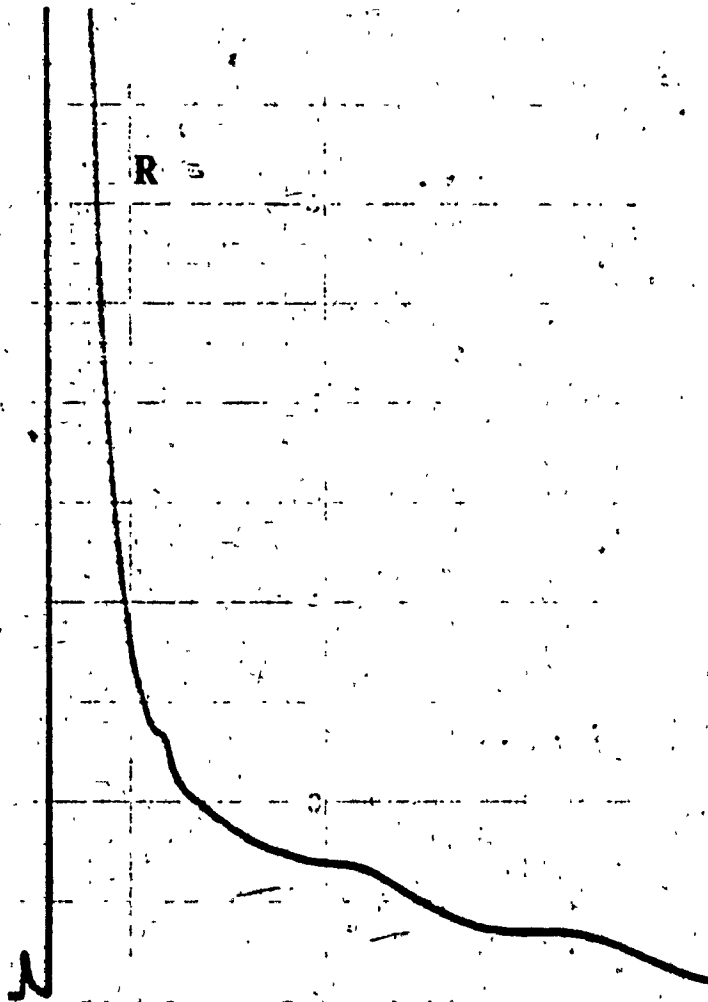


FIGURE 18(R) Chromatogram of Prometone (4.0ug) on C-103 at 170°C (FID).

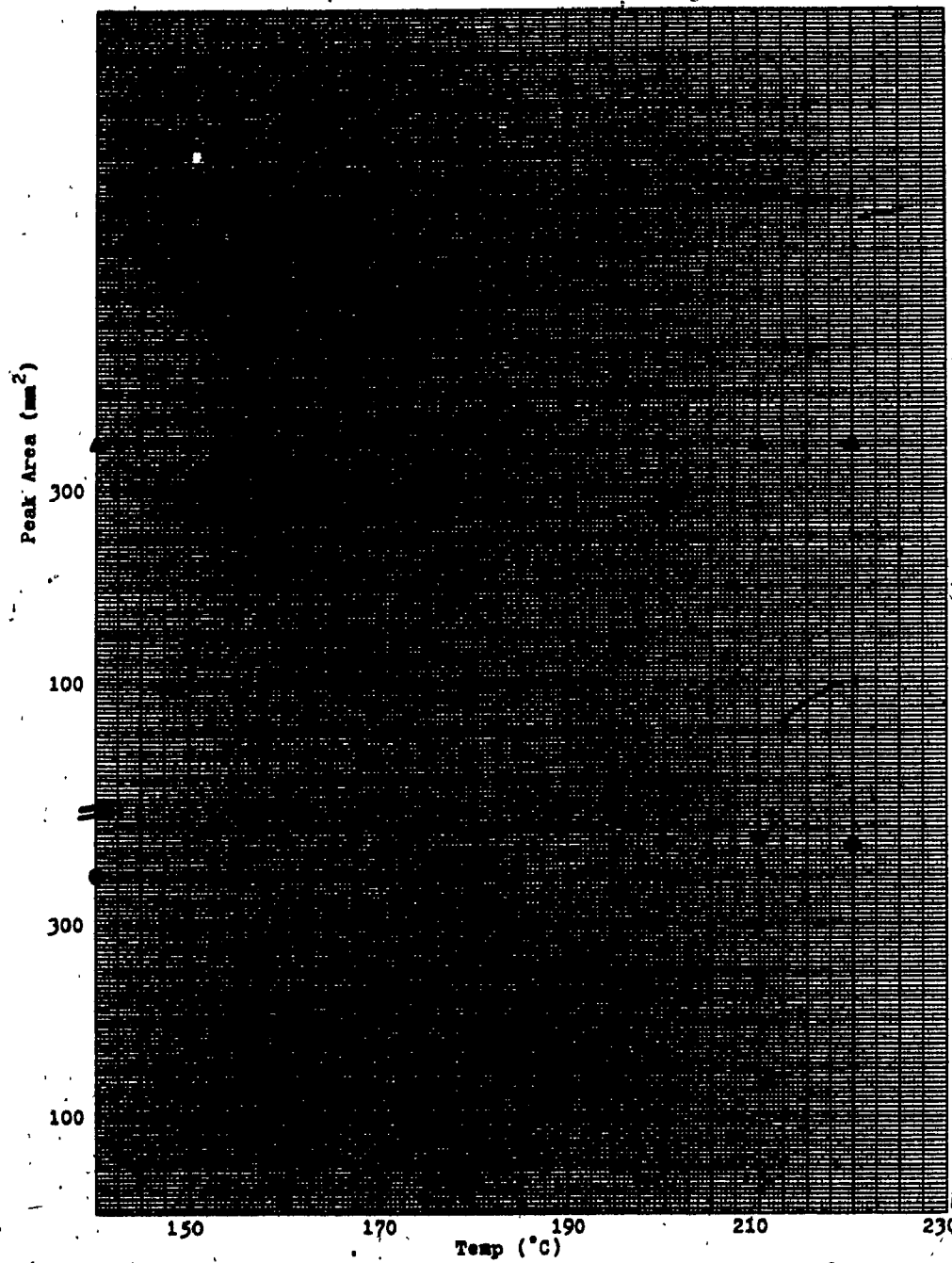


FIGURE 19. First and Second Run Thermograms for Ametryne on C-103 Using the FID.

strange that the same impurities would be in both solvents. Since there is no liquid phase bleeding involved, whatever minute impurities were present would be readily detected at the resultant higher sensitivity of the detector. Since these "impurity" peaks interfered with peaks for atrazine and ametryne, work with C-103 and the ECD was terminated.

4.7. CSP-20M.

This Carbowax coated support gave a good separation of "high" concentrations of the three s-triazines using the FID. All three peaks showed some tailing, however, which indicated adsorption (see Fig. 20). This adsorption was emphasized when lower s-triazine concentrations were tested using the ECD (Fig. 21N). Peaks for prometone and ametryne were distorted indicating severe of solute - column interaction. Atrazine, however, gave almost symmetrical peaks at "low" concentrations (Fig. 21M). Therefore, a thermogram run was carried out with atrazine using the ECD (Fig. 22). The decreasing half of the thermogram after the peak maximum did not show a drastic decrease, an indication of a slow rate of liquid phase bleeding. This is in agreement with the manufacturer's claim of low bleed for CSP-20M.

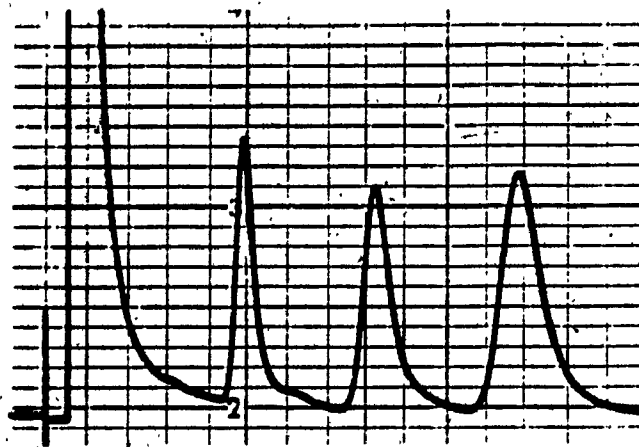


FIGURE 20. Chromatogram of Prometone (1.3ug), Atrazine (2.2ug), and Ametryne (3.0ug) on CSP-20M at 200 °C. (FID).

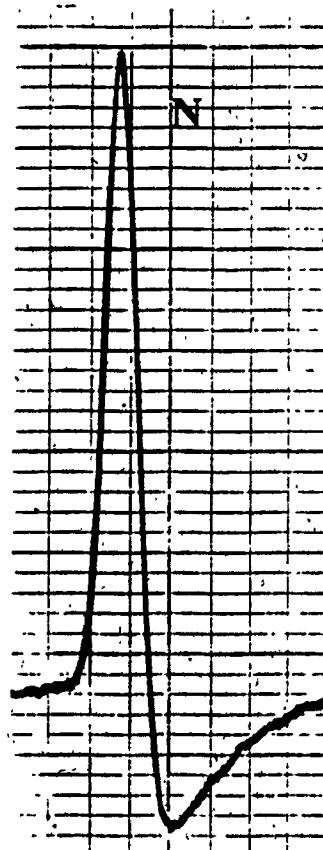


FIGURE 21. (M) Peak Shape of Prometone (6.0ng) on CSP-20M at 170 °C; (N) Peak Shape of Atrazine (6.0ng) on CSP-20M at 200 °C (ECD)

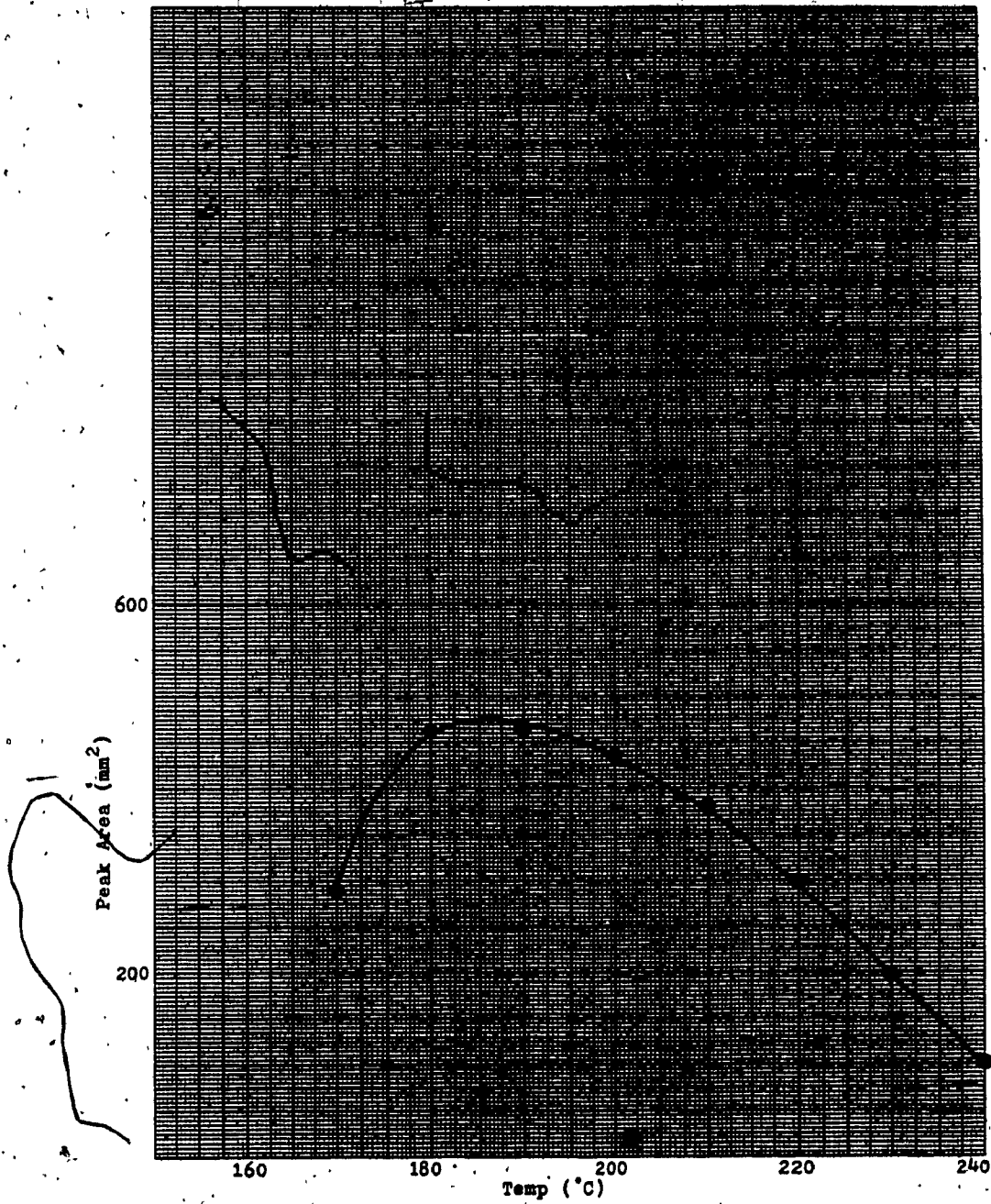


FIGURE 22. Thermogram of Atrazine (6.0ng) on CSP-20M
Using the ECD.

CHAPTER

5

THE EFFECT OF COLUMN BLEED ON THE RESPONSE OF THE ECD AND
POSSIBLE WAYS OF REDUCING THE AMOUNT OF BLEEDING

From Chapters 2 and 3 it is clear that column liquid phase bleed has a definite effect on the column performance as well as detector response. In this chapter are reported results of further experiments that were carried out to determine more precisely the effect of bleeding on the shape of the thermogram, how increasing or decreasing column temperature affects bleeding and how the rate of bleeding changes after exposure of a column to a constant temperature over a long period of time.

5.1. EFFECT OF THERMAL PRETREATMENT OF A COLUMN UP TO PEAK MAXIMUM TEMPERATURE ON THE OVERALL RESPONSE OF THE ECD.

Duplicate thermograms for the s-triazines ("moderate" concentrations) were recorded on a CG-AW column. The first runs were cut off at the temperature of peak maxima. The aim was to determine whether prior exposure of the column to the higher temperatures studied during a regular thermogram run would affect column behaviour. Results obtained are shown in Fig. 23. There was no apparent difference in the duplicate thermograms, and hence in the response behaviour of the ECD over the temperatures range studied. This indicated that subjecting a column to temperatures up to the peak maximum temperature do not cause significant bleeding and the number of new active surface sites exposed by any such bleeding is therefore minimal. This is important since extensive liquid phase

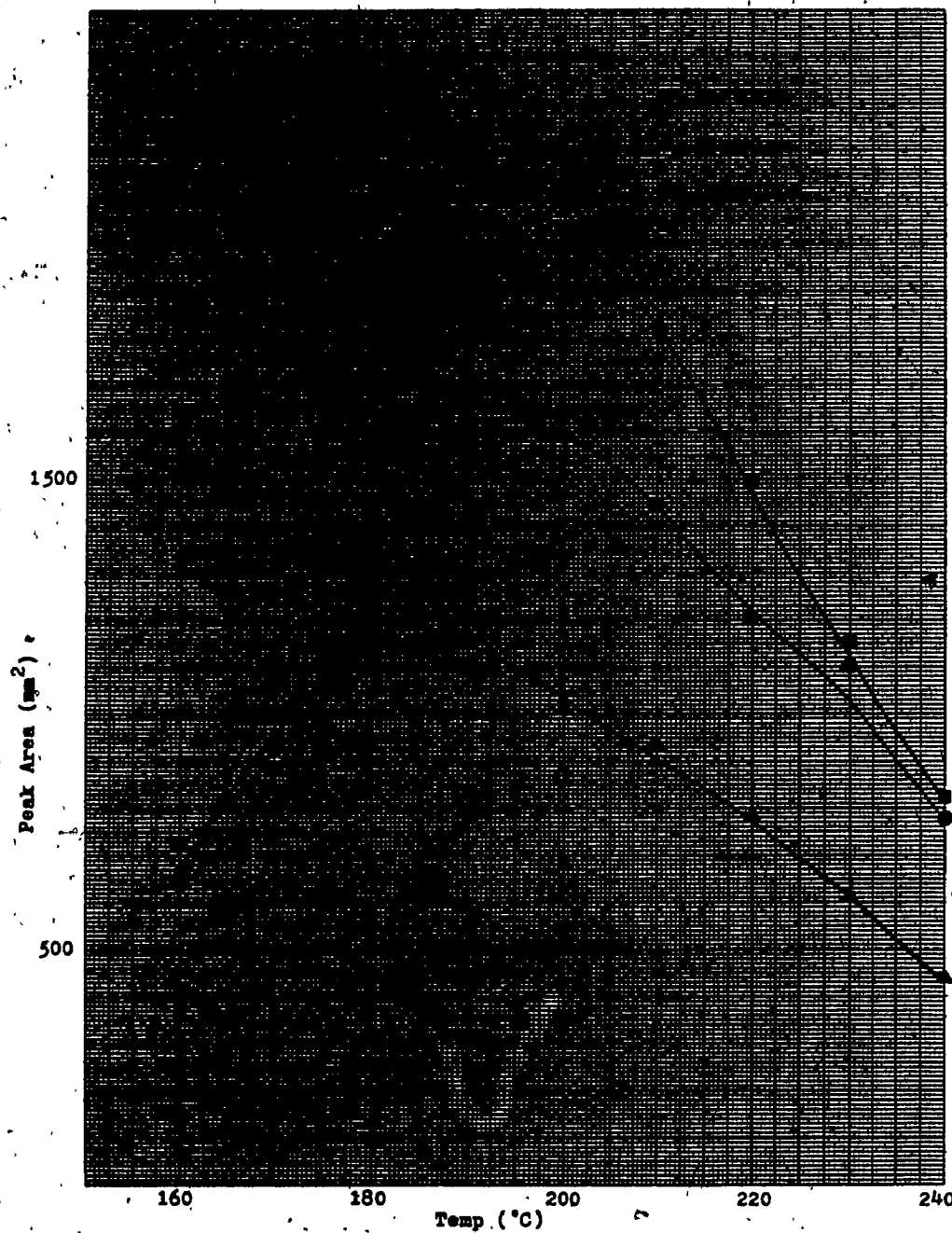


FIGURE 23. Thermograms of Prometone (50.6ng), Atrazine (6.0ng), and Ametryne (50.0ng) on a CG-AW Support Using the ECD.

bleeding changes column performance and is detrimental to detector response, and therefore, to quantitative analysis of s-triazines. Column life can be extended considerably if the column is never operated at temperatures above the peak maxima temperatures.

5.2. RESPONSE OF THE ECD DURING A REVERSE THERMOGRAM RUN.

The term "reverse thermogram" (RTG) as used here is intended to signify a thermogram run carried out starting at the highest column temperature to be investigated and then decreasing the temperature at 10 degree intervals to the lowest column temperature used. After each temperature decrease, the column was allowed to stabilize for 10 minutes. The aim of this test was to establish whether column bleeding effects would be the same as previously observed for "forward" thermogram (FTG) runs. Typical RTG on a CG-AW support as shown in Fig. 24 confirm this to be the case. As column temperature was decreased, liquid phase bleeding decreased down to the temperature of the peak maxima. The reduced bleeding caused an increase in the number of electrons in the detector which was probably the single most important factor causing the increase in detector response. Priming is taking place to a small extent only at high column temperatures, since adsorptivity is relative low at these elevated temperatures. Adsorptivity increased at temperatures below that of peak

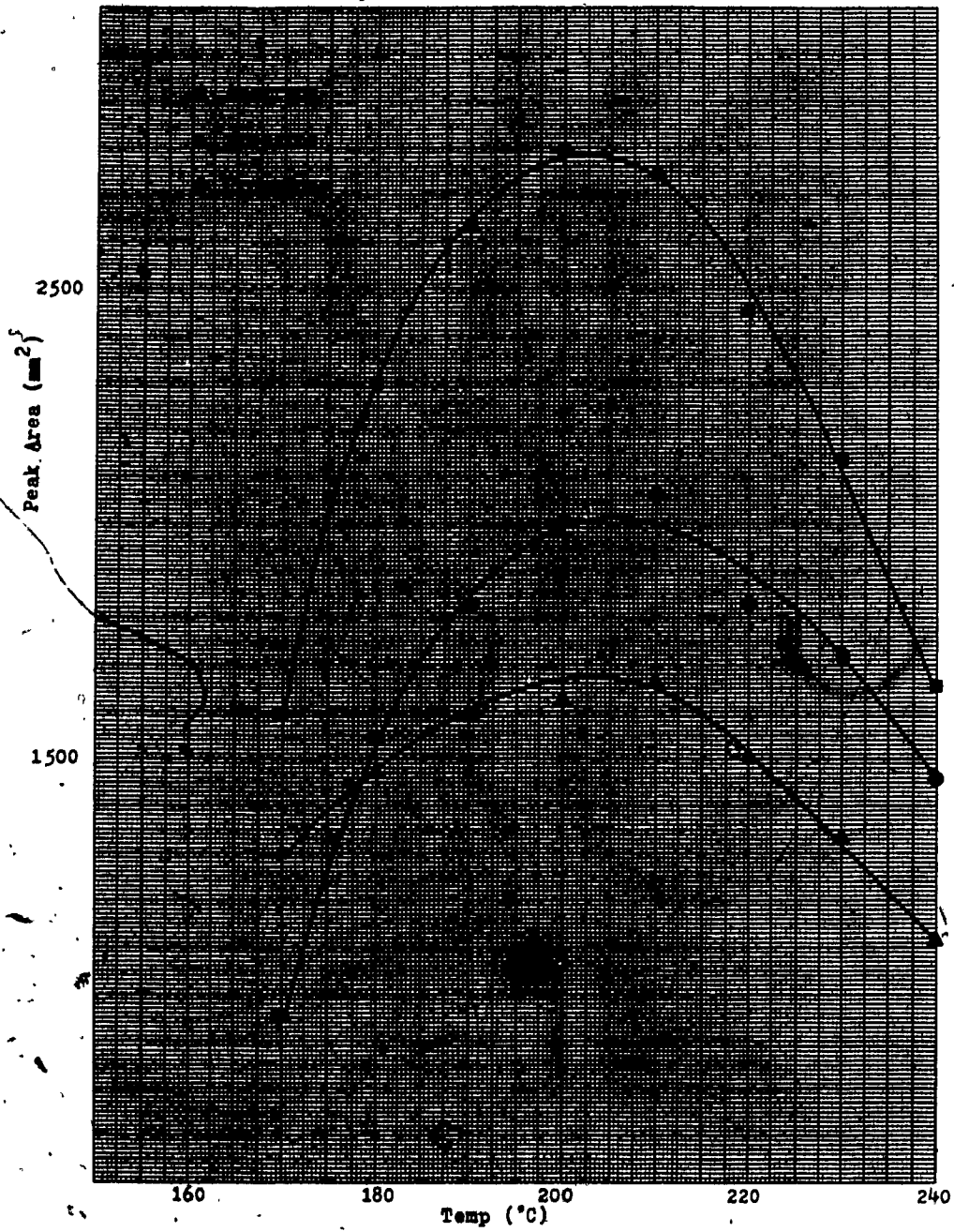


FIGURE 24. Reverse Thermogram of s-Triazines on a Column Packed With CG-AW Packing (ECD).

a decrease in detector response.

The reverse and forward thermograms for s-triazines on Figs. 24 and 47 have been reproduced in Fig. 25 for ease of comparison. The RTG was carried out after the forward one and details of the two do not match, beyond the fact that both were bell-shaped curves. From Fig. 25 it is evident that:

1. the overall response of the ECD was much greater during the RTG run than during the forward one; and, consequently
2. the degree of liquid phase bleeding must have been decreased in the cause of the RTG run, and more significantly, an appreciable amount of bleeding took place during the FTG run.

Further proof of liquid phase bleeding during the FTG run is provided from comparison of the bell shape thermograms for the forward and reverse runs. The sharpness of these curves is an indication of the degree of liquid phase bleed (Sec. 4.3). From Fig. 25 the RTG curves are broader than the forward ones, showing less liquid phase bleed occurred during the reverse run. Decreased liquid phase bleeding will also be expected to shift the temperature at which the peak maxima occurred to higher column temperatures meaning that a higher column temperature can be achieved before liquid phase bleeding becomes extensive. This was in fact

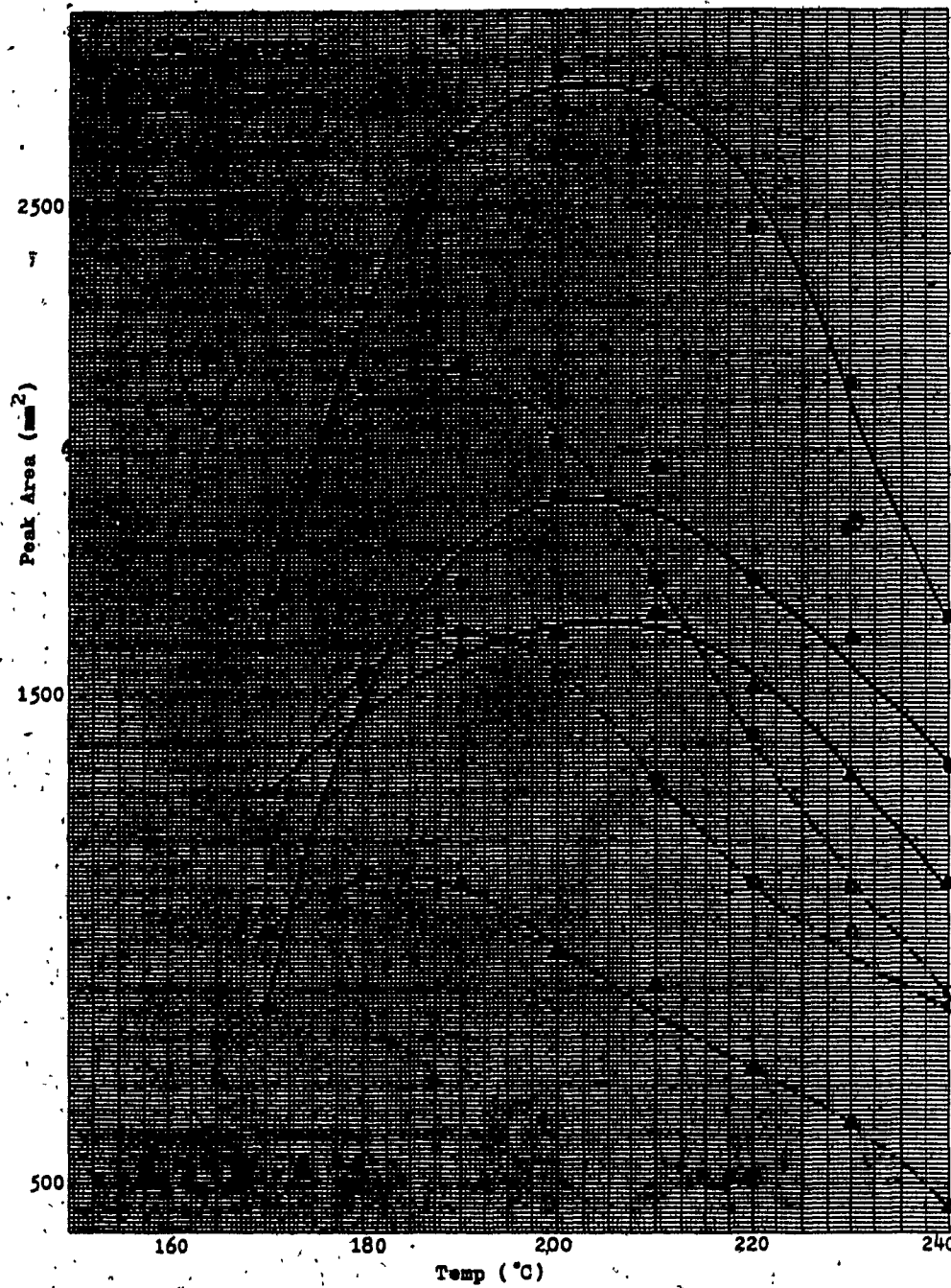


FIGURE 25. Comparison of FTG and RTG's of s-Triazines on a GG-AW Support (ECD).

observed ; peak response maxima being about 20 °C higher in the RTG.

A further experiment was carried out with coated CW-AW support. A FTG was performed, followed by a period of 90 hours of column equilibration at 240 °C with a normal flow of carrier gas (30 ml/min) passing through. The "moderate" concentration level s-triazine solution was then injected (in triplicate) at 240 °C. Column temperature was lowered to that at the previously observed response maxima (190 °C); recorder baseline was allowed to stabilize and triplicate injections made again. As can be seen from Fig. 26 response was considerably greater for injections made after the very lengthy column equilibration period, further proof of loss of a portion of the liquid phase by bleeding during conditioning.

5.3. VARIATION IN LIQUID PHASE BLEEDING WITH THERMAL CONDITIONING TIME.

The first study was with a coated CG-AW column which had already been preconditioned for 24 hours according to standard GC practice. The procedure was to condition the column for further periods of time at 240 °C, injecting s-triazines periodically, and from the responses observed establishing the extent of liquid phase bleeding in progress. Fig. 27 shows the results obtained. It seems that

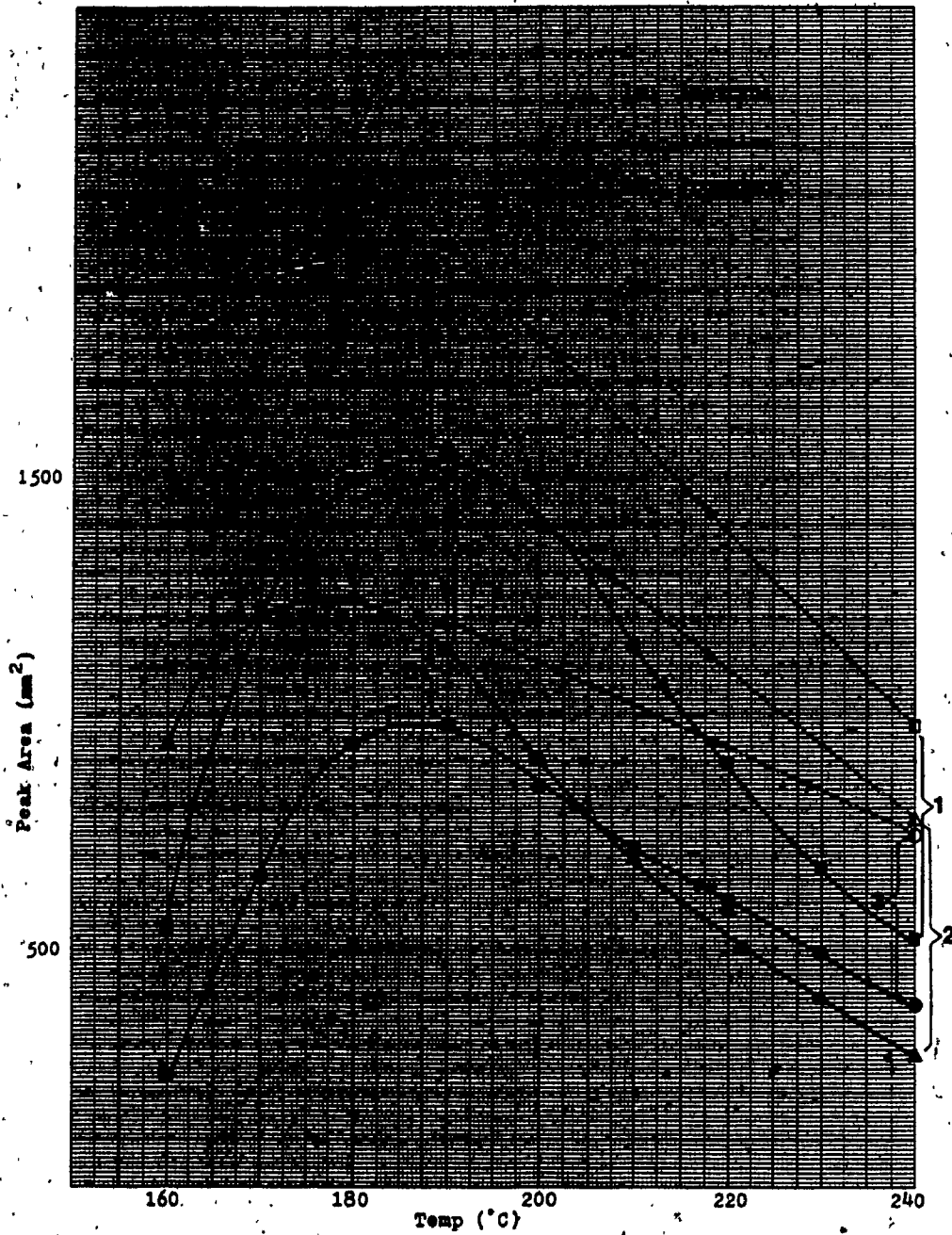


FIGURE 26. Thermograms on a Column Packed with CW-AW Support Followed by Temperature Equilibration and Injections at 240 and 190°C (ECD).

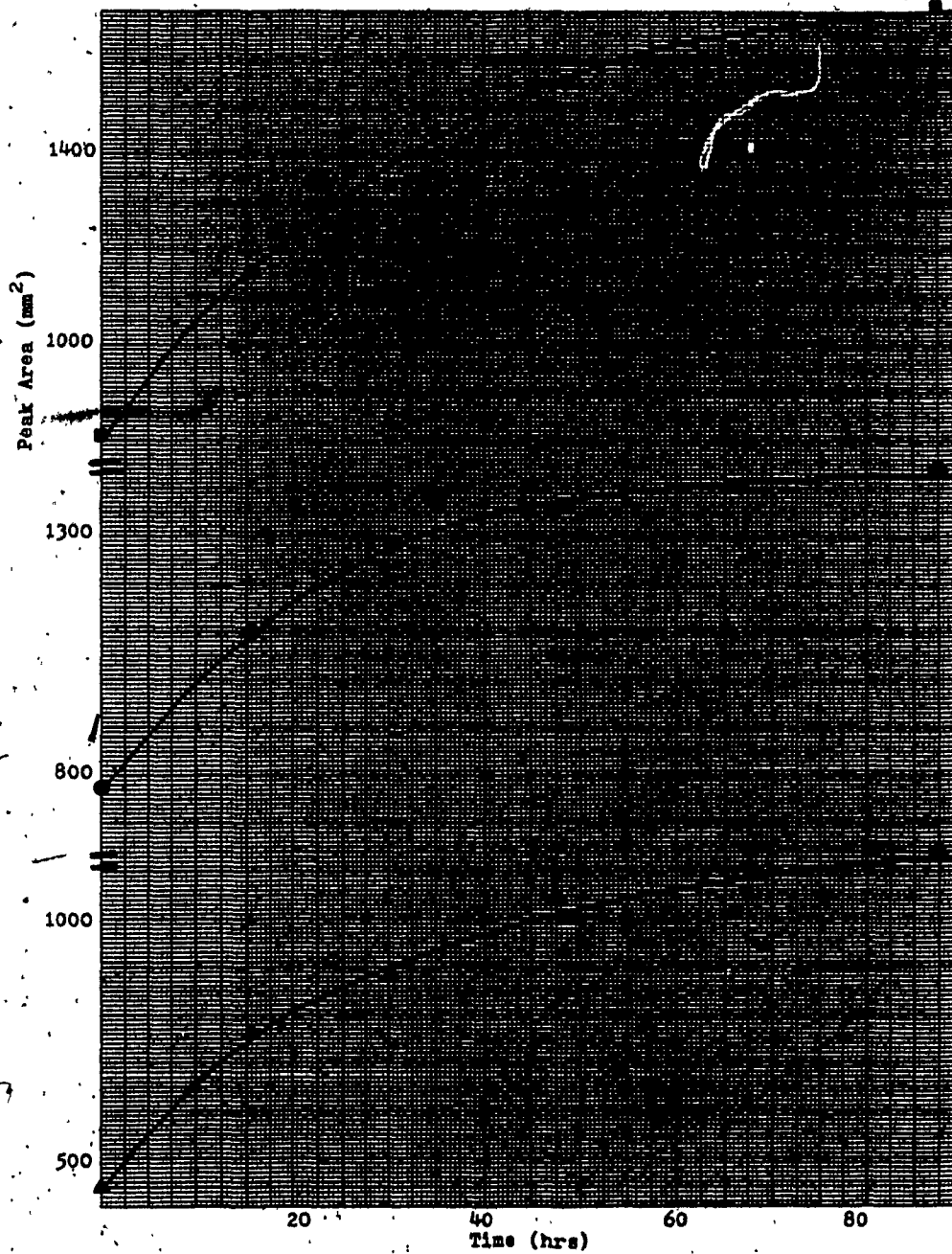


FIGURE 27. Detector Response as a Measure of Liquid Phase Bleeding During Thermal Conditioning of a Coated CG-AW Support Column at 240°C (ECD).

after 90 hours of conditioning the detector response, initially increasing, leveled off. This indicates that liquid phase bleeding had ceased altogether, or decreased to a constant minimum rate dependent on liquid phase vapour pressure at 240 °C. "Massive" liquid phase bleeding, however, was no longer in effect. The conclusion from this test was that a support coated with 3.5% OV-225 must be preconditioned at the operating temperature for at least 90 hours in order to optimize subsequent analysis using the ECD. To confirm this finding, tests were repeated with a coated CW-AW support column. Triplicate injections of s-triazines were made at 240 °C after 24 hours of column preconditioning at 250 °C. The column was allowed to condition for a further 90 hours at 240 °C and injections repeated. To confirm that liquid phase bleeding was, for most part, complete at this time, conditioning of the column was continued for still another 90 hours, with the s-triazines being analyzed at several time intervals. Results obtained are shown in Fig. 28. After 90 hours the column had reached a minimum bleed rate condition, the response remaining constant from that point up to 180 hours. It is worthy of note that column performance did not change during the 180 hours of conditioning. Peaks for s-triazine were still symmetrical (Fig. 29) and the resolution remained constant as did retention times.

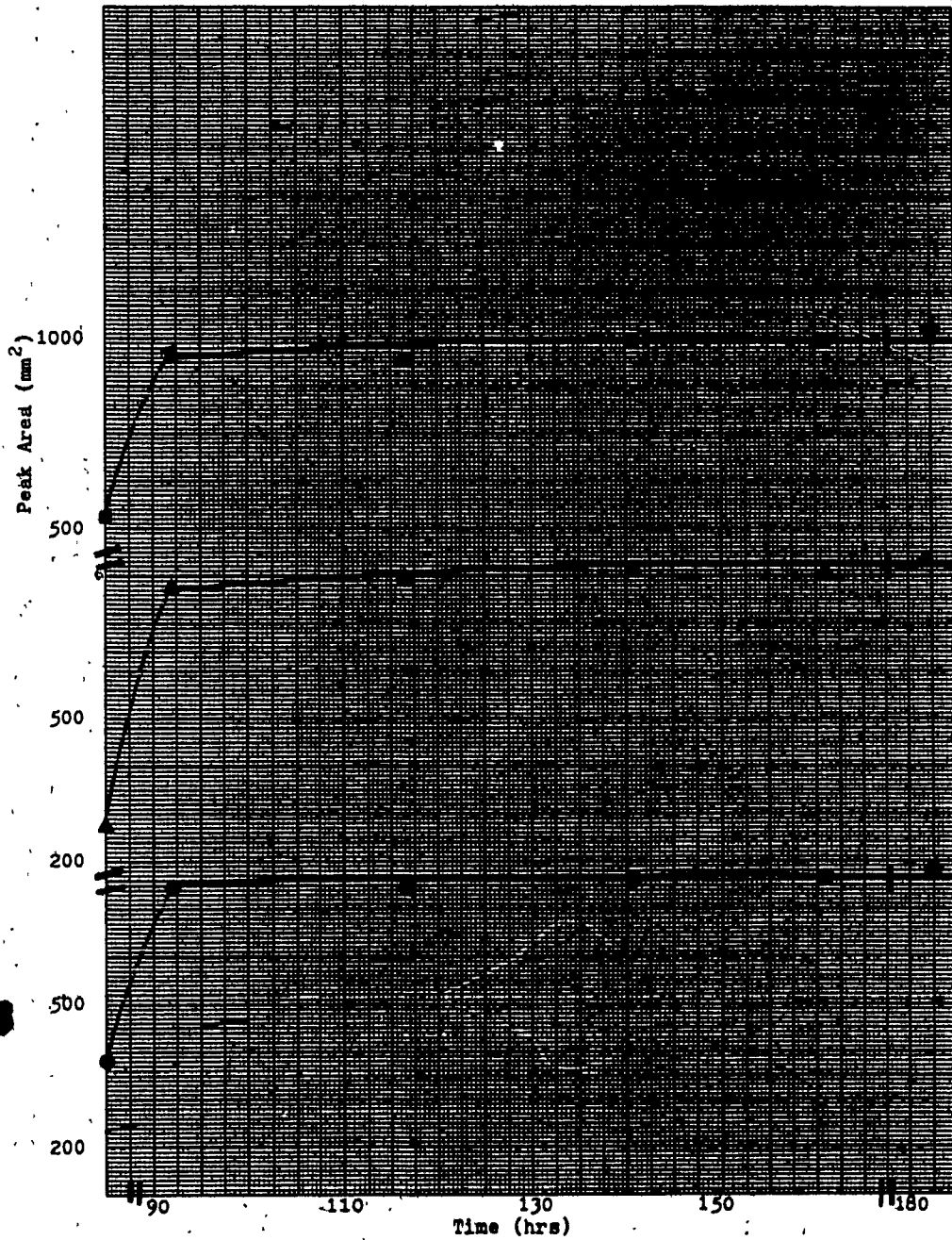


FIGURE 28. Detector Response as a Measure of Liquid Phase Bleeding During Thermal Conditioning of a Coated CW-AW Support Column at 240°C for 180hrs (ECD).

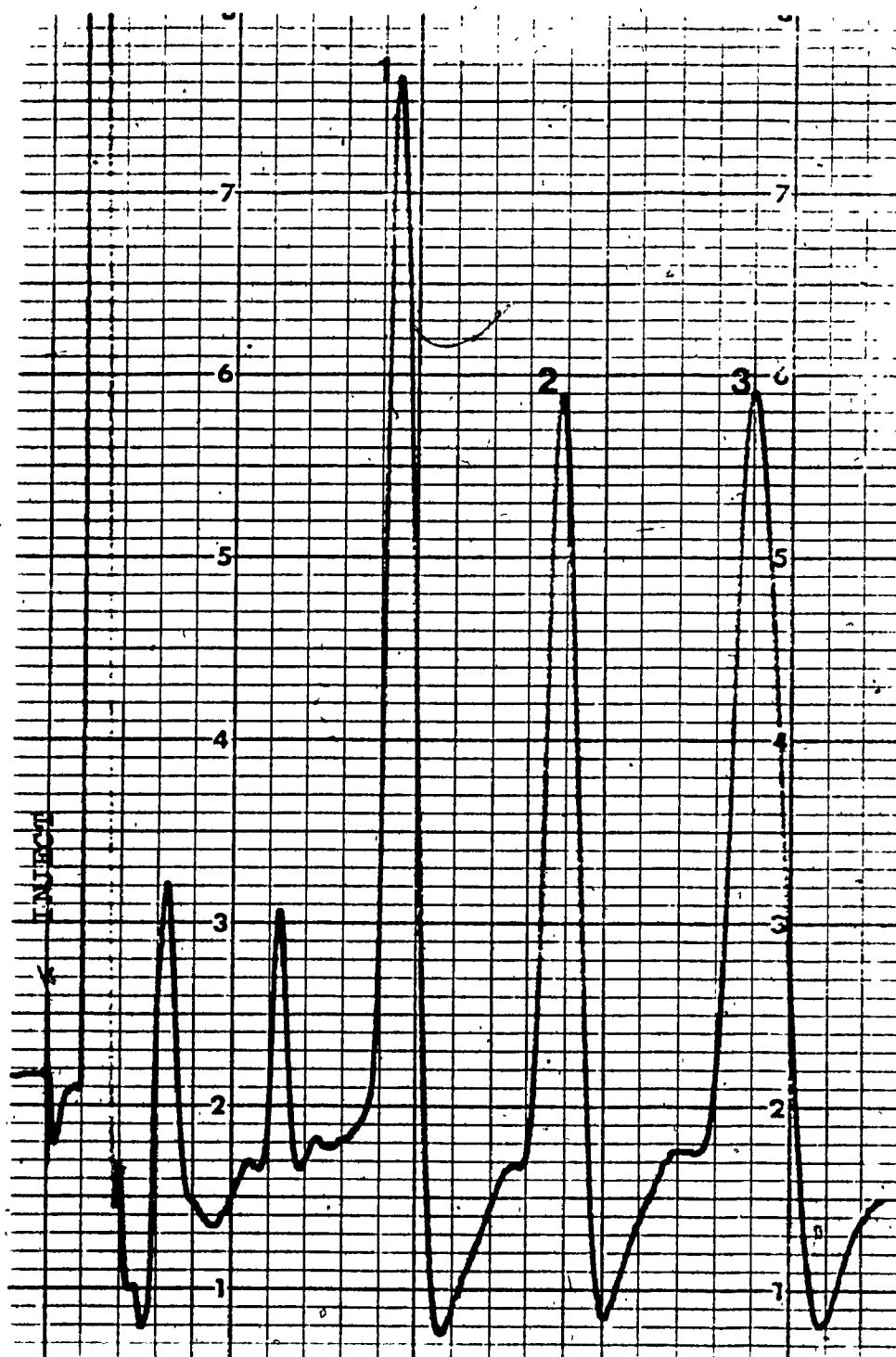


FIGURE 29. Chromatogram of s-Triazines at 240°C on a CG-AW Support Column After 90 hrs of Conditioning;
1. Prometone; 2. Atrazine; 3. Ametryne.

5.4. MASS SPECTROMETRIC EVIDENCE FOR LIQUID PHASE BLEEDING.

To confirm the observations made in the previous sections, mass spectrometry was used to analyse carrier gas eluting from a CG-AW-DMCS column. The column was raised to and stabilized at the temperatures of interest before mass spectra of column effluents were measured. There was no injection of any s-triazines into the column which eliminated any possibility of solute-liquid interactions as being responsible for the observed liquid phase bleeding. Spectra were obtained initially at 20 degree column temperature intervals in the 140 - 220°C range. The lower temperature effluents were analyzed first. A duplicate mass spectral study was done in the temperature range of 180 to 220°C only.

Fig. 30 shows the mass spectrum of effluent from the CG-AW-DMCS column thermostated at 160 C. Any mass spectra of column effluent measured in the 140 to 160°C range had the same peaks. These peaks are attributable to background noise [92]. Peaks due to liquid phase bleeding began to appear at 180°C. At lower temperatures whatever bleeding occurred (as evident in tests with the ECD) was not sufficient to be detected by the lower sensitivity mass spectrometry technique. Hence, bleeding may have been occurring, but to a small extent only. Fig. 31 shows the

FIGURE 30. Mass Spectrum of Effluent from a 3.5% (w/w) OV-225 on CG-AW-DMCS Support Column at 160 °C.

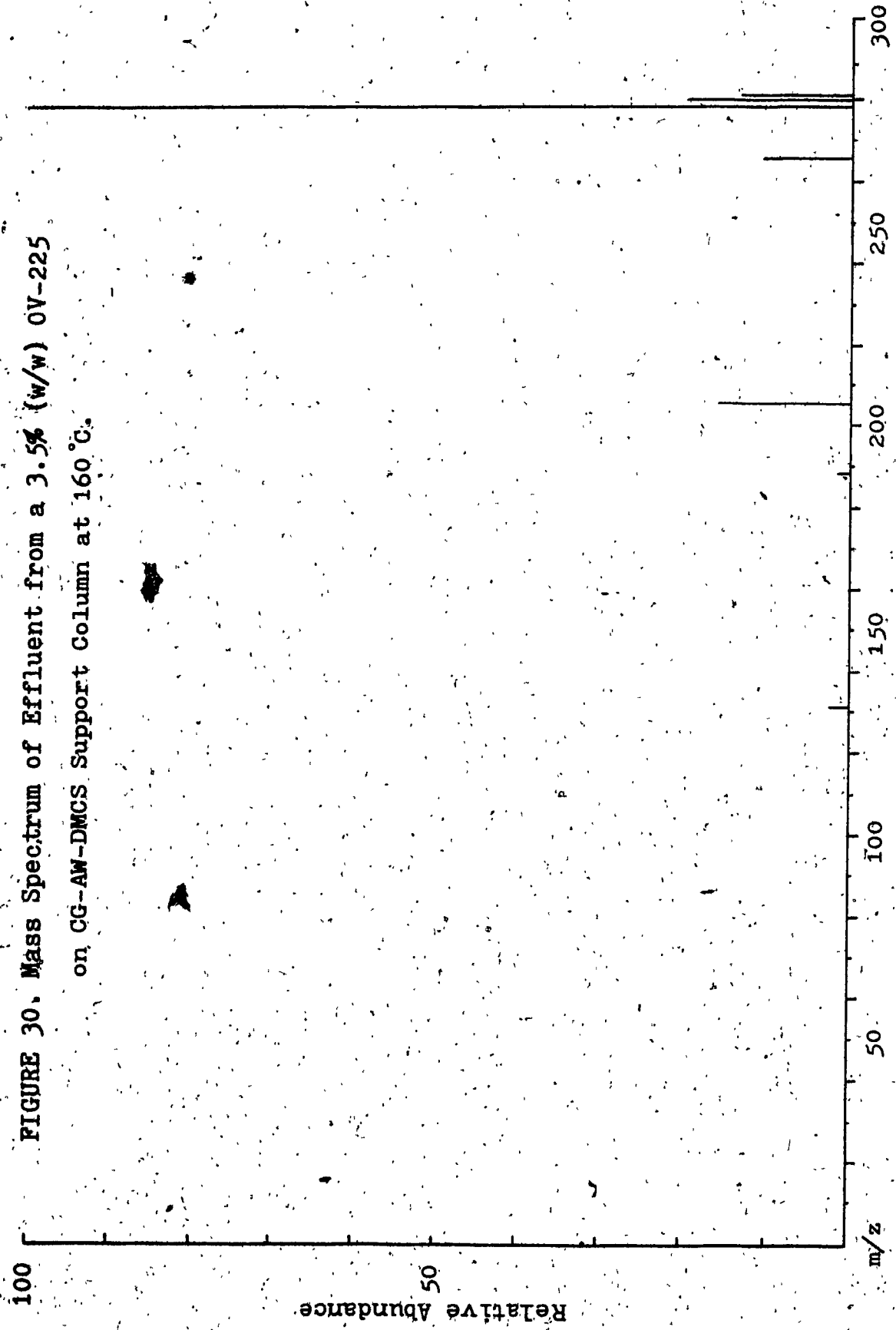
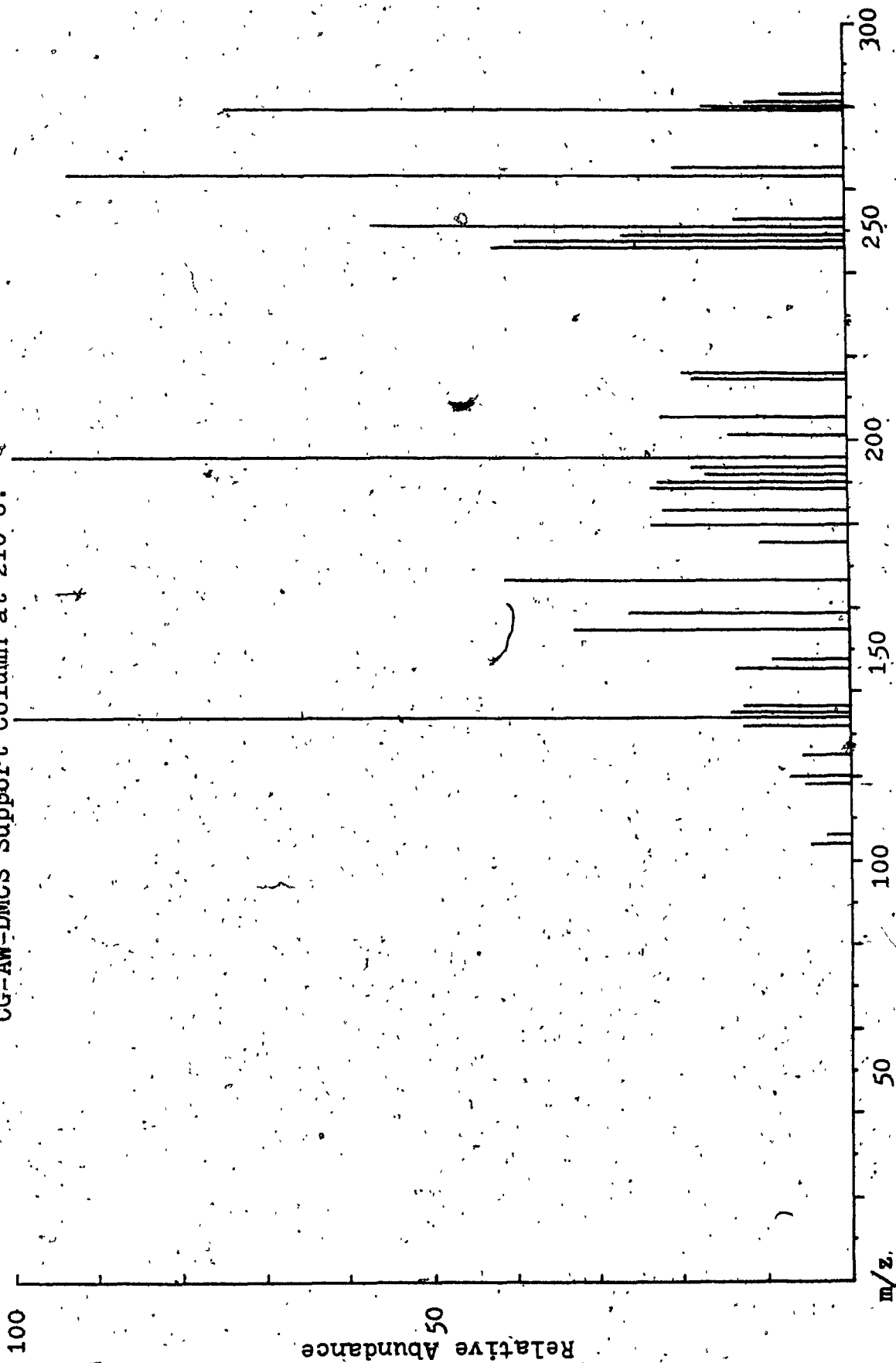


FIGURE 31. Mass Spectrum of Effluent from a 3.5% (w/w) OV-225 on

CG-AW-DMCS Support Column at 210°C.



mass spectrum of the column effluent at 210°C. From this mass spectrum it is quite evident that liquid phase is coming off the column. No attempt was made to identify all the mass spectral peaks, since the purpose of the experiment was to confirm bleeding and this was accomplished. Identification of the peaks in the mass spectrum would be very useful, however, in determining whether or not the liquid phase undergoes decomposition. It should be noted that mass spectra obtained at still higher temperatures, for example, 220°C, showed even more mass peaks than the one at 210°C, an indication of increased bleeding.

To attempt quantitation of the bleed rate using mass spectral data, the mass peak (m/z 146) was chosen arbitrarily, its peak height measured on each mass spectrum obtained and results plotted vs the column temperature (Fig. 32). An exponential increase in liquid phase bleeding is suggested in both runs, being more severe in the first. Notice that during the first run the bleed rate increased drastically above 180°C. This coincides with the temperature of the peak maxima shown in the thermogram obtained for s-triazines on this same column (Fig. 50). This confirmed the hypothesis that extensive liquid phase bleeding occurs after the peak maxima. The second run was performed after the column had been further conditioned for

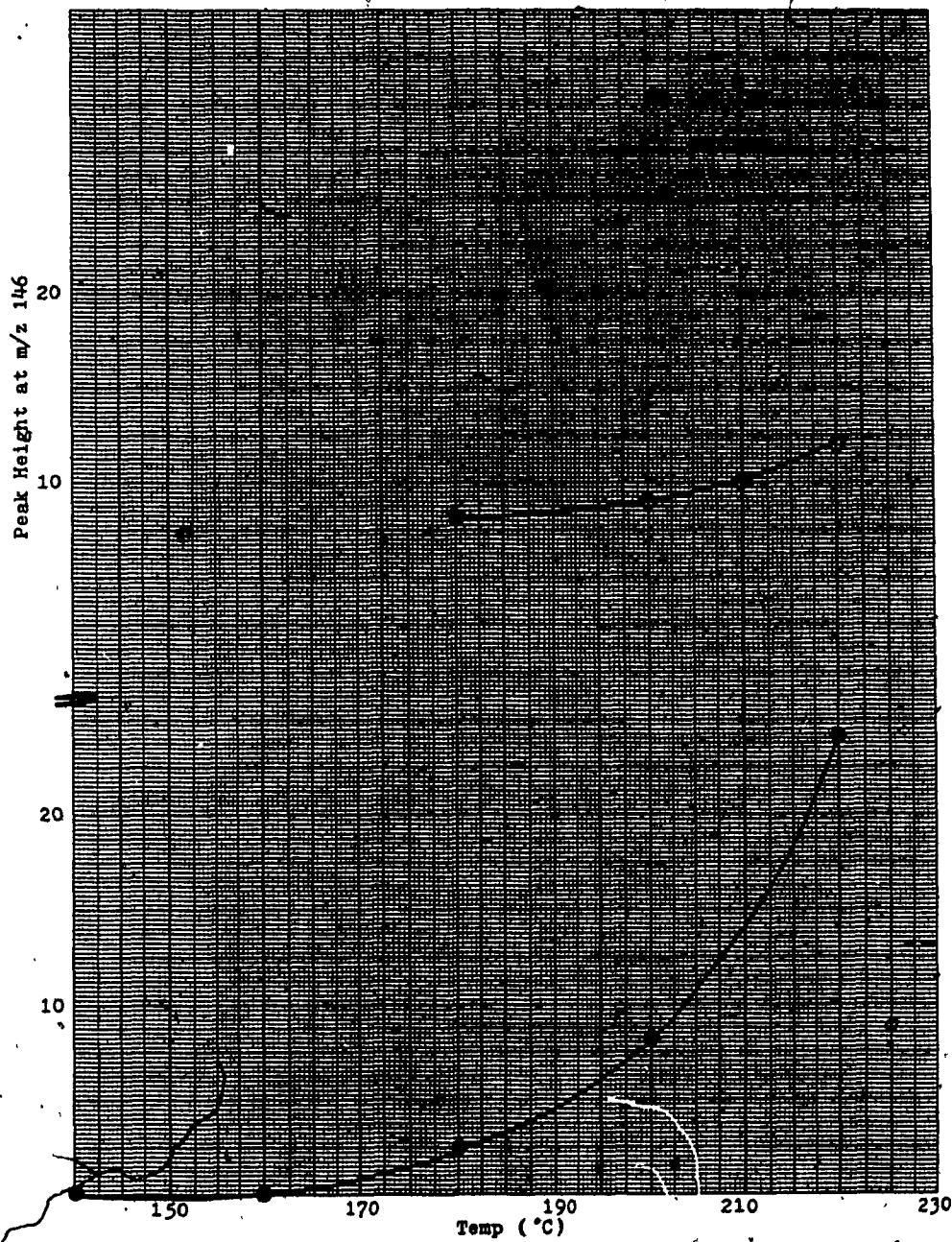


FIGURE 32. Graph of Peak Height of m/z 146 Peak in Effluent Versus Temperature of a 3.5% (w/w) OV-225 on CG-AW-DMCS Support Column.

another 44 hours. The bleed rate was significantly less than during the first run. However, at the lower temperature tested during the second run more bleeding was observed than during the first run. This anomolous result was probably due to contamination of the mass spectrometer by liquid phase at high temperatures used during the first run, and consequently is not considered significant. The second run certainly confirmed that liquid phase bleeding decreases with column conditioning time. Futher conditioning at 240°C for longer periods of time showed that the mass peaks at 180°C, disappeared completely. The mass spectrum obtained at this point was identical to Fig. 30.

CHAPTER 6

THERMODYNAMIC PROPERTIES OF COLUMNS PACKED WITH COATED
CHROMOSORB SUPPORTS

In the previous chapters it was established that at some temperature which varied with the support, bleeding of the liquid phase from any support surface became quite extensive. While such increased bleeding could be related to phase decomposition, it can frequently be assumed from our experimental evidence that decomposition was not taking place since no extraneous peaks were observed in the gas chromatograms. That being the case it became necessary to explain what happens to the liquid phase at the temperature of peak response maxima and above, which results in an onslaught of liquid phase bleeding.

Plots of $\log V_R$ vs $1/T$ and $\log t_R$ vs T were prepared starting with thermogram data for the s-triazines on various Chromosorb supports. Typical plots are illustrated in Fig. 33 for prometone on a coated CW-AW column. Upon close study it becomes apparent that both plots on Fig. 33 show a break in the curve at 190°C . This temperature occurs strikingly at the same temperature as the peak response maximum in the thermogram for prometone on this column. This same correspondence was observed on all the supports studied except for CW-NAW. Similar effects have been reported in the literature. Smidsrod and Guillet [27] have done a study of the interaction of solutes with poly (N-isopropylacrylamide). They attributed the breaks observed in the logarithm of the specific retention volume vs the reciprocal temperature curve to a glass transition

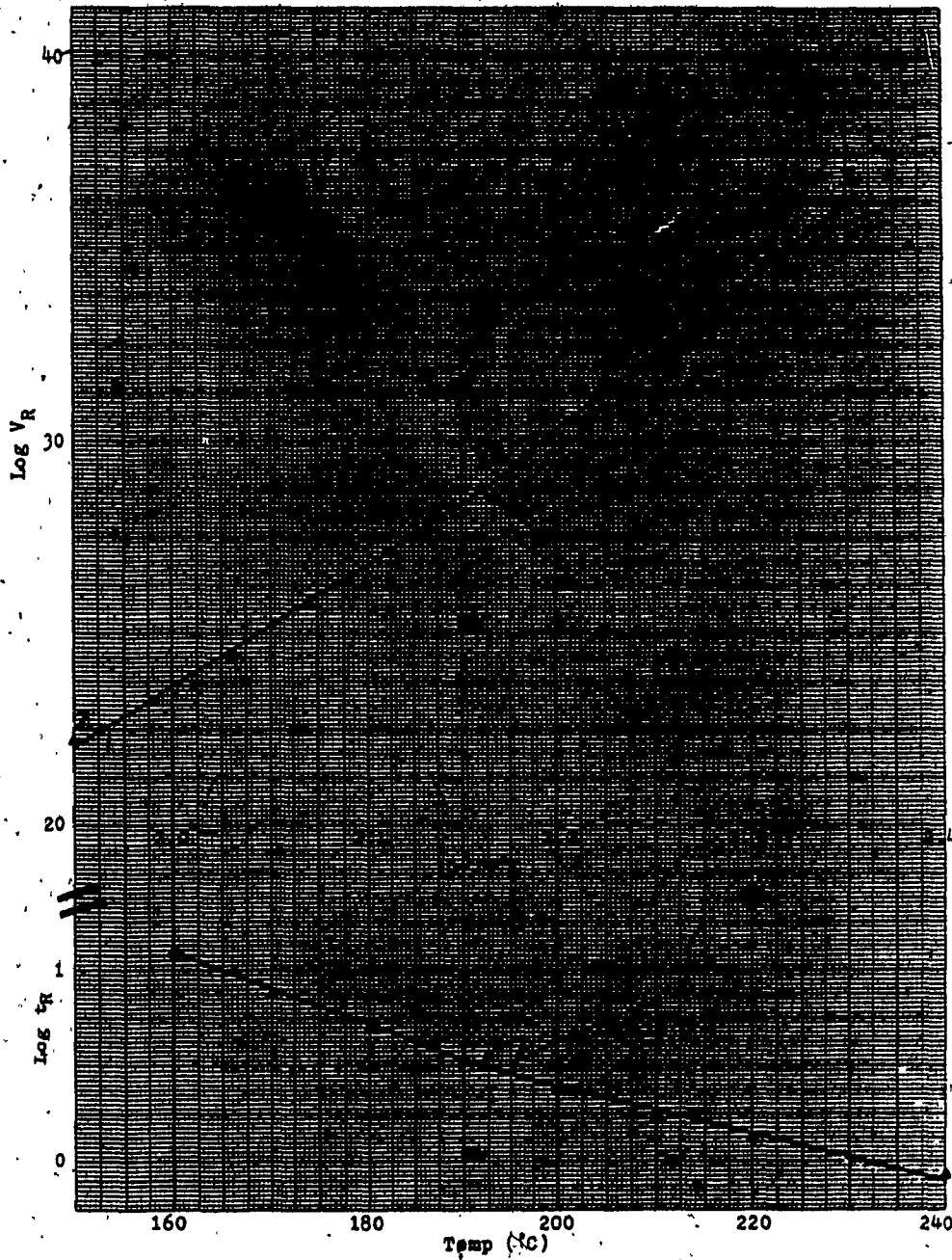


FIGURE 33.(a) Variation in $\log t_R$ of Prometone (50.6ng) vs Temperature on a Column Containing CW-AW Support;
 (b) Variation of $\log V_R$ of Prometone vs Reciprocal of Temperature on a Column Containing CW-AW Support

temperature of the polymer, i.e., a solid - liquid transition. The breaks obtained in this thesis could not be attributed to a glass transition, however, since OV-225 exists already as a viscous liquid at room temperature. Guran and Rogers [93] studied the adsorption behaviour of C_8 hydrocarbons on the thermochromic solids, Cu_2HgI_4 and Ag_2HgI_4 . They explained the breaks in their retention data curves as being due to a solid-solid transition (i.e., between the α and β forms of these solids). Again this is not directly applicable to the OV-225 liquid phase that we worked with. What is clear from the above studies, however, is that at the break in the retention curve, some structural change is taking place. Haniff and Zienius [5] in a study of organophosphorus pesticides found similar breaks in the retention curves obtained using an OV-1 liquid phase. They explained the break as corresponding to a solid-solid transition in which the compact solid is changed to a swollen solid. Chen and Gacke [94] in a study of retention behaviour with change in temperature, suggested that above $170^\circ C$ conformational/spatial changes occur in a XE-60 (silicone nitrile with 100% cyanoethylmethyl siloxy units) polymer. These spatial changes are reversible if the temperature is decreased.

Similarly the breaks in the retention curves for s-triazines may be attributed to a conformational change in the structure of the OV-225 polymer. It may be that the

liquid phase arranges itself in a particular manner on the solid support at a relatively low temperature, but transforms into a different arrangement at a high temperature. This reorientation of various groups of the polymer, causing a conformational change and thus altering the characteristics of the column may be caused by thermal agitation. The structure of the OV-225 is such that it has fairly bulky polar (cyano) side chains beside nonpolar methyl groups all attached to the main polymer chain. Such a structure attaches itself onto the solid support partly by Van der Waals forces but, particularly by hydrogen bonding with silanol groups on the diatomite surface [94]. Even pre-silanized diatomite supports still contain a considerable fraction of free silanol groups. As can be seen from the structure of OV-225 (Sec. 1.9.1.), it is possible that all the side chains of OV-225 project outward from the main chain. The smaller methyl groups may oscillate to some degree at relatively low temperatures. The bulkier polar groups, because of steric reasons, would be more restricted in their motion. At a high temperature, a randomization and reorientation of the polymer molecules attached to the support could be brought about easily by a disruption of the Van der Waals' binding forces and hydrogen bonding between the silanol groups and the polymers of the first layer as a result of a rearrangement and perhaps a random coiling of the polymer backbone. A process such as this could account for bleeding of the

liquid phase after the peak response maxima temperatures are exceeded. Results obtained by Chen and Cacka [94] have showed that if the propyl-nitrile was substituted with a phenyl group heat had very little influence on for example the elution order of fatty acids. They attributed this to the fact that it would be more difficult to achieve extensive randomization of two phenyl groups on one silicon atoms. Although this hypothesis was not proven in our experiments, it presents a model of what could possibly happen at temperatures above the peak maximum.

Table 14 shows heats of adsorption values calculated for all the supports studied using the three s-triazines. The values ΔH_{XY} are calculated for the XY portions of retention plots, and ΔH_{YZ} for the YZ portions as illustrated in Fig. 33. Equation 1 is used to calculate ΔH . The slope of YZ was smaller than that of XY on all plots, and hence ΔH_{YZ} is smaller than ΔH_{XY} . These lower values of ΔH_{YZ} agrees with our claim that above the temperature of peak response maxima there is a decrease in adsorptivity when the temperature is increased. This decrease in adsorptivity after the peak maxima may even be enhanced by a possible conformational change in the liquid phase. Hence, the decreased slope for YZ in Fig. 33b. On the supports CG-HP and CW-AW-DMCS, the retention curve for atrazine shows two breaks, and hence, two ΔH_{YZ} values.

There is a correlation between heats of adsorption and the RRT. A greater ΔH corresponds to longer solute retention. This is illustrated by comparison of Tables 10 and 14. Generally, the G supports had higher heats of adsorption, and longer retention times compared to the W supports. No consistent correlation between the detector responses and the heats of adsorption of s-triazines could be drawn, however.

At the transition temperature, where the change in free energy, ΔG , between the XY and YZ forms of the liquid phase is zero, the change in entropy, ΔS , can be obtained directly from the difference in ΔH values:

$$\Delta S = (\Delta H_{YZ} - \Delta H_{XY}) / T_{\text{transition}} \quad 13$$

As shown in Table 15, ΔS values were largest for the CW supports. These higher ΔS values suggests a greater interaction between the s-triazines and the liquid phase at the liquid phase surface. This greater interaction is probably caused by the greater surface area of CW, compared to that of the CG supports.

From Tables 14 and 15 it can be seen that ΔH values are highest for ametryne and lowest for prometone, while the ΔS is lowest for ametryne and highest for prometone. This is due to the greater adsorption of ametryne onto the liquid

Table 14. Heats of Adsorption for s-Triazines Coated on Various Supports.

<u>Support</u>	<u>Prometone</u>		<u>Atrazine</u>		<u>Ametryne</u>	
	<u>ΔH_{XY}^*</u>	<u>ΔH_{YZ}</u>	<u>ΔH_{XY}</u>	<u>ΔH_{YZ}</u>	<u>ΔH_{XY}</u>	<u>ΔH_{YZ}</u>
CW-NAW	16.37	16.37	17.00	17.00	18.12	18.12
CW-AW-DMCS	16.88	14.74	17.91	16.3/14.7	18.88	16.84
CG-AW	17.62	16.52	17.66	17.01	18.03	18.03
CW-AW	17.82	14.27	18.76	15.41	19.06	16.68
CW-HP	17.87	14.60	18.59	15.85	19.54	16.84
CG-AW-DMCS	17.88	16.21	18.01	16.80	18.75	17.71
CG-NAW	17.94	15.22	19.68	16.41	19.13	17.39
CG-HP	18.97	16.17	26.81	17.1/15.3	19.39	17.69
C-750	19.22	14.97	18.40	15.42	19.52	16.69

* - ΔH values are all negative with kcal/mol as units.

Table 15. Entropy Values for s-Triazines on Various Coated Supports.

Support	ΔS^{++}		
	Prometone	Atrazine	Ametryne
CW-NAW	+	+	+
CW-AW-DMCS	4.43	3.46/3.25	4.31
CG-AW	2.38	1.43	*
CW-AW	7.67	7.40	5.14
CW-HP	7.30	6.19	5.77
CG-AW-DMCS	3.60	2.70	2.25
CG-NAW	5.75	7.22	3.75
CG-HP	5.92	22.0/3.51	3.67
C-750	9.38	6.58	6.25

+ - CW-NAW did not show a break in the $\log V_g$ curve

++ - all ΔS values are positive with cal/K as units

* - no ΔS obtained for ametryne

phase, and hence, relatively lower diffusivity within the liquid phase, and therefore longer retention time.

CHAPTER

CONCLUSIONS

7.1. COLUMN PERFORMANCE USING DIFFERENT SUPPORT MATERIALS.

7.1.1. RELATIVE RETENTION TIMES.

For CW supports:

$$\text{CW-AW-DMCS} > \text{CW-AW} > \text{CW-HP} > \text{CW-NAW}$$

for CG supports:

$$\text{CG-HP;CG-AW} > \text{CG-AW-DMCS} > \text{CG-NAW}$$

CW-NAW has the shortest retention time of all the supports tested. The CW have generally shorter retention times when compared to the CG supports.

7.1.2. COLUMN EFFICIENCIES (n).

CW supports; "high" concentrations:

$$\text{CW-AW-DMCS} > \text{CW-NAW} > \text{CW-HP} > \text{CW-AW}$$

"moderate" concentrations:

$$\text{CW-HP} > \text{CW-AW-DMCS} > \text{CW-AW} > \text{CW-NAW}$$

CG supports; "high" concentrations:

$$\text{CG-AW-DMCS} > \text{CG-HP} > \text{CG-NAW} > \text{CG-AW}$$

"moderate" concentrations:

$$\text{CG-AW} > \text{CG-NAW} > \text{CG-AW-DMCS} > \text{CG-HP}$$

7.1.3. RESOLUTION.

Resolution using both "high" and "moderate" concentrations of s-triazines on all supports was good with no overlap of peaks.

7.1.4. GENERAL CONCLUSIONS.

The CW supports gave more efficient columns than the CG supports for analysis of s-triazines using OV-225 liquid phase. It was also observed that the concentration of s-triazines tested affected the column efficiency. Overall, the optimum support was found to be CW-AW-DMCS.

7.2. RESPONSES FOR "HIGH", "MODERATE" AND "LOW" CONCENTRATIONS OF S-TRIAZINES.

It has been concluded that the relative quantitative responses, on the different supports tested, are dependent upon the quantity of s-triazine and the type of detector used. For "high" (μg) concentrations of s-triazines with FID the best response overall was obtained on a C-750 support. For "moderate" and "low" (ng) s-triazine levels with the ECD the best response overall was obtained on the CG-AW support. Column bleeding does not adversely affect the sensitivity of the FID, and because of the relatively high concentrations of s-triazines used with this detector,

there was no significant decrease in response due to loss of solutes because of priming of exposed active surface sites.

The thermograms for s-triazines on the supports tested differed in shape using FID and ECD detectors. Bleeding of the liquid phase and priming of the exposed active surface sites are the main reasons for the decreased response observed after the peak maxima using the ECD. The shape of an ECD thermogram, in particular the rate of decrease of response beyond the peak maxima, could be related to the degree of liquid phase bleeding, and hence to projected column lifetime. It was found that the AW supports suffered from extensive bleeding, NAW supports showed relatively little liquid phase bleed, and AW-DMCS and HP supports showed intermediate amounts of bleeding.

Adsorption of s-triazines was found to be particularly severe on CP supports. Chromosorb 103 was found unsuitable for the separation of the s-triazine mixtures that we were dealing with. An atrazine thermogram on this support showed no apparent column effects on the response of the FID over the temperature range studied. Attempts to use this column with the ECD were not successful. Although the CSP-20M support showed a low liquid phase bleed rate, it seemed that at lower s-triazine concentrations, using the ECD, only atrazine could be analyzed quantitatively. The peaks

for ametryne and prometone showed distortion, which make manual measurement of their areas rather difficult. Analysis of "high" s-triazine concentrations with an FID were feasible on CSP-20M, only slight tailing of peaks being observed.

7.3. THE EFFECT OF COLUMN BLEED ON THE RESPONSE OF THE ECD AND POSSIBLE WAYS OF REDUCING THE AMOUNT OF BLEEDING.

The results obtained in this section are especially significant since the evidence confirms liquid phase bleed. The adverse effect of liquid phase bleeding on the response of an ECD has been proven. The longer the thermal conditioning period at the operating column temperature, after initial preconditioning, the lower the liquid phase bleed observed. Bleeding is not significant however, at temperatures below those of peak response maxima.

Mass spectrometry provided independent evidence which confirmed all conclusions regarding bleeding based on GC results, i.e., extensive bleeding at temperatures above response maxima, and decreased bleed rate after conditioning the column at the operating temperature for unusually long periods of time; e.g., 90 hours.

7.4. THERMODYNAMIC PROPERTIES OF COLUMNS PACKED WITH COATED CHROMOSORB SUPPORTS.

Retention data plots for s-triazines on the various coated supports showed a break in the curves which coincided with the temperatures at which the response maxima occur on the thermograms. These breaks are possibly due to a conformational change in the structure of the OV-225 liquid phase which may be responsible for the extensive liquid phase bleeding that is observed when the temperature of peak response maxima is exceeded. The decrease in ΔH values after the break in the retention data plots is due to decreased adsorptivity of the s-triazines onto the packing material. Heats of adsorption were greatest for ametryne and smallest for prometone with intermediate values for atrazine.

CHAPTER

8

SUGGESTIONS FOR FURTHER RESEARCH

The effect of prolonged column conditioning on the amount of liquid phase removed from the support, i.e., bleeding, should be determined. For example, after further conditioning of the column at 240°C for 90 hours, the amount of liquid phase left on the support should be determined and compared with the initial amount of liquid phase on the support. This study will help to quantitize the severity of bleeding of the liquid phase on any particular support.

Studies on thermal conditioning of columns should be carried out at temperatures lower than 240°C. Of interest would be the time it will take for bleeding curves to level off and how this will compares with time taken at 240°C.

Thermal analysis of OV-225 liquid phase (in liquid form, i.e., not coated on any support) should be done to see whether any conformational changes in the liquid phase can be detected. This result should then be compared with the thermal analysis of a particle of support coated with OV-225 liquid phase. This would indicate any catalytic activity on the part of the support.

More work should be done with Chromosorb 103 using the ECD. A method should be found to eliminate the spurious peaks which interfered with the analyte peaks in our work.

Thermograms should be obtained using columns containing various liquid phase loadings. It would be especially advantageous to obtain the thermograms at lower liquid loads than those used in this thesis.

An attempt should be made to analyze the mass spectra obtained from the effluent gas coming off the column. This could indicate whether decomposition of the liquid phase is taking place or not. One could compare the mass spectrum of the neat OV-225 liquid phase with that contained in the effluent gas coming off an OV-225 coated support.

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APPENDIX

I

CLASSIFICATION OF CHROMOSORB SUPPORTS USING "HIGH",
"MODERATE" AND "LOW" CONCENTRATIONS OF S-TRIAZINES

Table 16. Classification of CW Supports Using "High" Concentrations of s-Triazines at 170 and 210 °C (CID).

<u>s-triazine</u>	<u>Peak Area Response (mm²)</u>				
	<u>CW-NAW</u>	<u>CW-AW</u>	<u>CW-AW-DMCS</u>	<u>CW-HP</u>	<u>C-750*</u>
Prometone					
(1.3ug)					
170 °C/Rank	87/2	88/2	39/5	78/4	131/1
210 °C/Rank	81/2	87/2	67/5	74/4	131/1
Atrazine					
(2.2ug)					
170 °C/Rank	130/2	126/2	85/5	113/4	193/1
210 °C/Rank	212/2	126/2	109/5	117/4	189/1
Ametryne					
(3.0ug)					
170 °C/Rank	196/2	181/3	110/5	162/4	293/1
210 °C/Rank	165/3	192/2	163/3	167/3	285/1

* - C-750 included for comparative purposes

Table 17. Classification of CW Supports Using "Moderate" Concentrations of s-Triazines at 170 and 210 °C (ECD).

<u>s-triazine</u>	<u>Peak Area Response (mm²)</u>				
	<u>CW-NAW</u>	<u>CW-AW</u>	<u>CW-AW-DMCS</u>	<u>CW-HP</u>	<u>C-750</u>
Prometone (50.5ng)					
170 °C/Rank	659/3	931/1	439/5	793/2	461/4
210 °C/Rank	491/4	814/2	1020/1	527/3	294/5
Atrazine (6.0ng)					
170 °C/Rank	803/3	1327/1	814/3	1153/2	669/5
210 °C/Rank	598/4	997/1	937/2	778/3	385/5
Ametryne (50.0ng)					
170 °C/Rank	906/3	1313/1	816/5	1167/2	832/4
210 °C/Rank	504/5	1272/1	1268/1	829/1	542/4

Table 18. Classification of CW Supports Using "Low" Concentrations of s-Triazines at 170 and 210 °C (ECD).

<u>s-triazine</u>	<u>Peak Area Response (mm²)</u>				
	<u>CW-NAW</u>	<u>CW-AW</u>	<u>CW-AW-DMCS</u>	<u>CW-HP</u>	<u>C-750</u>
Prometone (25.3ng)					
170 °C/Rank	348/4	1203/1	*	823/2	407/3
210 °C/Rank	503/4	1173/2	1786/1	709/3	408/5
Atrazine (3.0ng)					
170 °C/Rank	670/4	1398/1	732/3	1064/2	655/5
210 °C/Rank	362/5	717/2	1030/1	578/3	550/4
Ametryne (25.0ng)					
170 °C/Rank	841/3	2250/1	240/5	1333/2	706/4
210 °C/Rank	602/5	1717/2	2184/1	1016/3	894/4

* - peak too flat to measure

Table 19. Classification of CW Supports Using "Moderate" Concentrations of s-Triazines at Temperature of Peak Area Maxima (PMT).

<u>s-triazine</u>	<u>Peak Area Response (mm²)</u>				
	<u>CW-NAW</u>	<u>CW-AW</u>	<u>CW-AW-DMCS</u>	<u>CW-HP</u>	<u>C-750</u>
Prometon					
(50.0ng)		190 °C ⁺	210 °C	170 °C	180 °C
PMT/Rank	*	1040/1	1020/2	850/3	490/4
Atrazine					
(6.0ng)		180 °C	210 °C	170 °C	180 °C
PMT/Rank	*	1443/1	1064/3	1153/2	680/4
Ametryne					
(50.0ng)		190 °C	200 °C	175 °C	180 °C
PMT/Rank	*	1685/1	1367/2	1175/3	870/4

* - no peak maximum observed in thermogram (see Fig. 43)

+ - Temperature of Response Maxima

Table 20. Classification of CG Supports Using "High" Concentrations of s-Triazines at 170 and 210 °C (FID).

<u>s-triazine:</u>	<u>Peak Area Response (mm²)</u>				
	<u>CG-NAW</u>	<u>CG-AW</u>	<u>CG-AW-DMCS</u>	<u>CG-HP</u>	<u>CSP-20M*</u>
Prometone (1.3ug)					
170 °C/Rank	63/5	98/1	100/1	76/4	82/3
210 °C/Rank	81/5	99/1	107/1	89/2	91/2
Atrazine (2.2ug)					
170 °C/Rank	89/5	153/1	153/1	113/3	103/4
210 °C/Rank	117/4	143/2	153/1	119/4	122/3
Ametryne (3.0ug)					
170 °C/Rank	121/5	212/1	217/1	142/4	157/3
210 °C/Rank	167/5	209/2	225/1	177/4	183/3

* - included for comparative purposes

Table 21. Classification of CG Supports Using "Moderate" Concentrations of s-Triazines at 170 and 210 °C (ECD).

<u>s-triazine</u>	<u>Peak Area Response (mm²)</u>			
	<u>CG-NAW</u>	<u>CG-AW</u>	<u>CG-AW-DMCS</u>	<u>CG-HP</u>
Prometone (50.5ng)				
170 °C/Rank	401/4	1114/1	903/2	679/3
210 °C/Rank	610/4	1390/1	1097/2	866/3
Atrazine (6.0ng)				
170 °C/Rank	530/4	936/1	833/2	702/3
210 °C/Rank	434/3	782/1	620/2	394/4
Ametryne (50.0ng)				
170 °C/Rank	746/4	1682/1	1425/2	1336/3
210 °C/Rank	820/4	1764/1	1283/2	941/3

Table 22. Classification of CG Supports Using "Low" Concentrations of s-Triazines at 170 and 210 °C (ECD).

<u>s-triazine</u>	<u>Peak Area Response (mm²)</u>			
	<u>CG-NAW</u>	<u>CG-AW</u>	<u>CG-AW-DMCS</u>	<u>CG-HP</u>
Prometone (25.3ng)				
170 °C/Rank	189/4	1583/1	798/2	544/3
210 °C/Rank	895/4	2226/1	1536/2	1514/3
Atrazine (3.0ng)				
170 °C/Rank	547/4	810/1	698/2	659/3
210 °C/Rank	400/4	998/1	533/2	540/2
Ametryne (25.0ng)				
170 °C/Rank	800/4	2202/1	1653/2	1498/3
210 °C/Rank	965/4	2916/1	1799/2	1528/3

Table 23. Classification of CG Supports Using "Moderate" Concentrations of s-Triazines at Temperature of Peak Area Maximum (ECD).

<u>s-triazine</u>	<u>Peak Area Response (mm²)</u>			
	<u>CG-NAW</u>	<u>CG-AW</u>	<u>CG-AW-DMCS</u>	<u>CG-HP</u>
Prometone (50.5ng)	200 °C ⁺	190 °C	190 °C	200 °C
PMT/Rank	635/4	1674/1	1170/2	875/3
Atrazine (6.0ng)	180 °C	190 °C	175 °C	220 °C
PMT/Rank	547/4	1097/1	833/2	702/3
Ametryne (50.0ng)	190 °C	190 °C	190 °C	190 °C
PMT/Rank	920/4	2300/1	1561/2	1256/3

+ - Temperature of Maximum Response

APPENDIX

II

THERMOGRAMS OBTAINED USING "HIGH" CONCENTRATIONS OF S-
TRIAZINES AND FID

i.e., 1.3ug Prometone

2.2ug Atrazine

3.0ug Ametryne

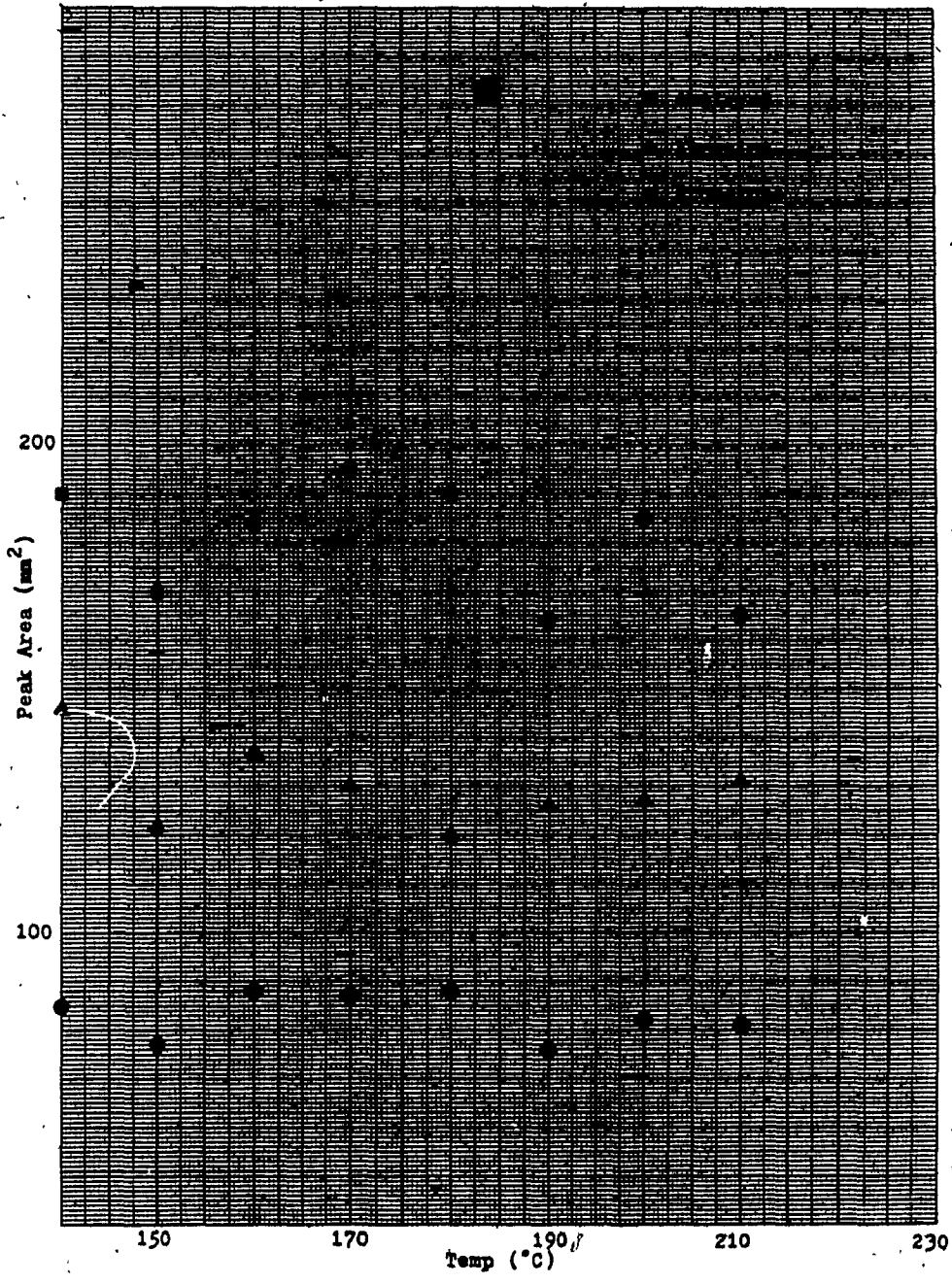


FIGURE 34. CW-NAW 1st Run (FID)

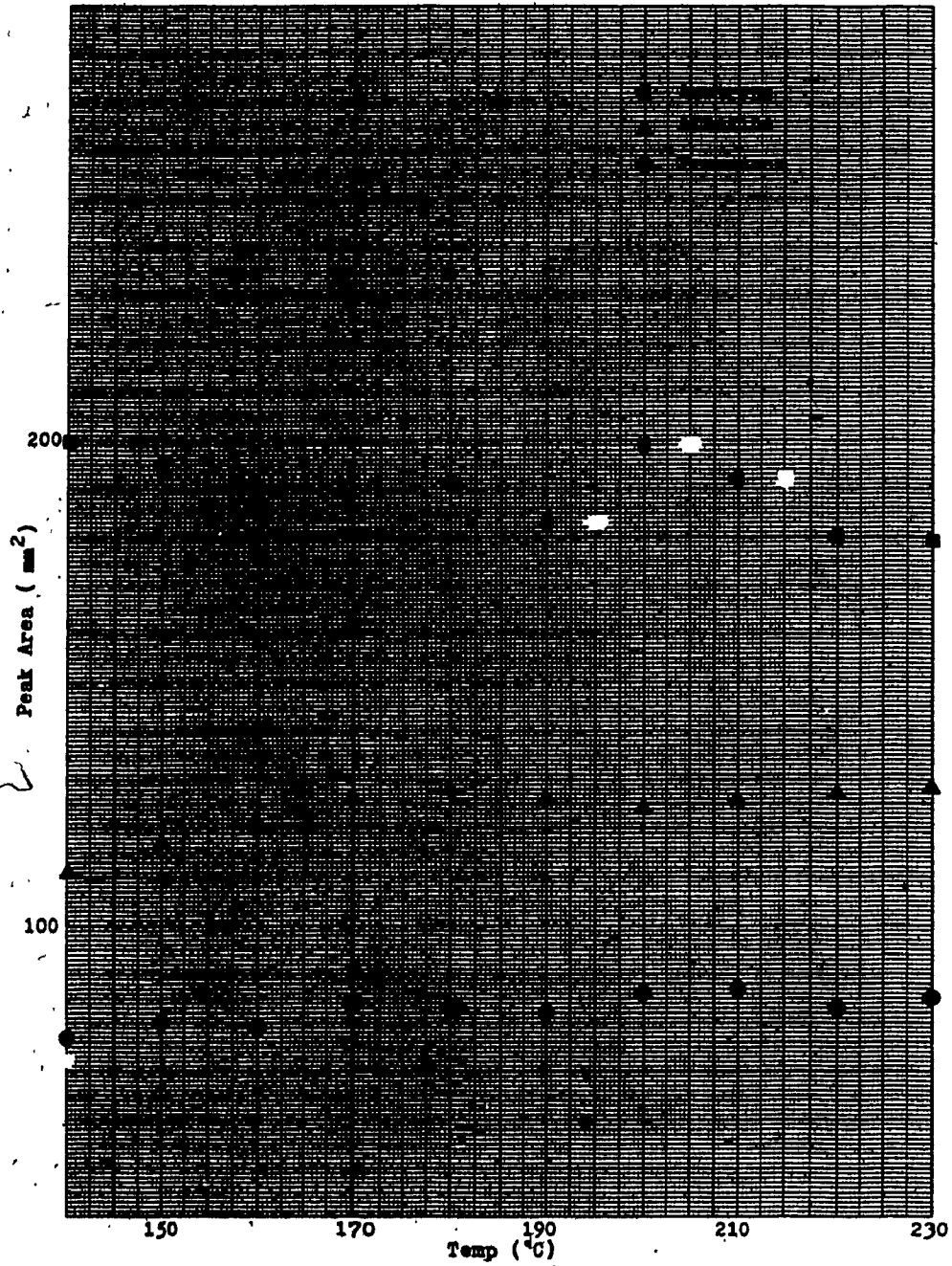


FIGURE 35. CW-AW 1st Run (FID)

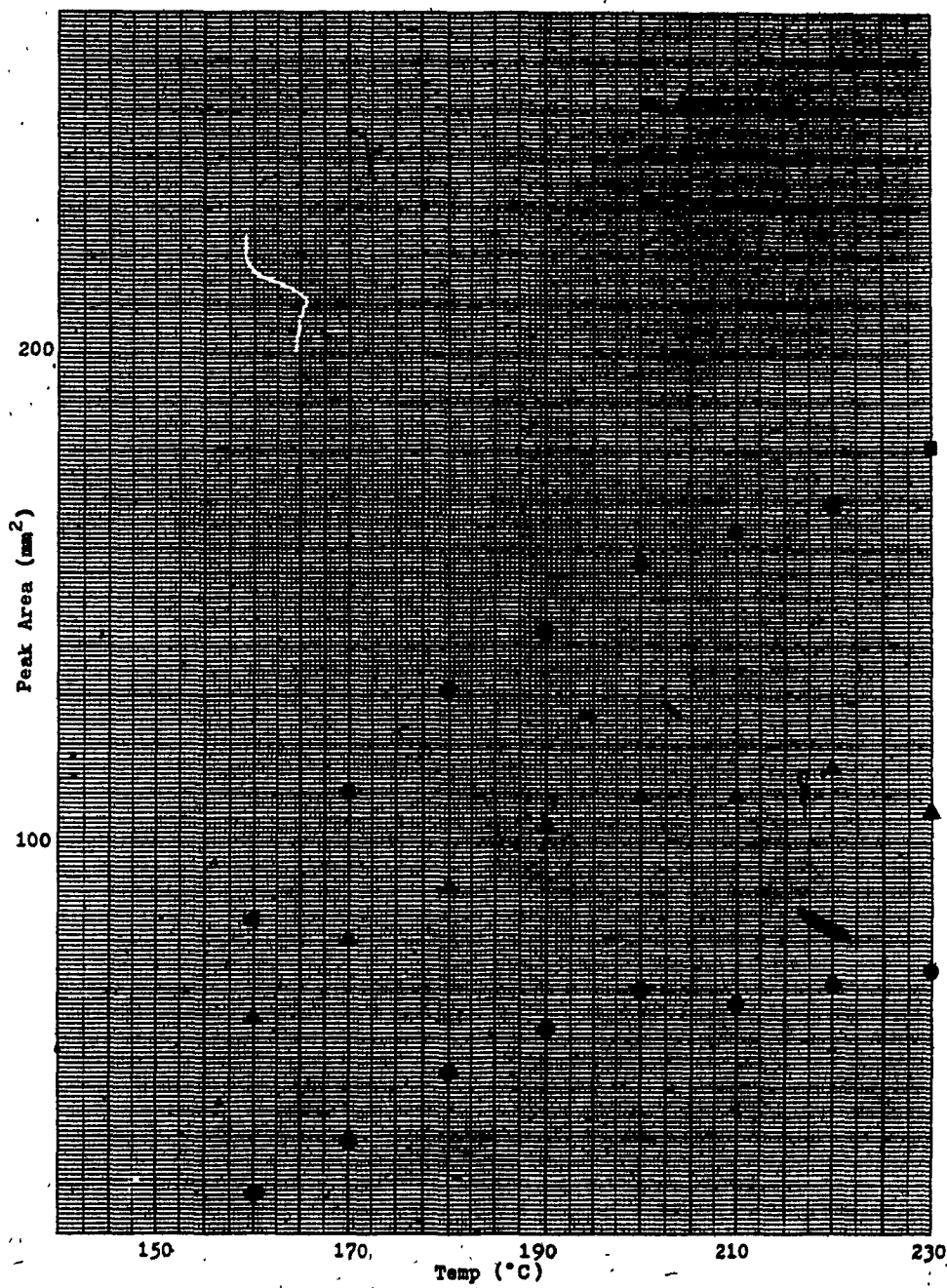


FIGURE 36. CW-AW-DMCS 1st Run (FID)

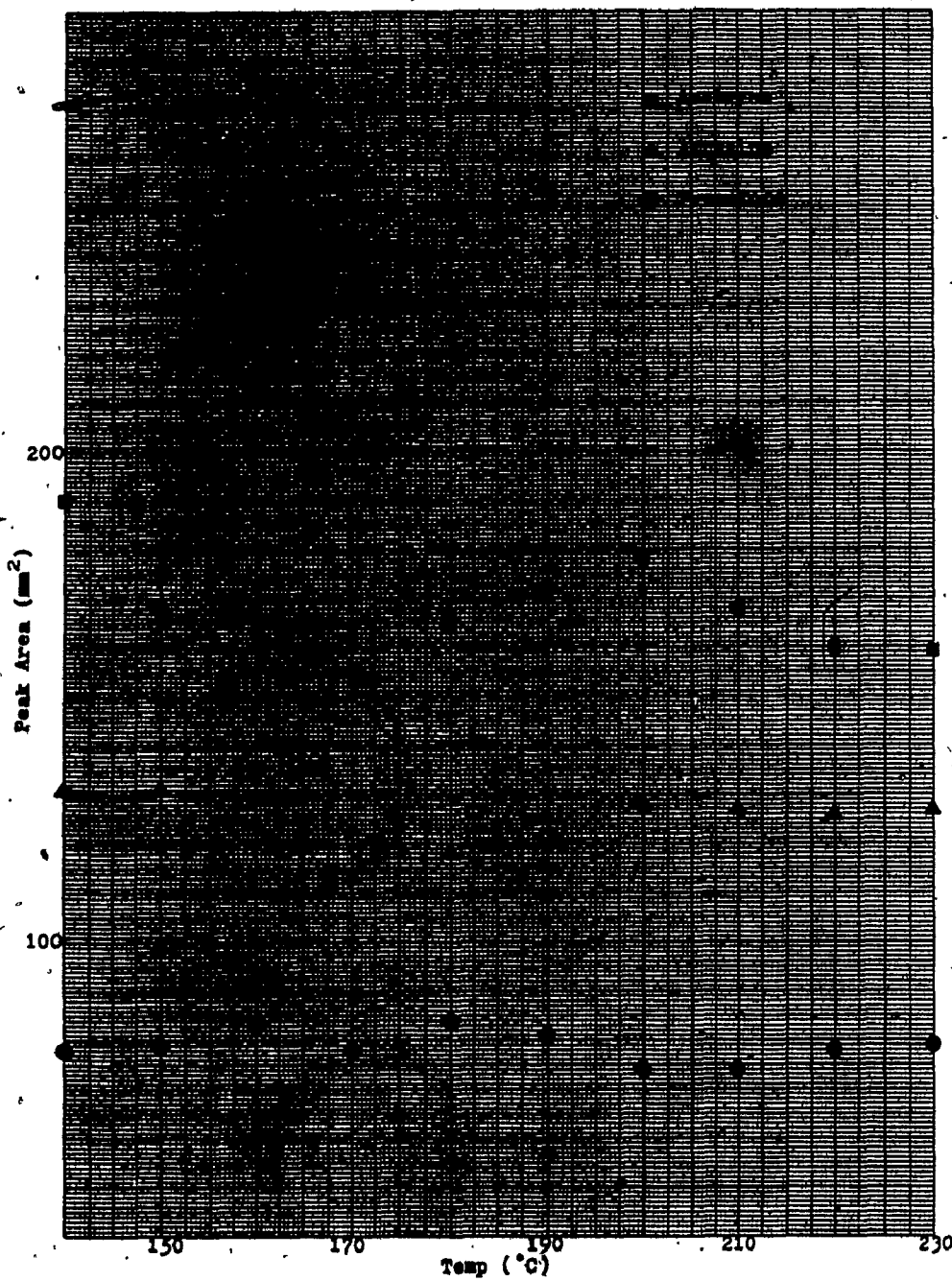


FIGURE 37: CW-HP 1st Run (FID)

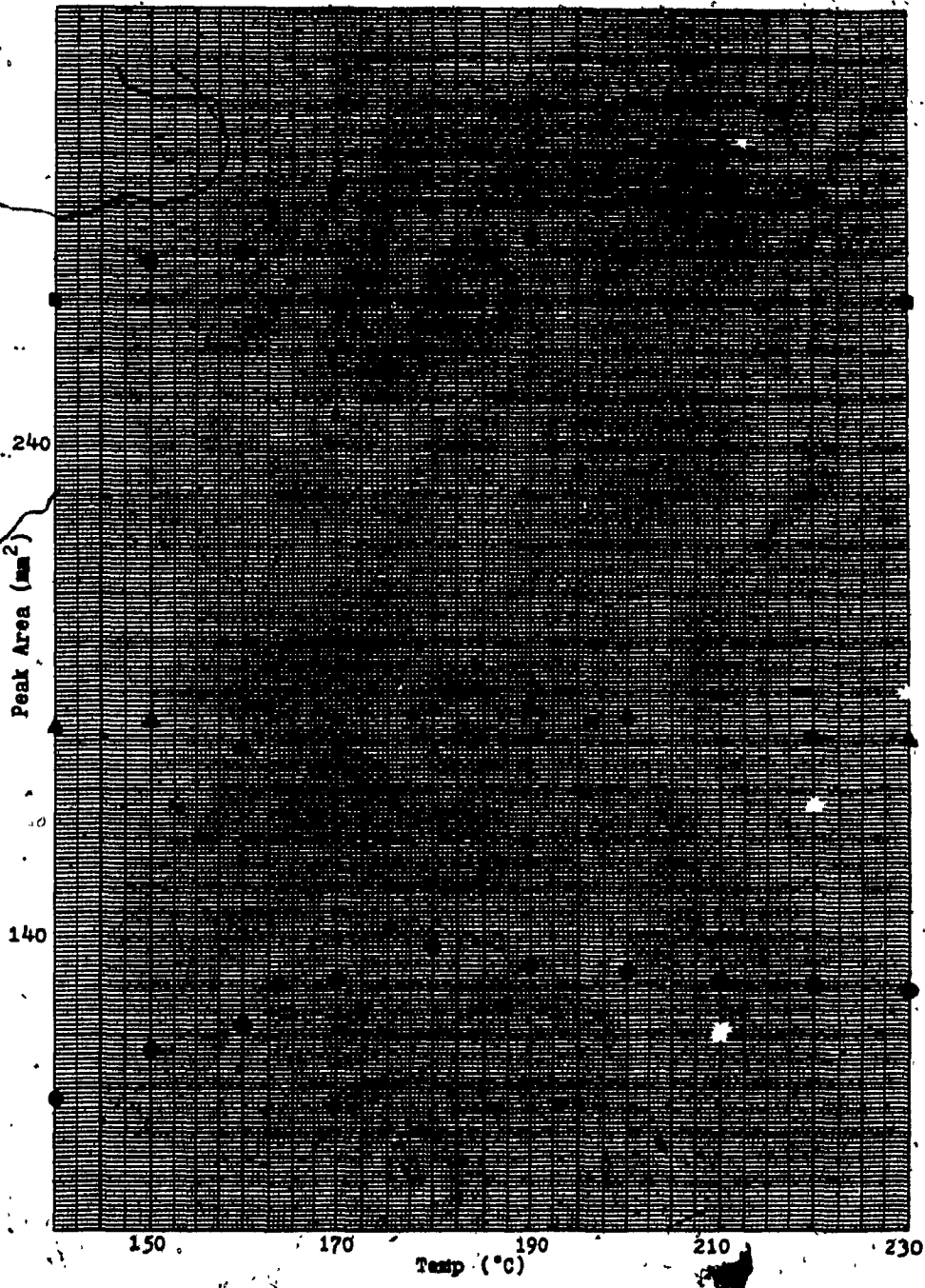


FIGURE 38. C-750 1st Run. (FID)

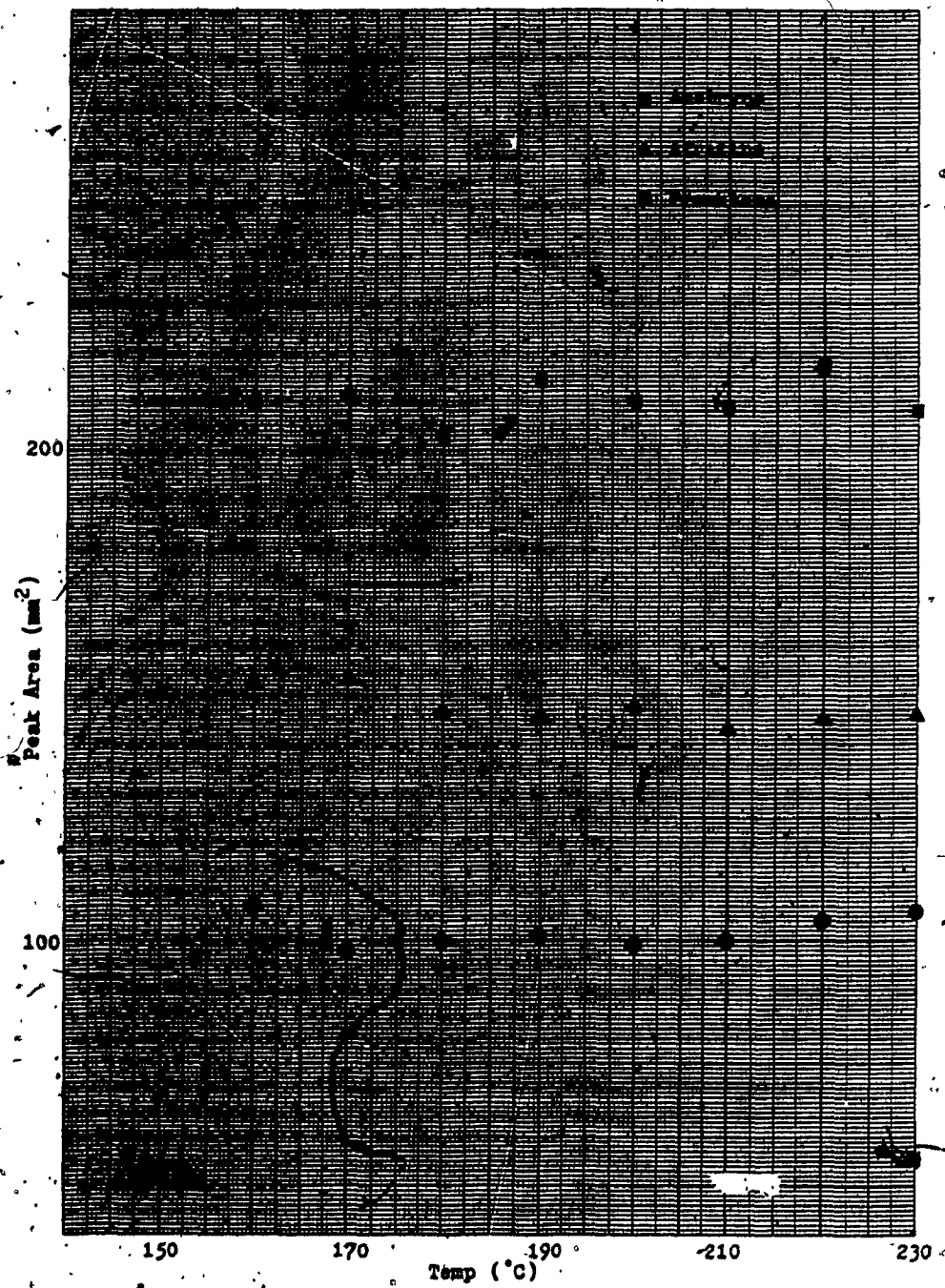


FIGURE 39. CG-NAW 1st Run (FID)

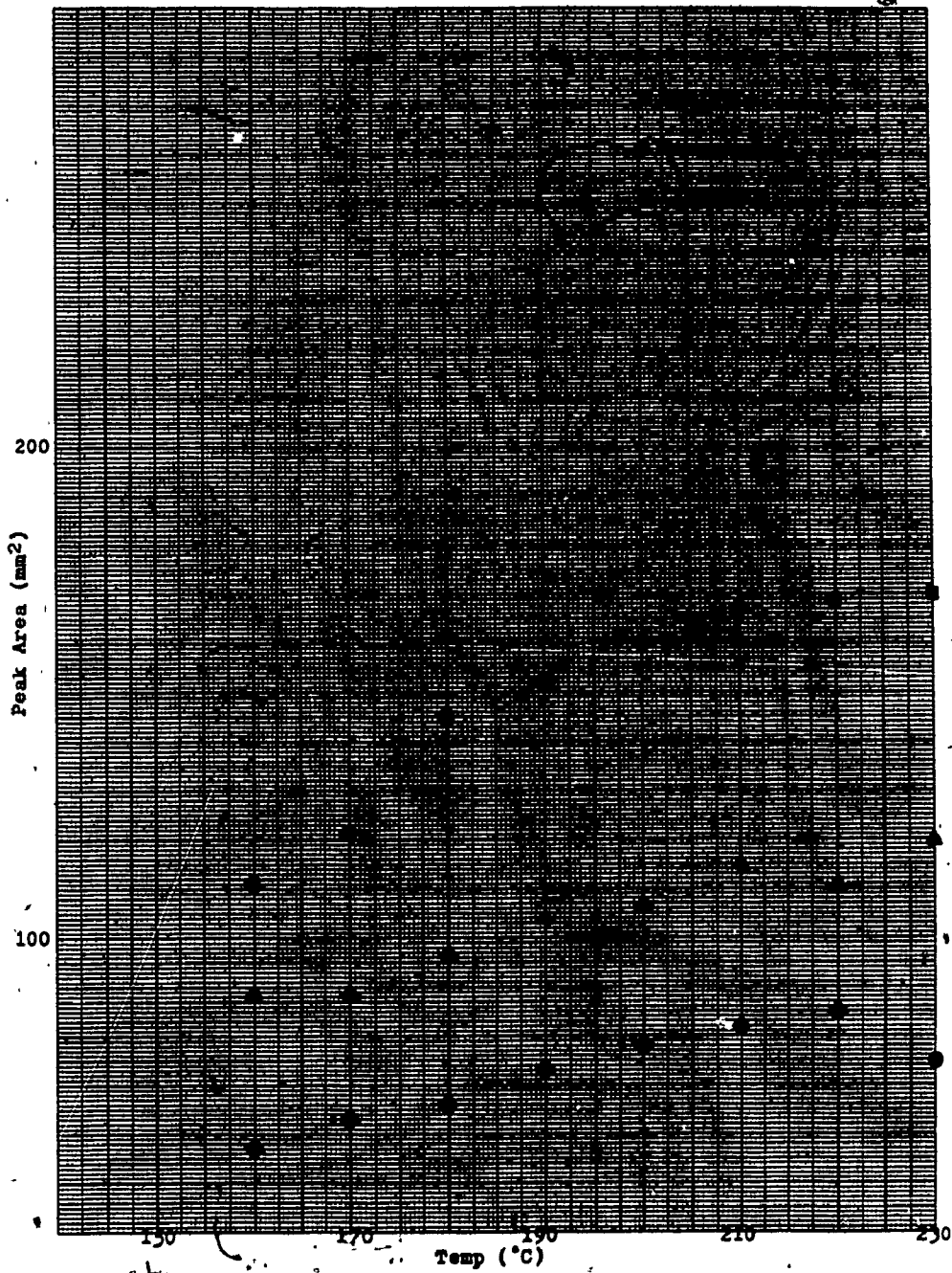


FIGURE 40. CS-AW 1st Run (FID)

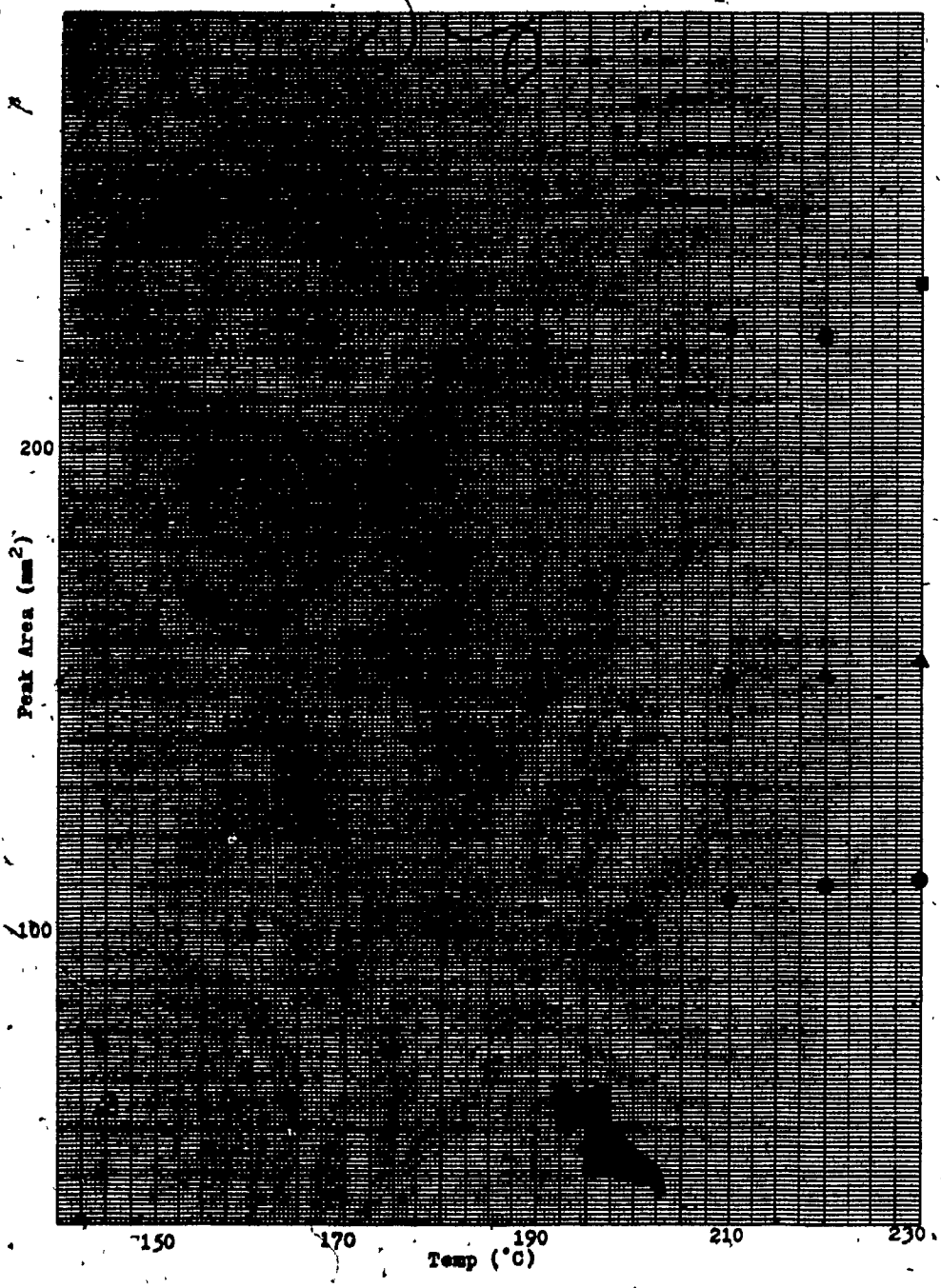


FIGURE 41. CG-AW-DMCS 1st Run (FID)

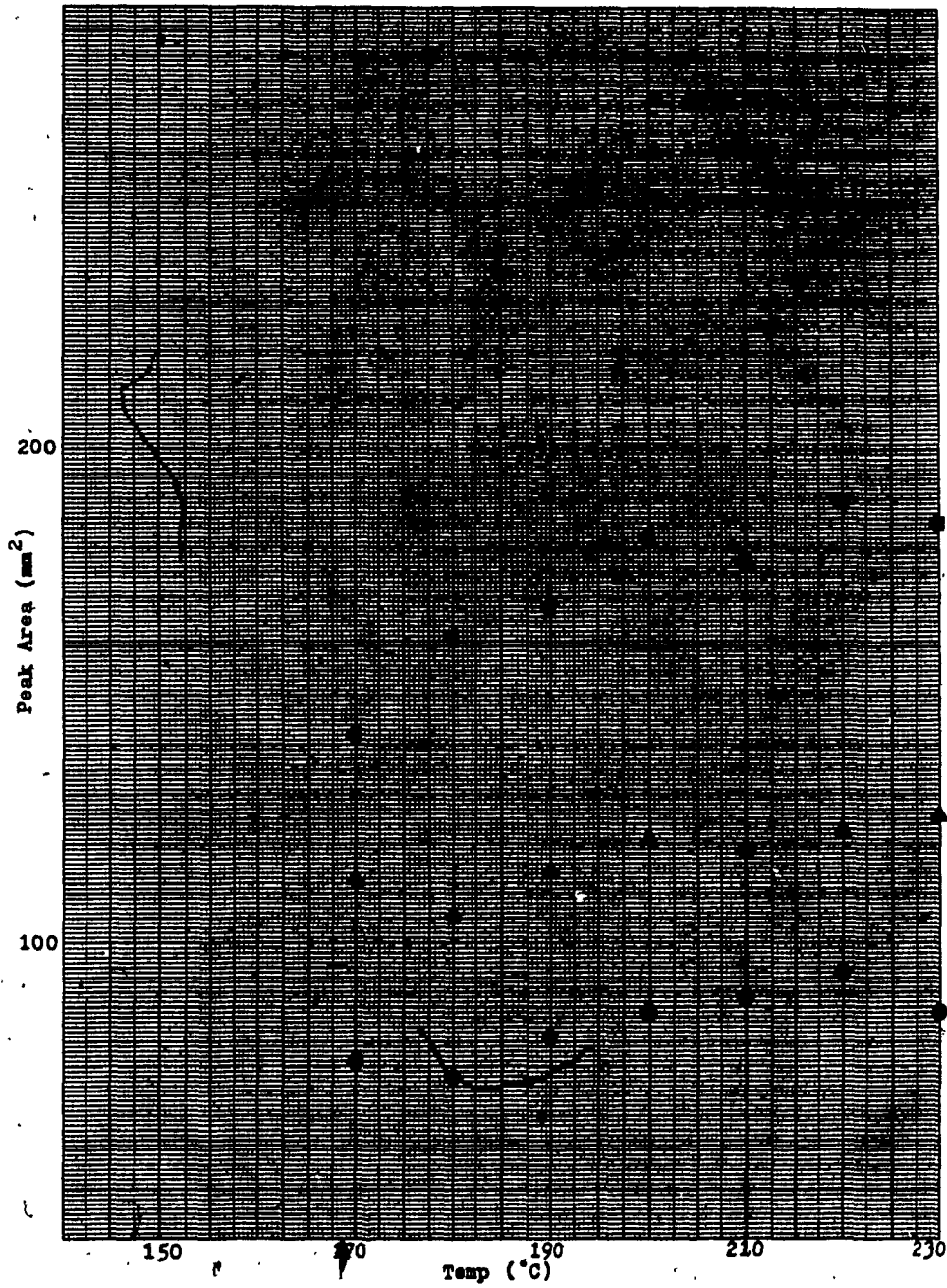


FIGURE 42. CG-HP 1st Run (FID)

APPENDIX

III

THERMOGRAMS OBTAINED USING "MODERATE" CONCENTRATIONS OF S-
TRIAZINES AND ECD

i.e., 50.6ng Prometone

6.0ng Atrazine

• 50.0ng Ametryne

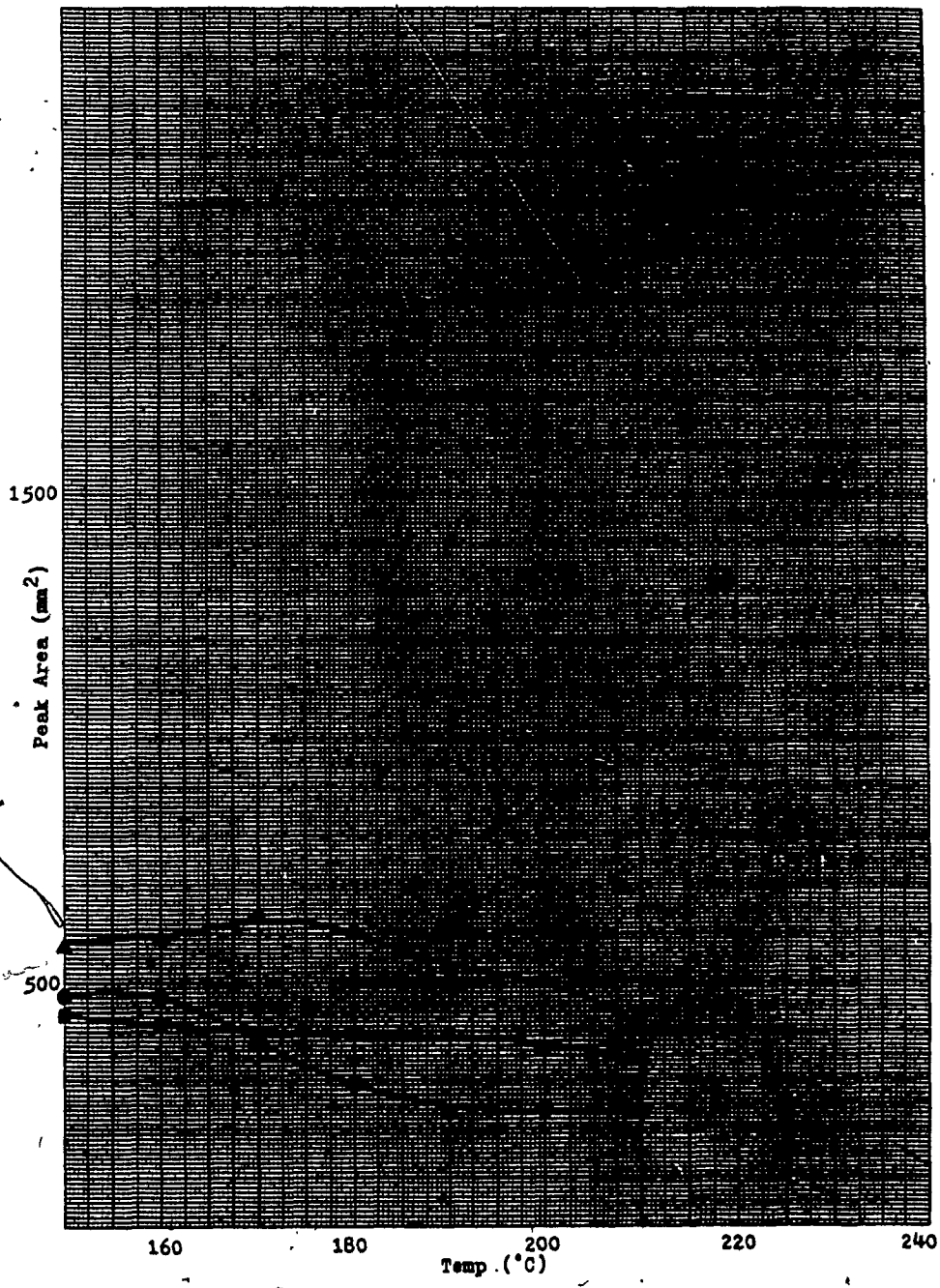


FIGURE 43. CW-NAW 2nd Run (ECD)

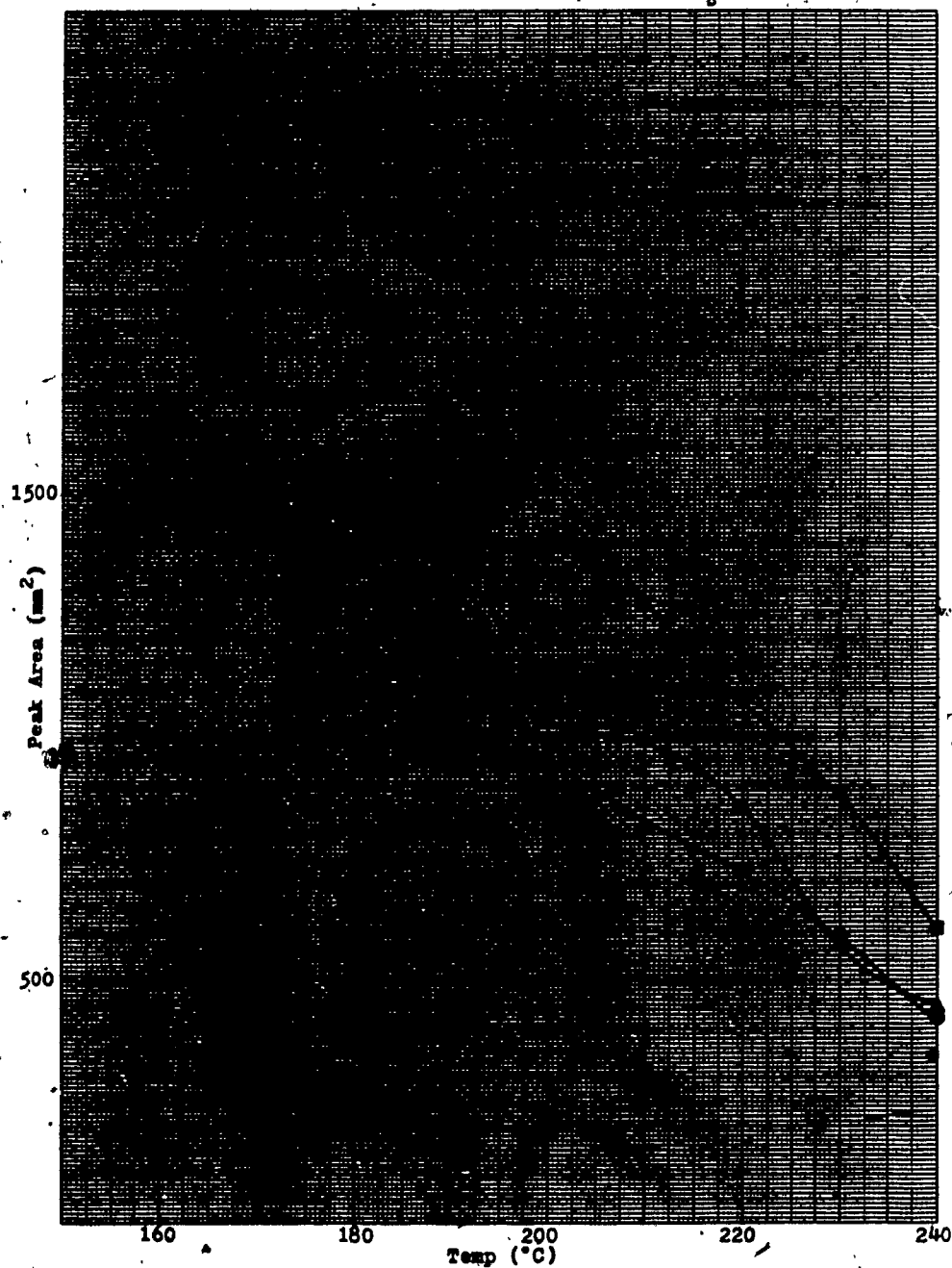


FIGURE 44. CW-AW 1st Run (ECD)

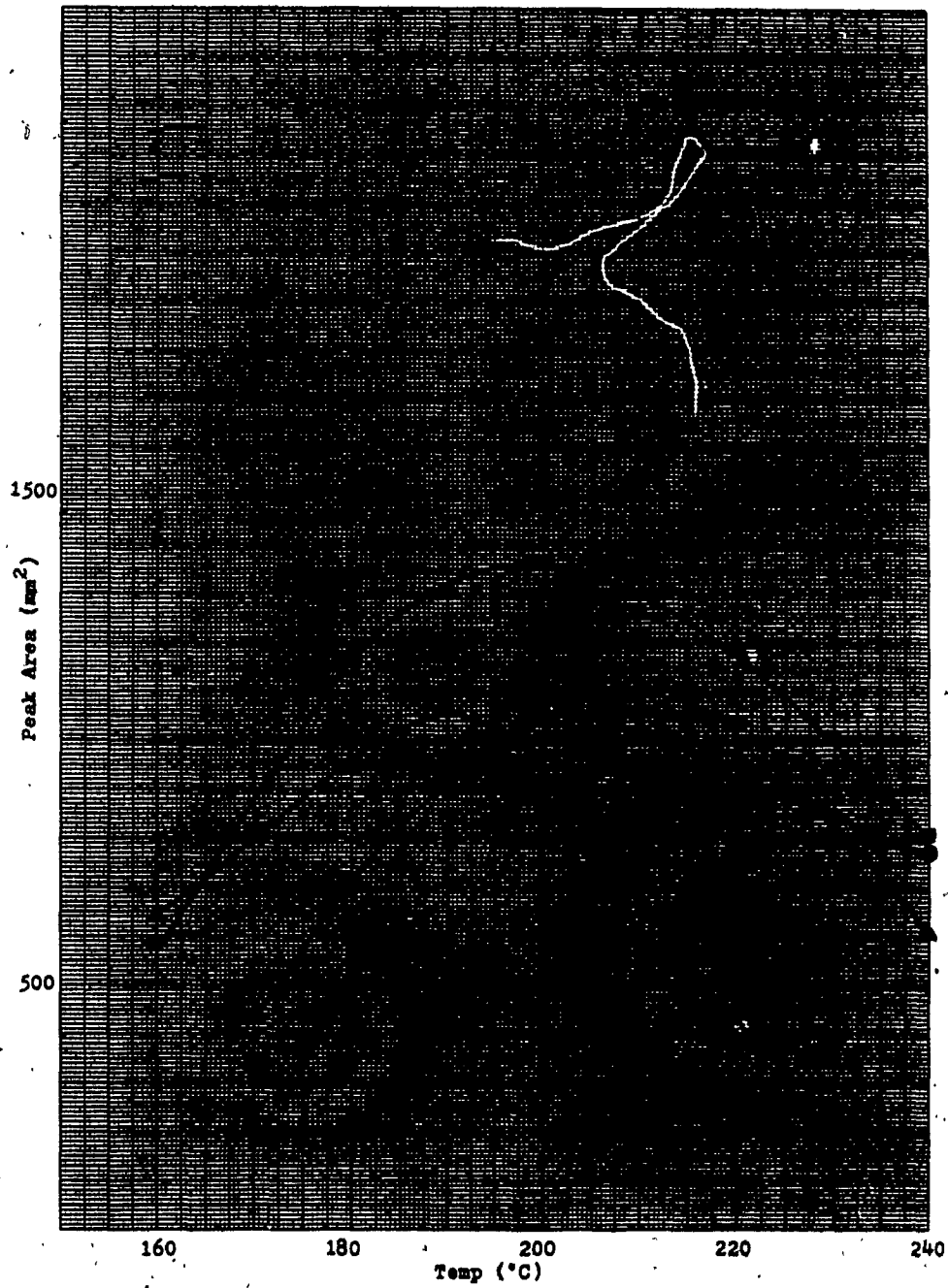


FIGURE 45. CW-AW-DMCS 1st Run (ECD)

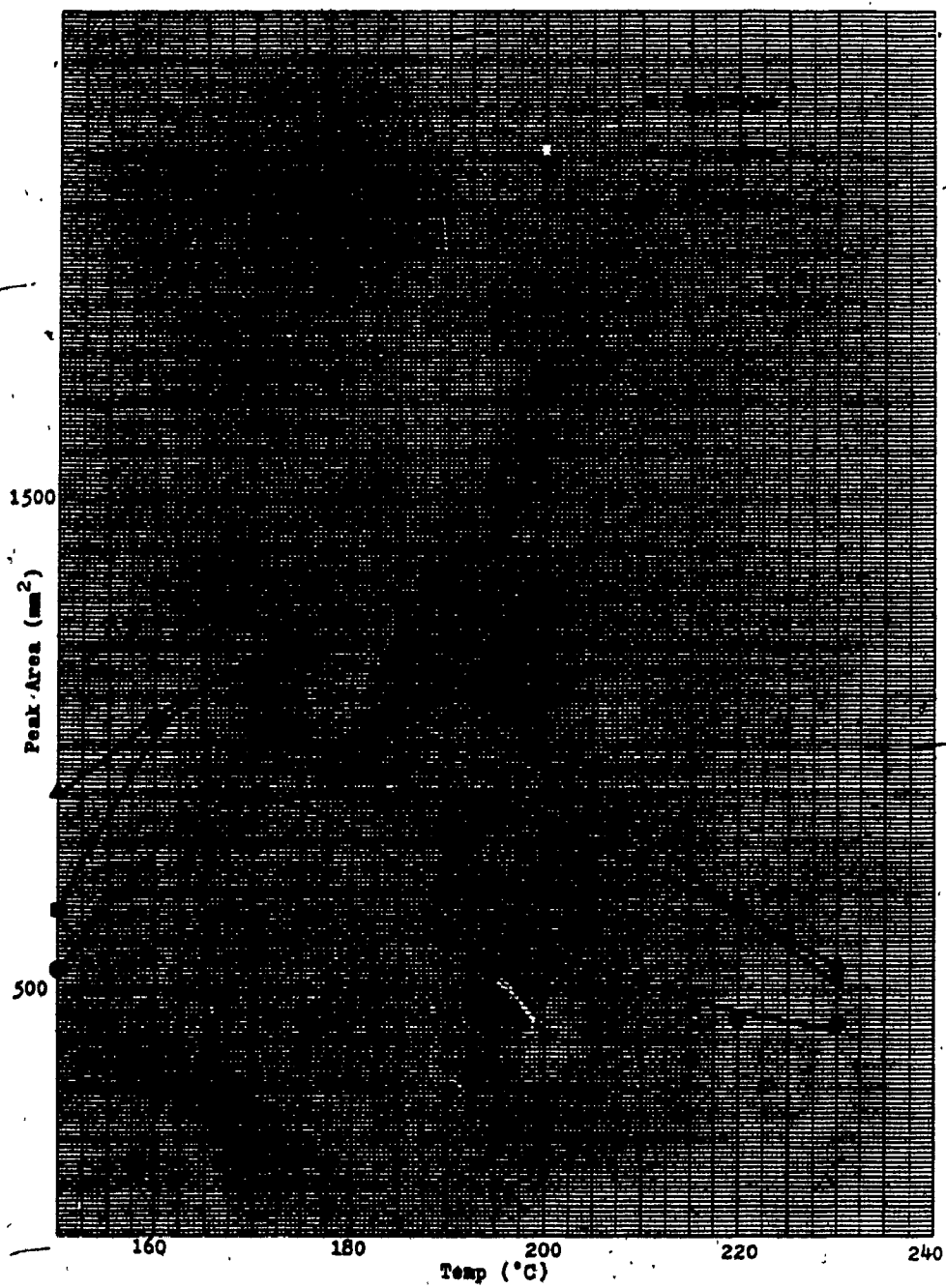


FIGURE 46. CW-HP 1st Run (ECD)

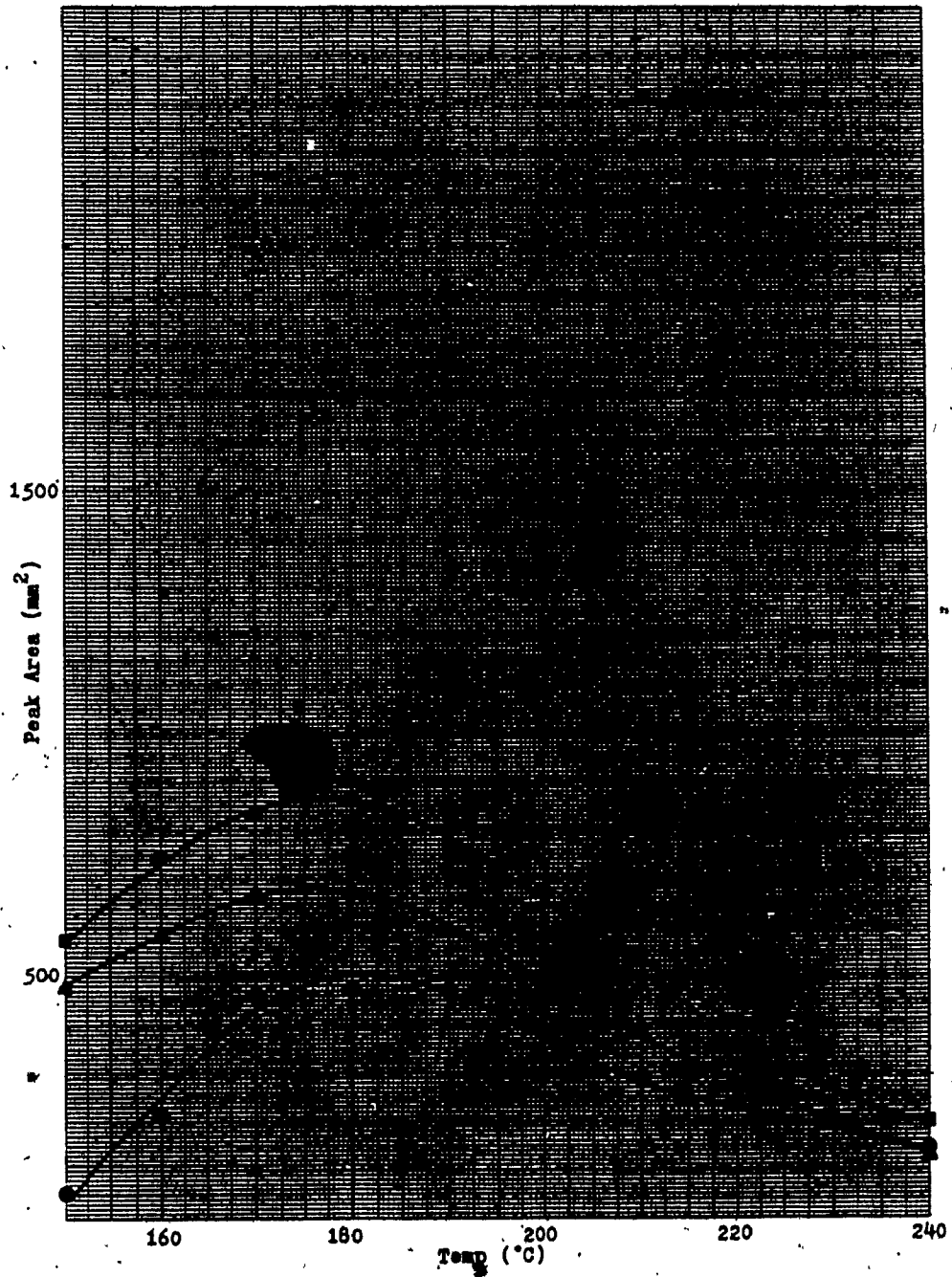


FIGURE 47. C-750 1st Run (ECD)

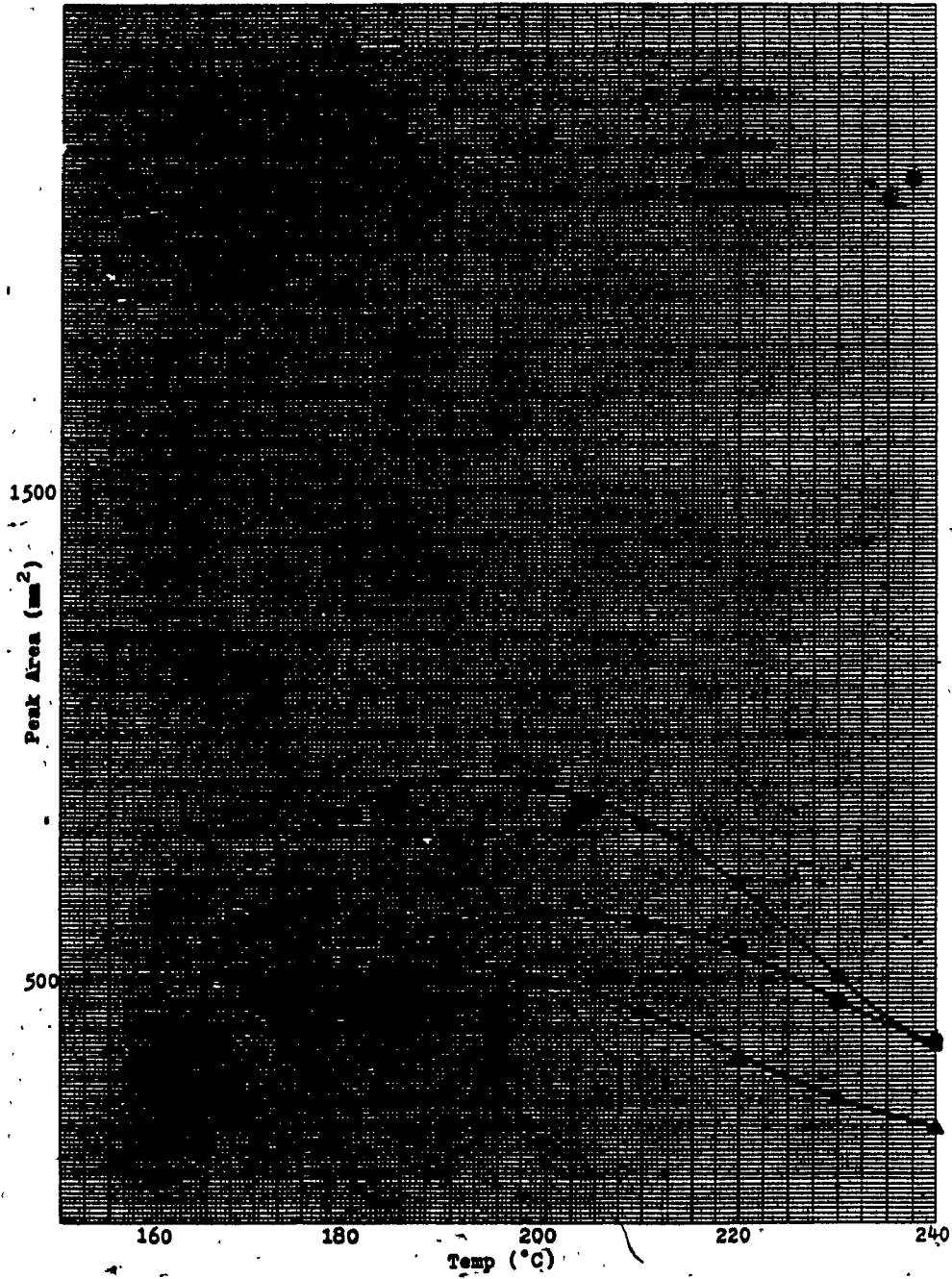


FIGURE 48. CG-NAW 1st Run (ECD)

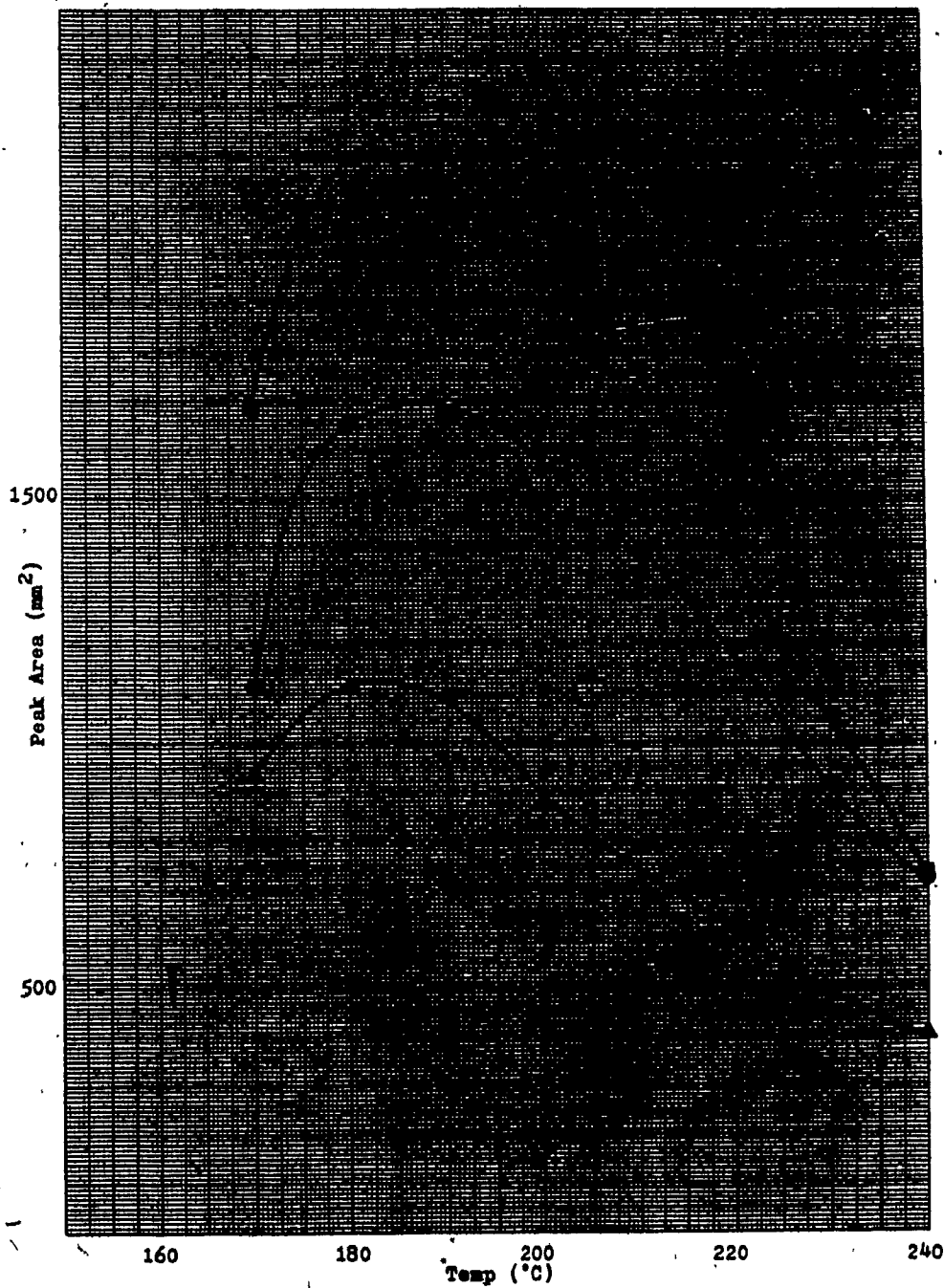


FIGURE 49. CG-AW 1st Run (ECD)

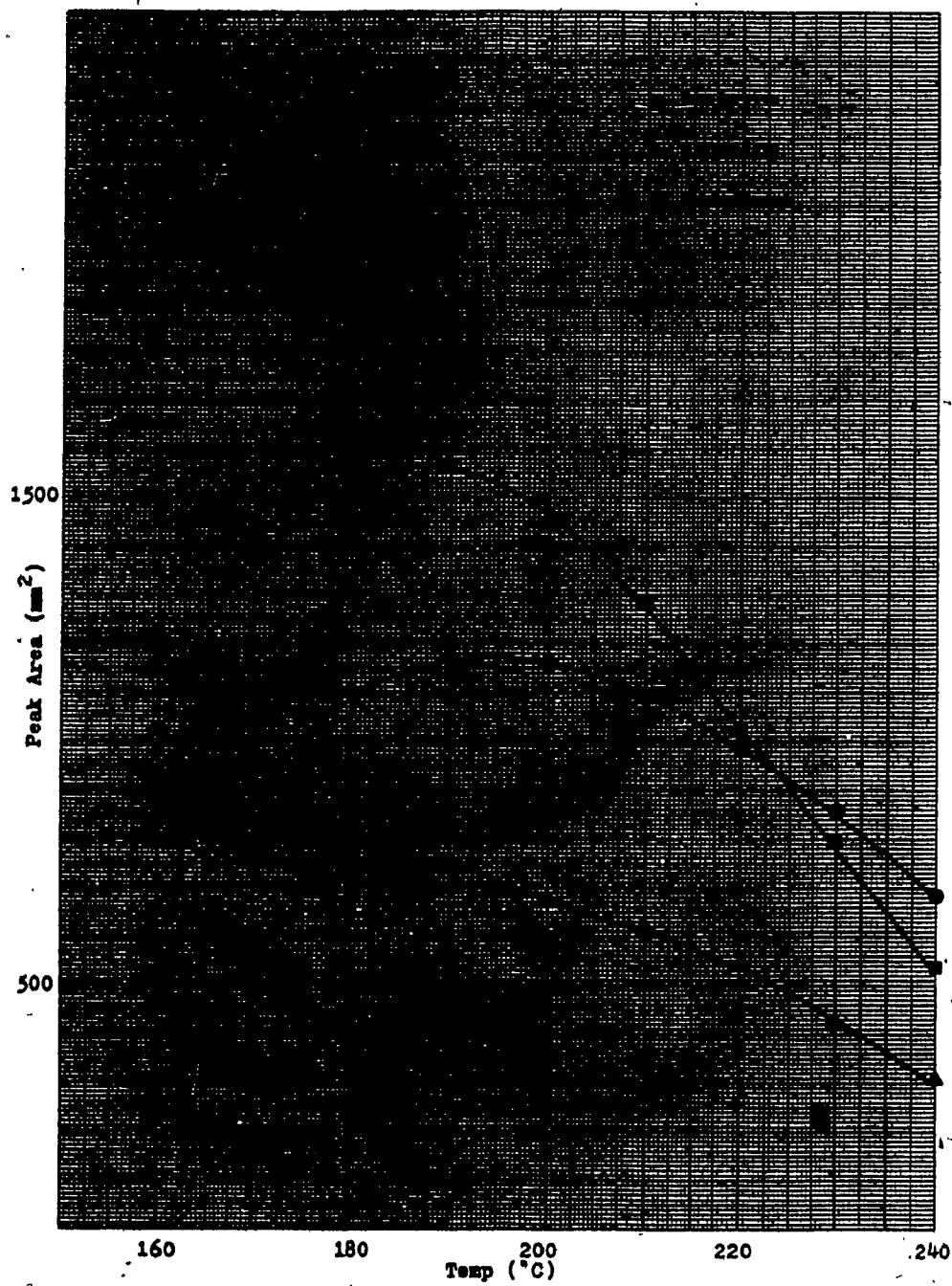


FIGURE 50. CG-AW-DMCS 1st Run (ECD)

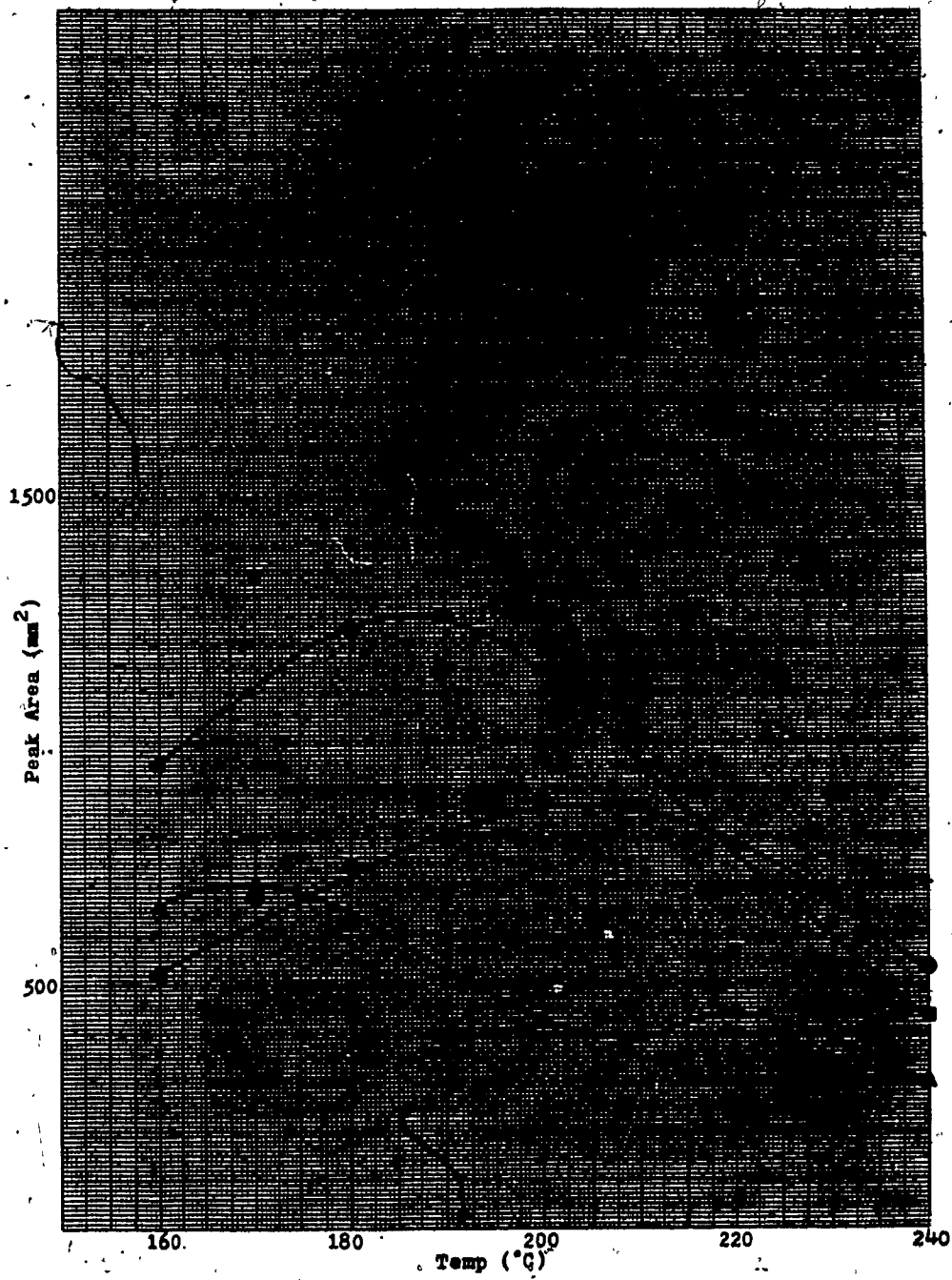


FIGURE 51. CG-HP

1st Run (ECD)

APPENDIX

IV

EFFECT OF A CONTAMINATED FID ON THE RESPONSE OF S-TRIAZINES

The importance of proper maintenance of the FID is illustrated in this section. A series of experiments were carried out with s-triazines on a CW-AW support column using the operating conditions as outlined in Table 8, immediately following the use of the GC instrument for the analysis of diethylthiocarbamates by another investigator. The detector had not been cleaned after its use for the diethyldithiocarbamate work. On performing FTG runs for the s-triazines, strange and rather unexpected response patterns were obtained (see Figs. 52, 53 and 54). On repeating these FTG runs, the same patterns resulted. It was then decided to do RTG's. The RTG's gave the same response profiles. This type of response was also observed with other supports, and could be attributed only to the detector. At this point the detector electrodes were cleaned with methylene chloride, the experiments repeated, and the drastically different FTG patterns shown in Figs. 52, 53 and 54 obtained. The assumption that this is a detector phenomenon was confirmed. This phenomenon is still unexplained, since the normal consequence of a contaminated FID is greatly decreased response. It is worthwhile reporting, because it was so unusual and unexpected.

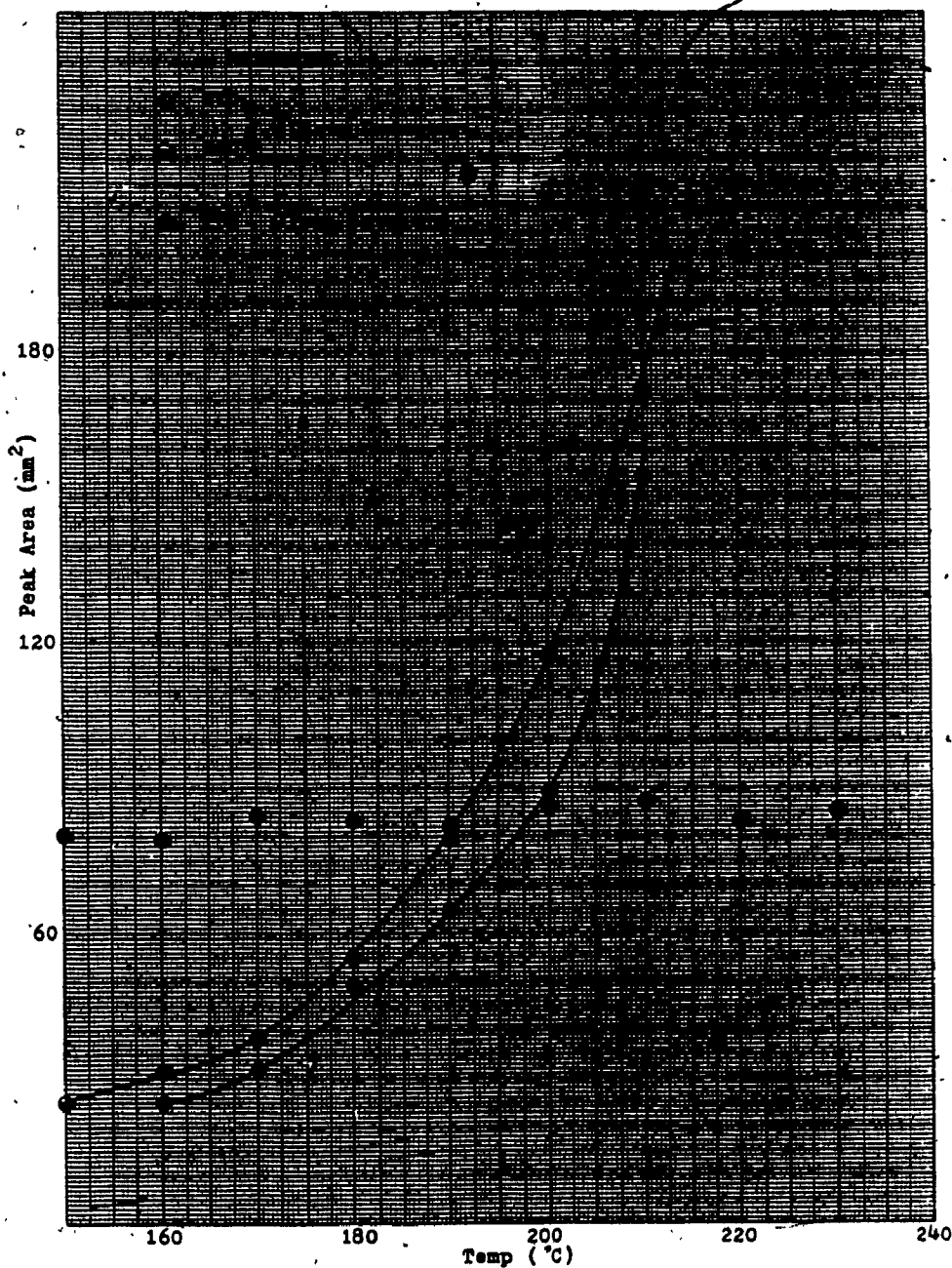


FIGURE 52. Thermograms of Prometone (1.3ug) on a CW-AW Support Column using a "Dirty" FID and a "Clean" FID.

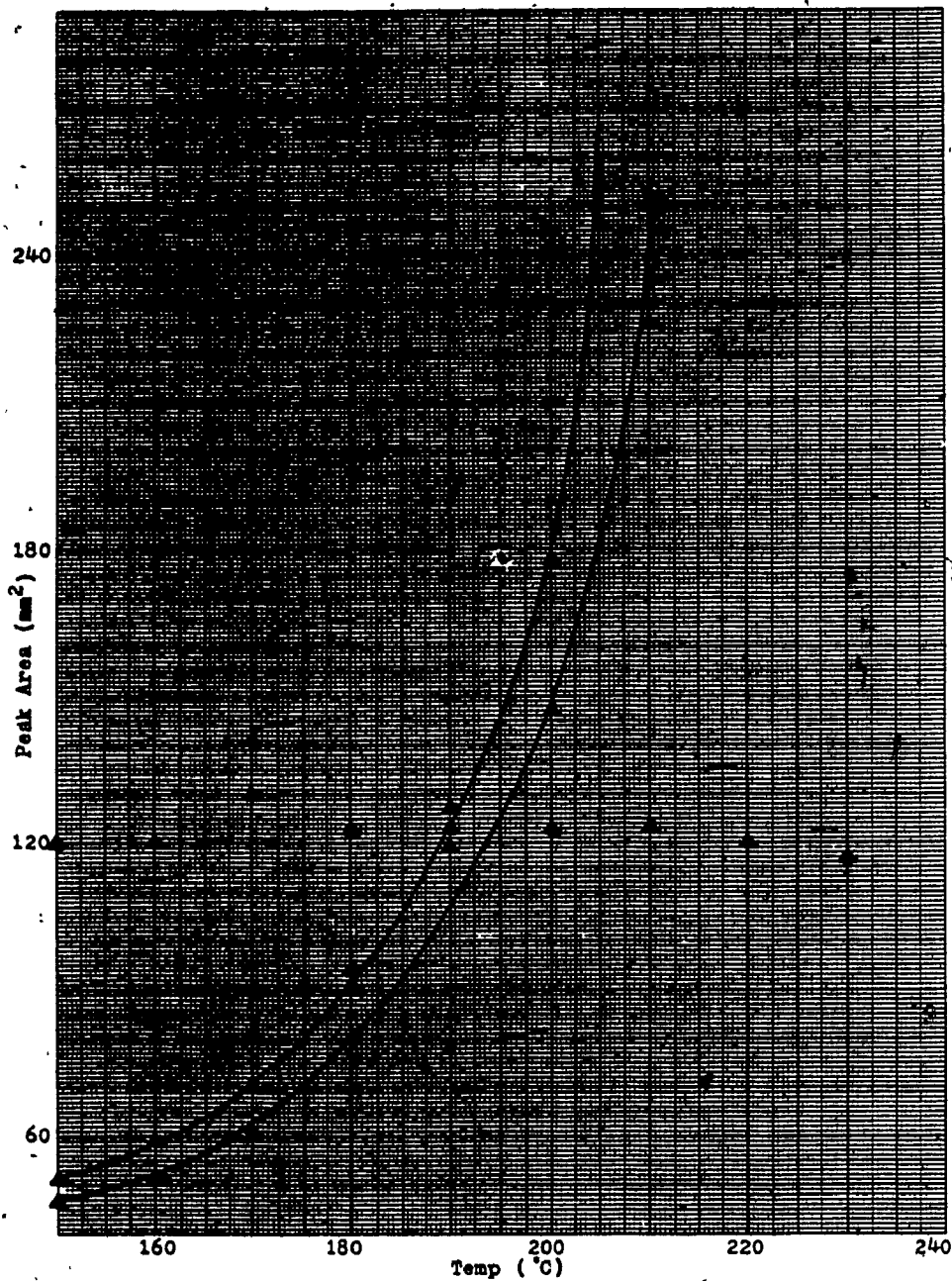


FIGURE 53. Thermograms of Atrazine (2.2ug) on a CW-AW Support Column using a "Dirty" FID and a "Clean" FID

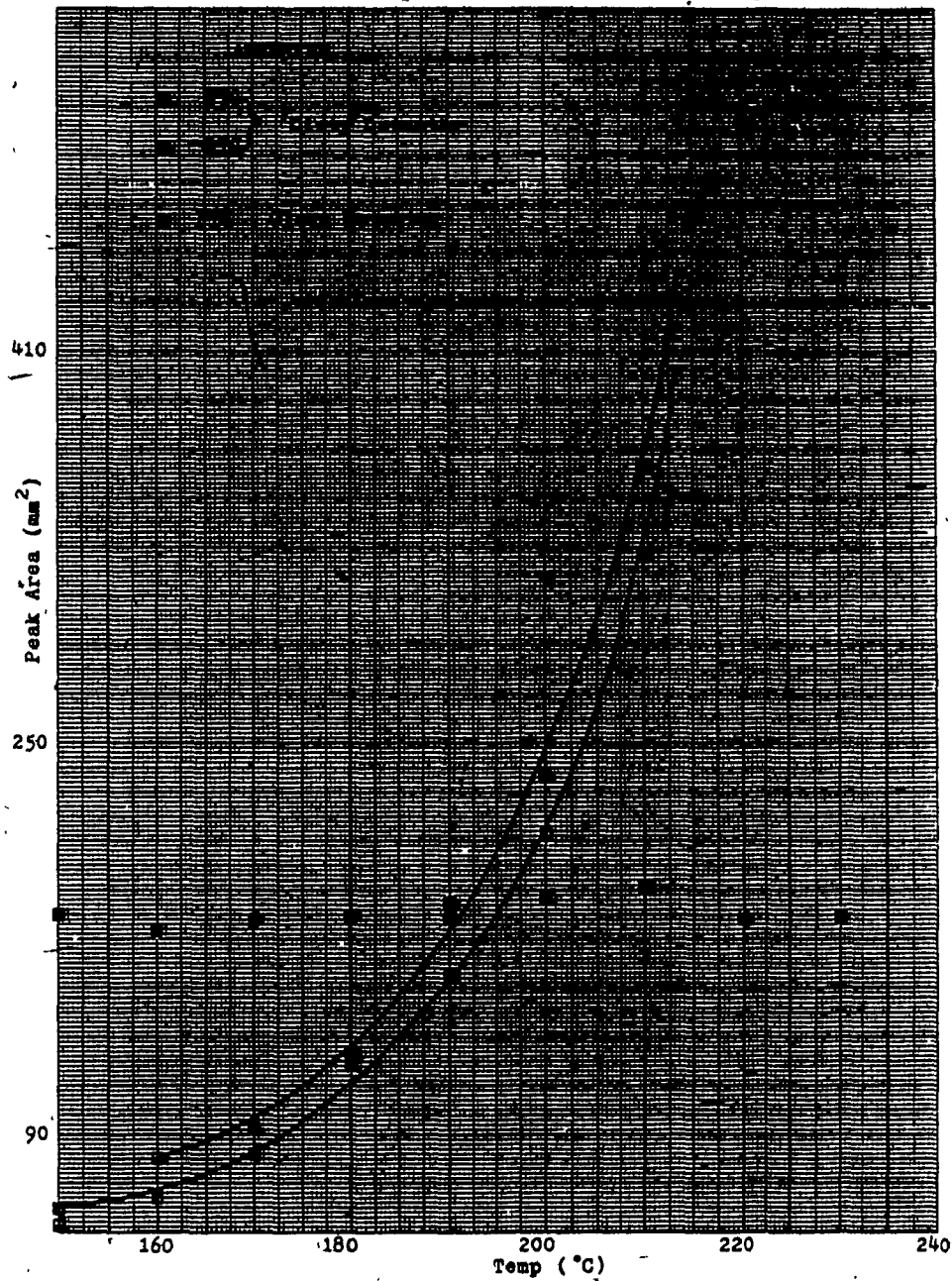


FIGURE 54. Thermograms of Ametryne (3.0ug) on a CW-AW Support Column using a "Dirty" FID and a "Clean" FID