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<u>THE ELECTRON CAPTURE DETECTOR:</u>

<u>SOME NEW MODES OF OPERATION</u>

by

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Submitted in partial fulfillment

of the requirements for the Degree of

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ABSTRACT

The influence of various operational parameters
on the response of an electron capture detector was
investigated. It is shown that under suitable conditions
an electron capture detector can be successfully employed
in temperature programmed gas chromatography.

Formation of products from electron capture
reactions has also been investigated. The effects of
various parameters on such products were studied in
detail. Possible use of these products and their product
patterns in confirmatory analysis of electron absorbing
compounds at trace levels is illustrated.

ABBREVIATIONS AND SYMBOLS

A	ampere
Ar^{o}	Argon (ground state)
Ar^{*}	Argon (excited)
atm	atmospheres
^{o} and ^{o}C	degrees centigrade
cm	centimetre
DC	direct current
E	change in energy
E_a	activation energy
ECD	electron capture detector
ED	electrolytic conductivity detector
e/m	peak area in faradays/mole analyte injected
eV	electron volt
fg	femtogram
FID	flame ionization detector
F/m	faraday/mole
FPD	flame photometric detector
g	gram
GC	gas chromatography
i.d.	inner diameter
IR	infrared
mg	milligram
min	minute

Abbreviations and Symbols continued

ml	millilitre
mm	millimetre
ms	millisecond
ug	microgram
ul	microlitre
us	microsecond
ng	nanogram
o.d.	outer diameter
pg	picogram
ppm	parts per million
TCD	thermal conductivity detector
TID	thermionic detector
UV	ultraviolet
V	volt

ACKNOWLEDGEMENT

INTRODUCTION, REVIEW OF LITERATURE AND THESIS OBJECTIVES

A. GENERAL INTRODUCTION

Since its introduction, in 1952, as a method of separation by James and Martin,[1] gas chromatography has grown into an analytical technique whose development and applicability have been unmatched. From a simple separation technique it has become a powerful analytical tool which surpasses most other techniques in terms of resolution, and compares favourably in terms of sensitivity.

Today gas chromatography as an analytical method includes separation, identification, and quantitative determination. In recent years it has often served as the method of choice in any field where analysis of a wide variety of organic or volatile inorganic compounds is required. It finds application in such diverse fields as organic chemistry, environmental studies, geochemistry, clinical analysis, petroleum and pharmaceutical industry, to name just a few.

The tremendous popularity of gas chromatography is a result in part of the rapid and continuous development of columns, detectors, and other instrumental hardware.[2-5] Columns capable of separating several hundred different components of complex mixtures, such as petroleum and biological fluids, have been developed;[6] however, without suitable means of detection, even the finest column resolution would be useless. Although classical spectroscopic techniques such as UV, IR, fluorescence and flame emission

have been employed for qualitative and quantitative determination of chromatographic effluents,[7-10] the union of gas chromatography and these techniques has proven to be quite cumbersome. This problem was soon realized by scientists involved in gas chromatography, and the period since the late fifties has seen the development and introduction of detection systems compatible with gas chromatography.

A gas chromatographic detector is essentially a transducer which generates an electrical (or in some special cases biological[10a]) signal which is indicative of the amount of analyte(s) present in the carrier gas.

Desired features of a gas chromatographic detector are full compatibility with the gas chromatographic system, high sensitivity, wide linearity, short response time, and in certain cases high selectivity.[11]

Compatibility with the gas chromatographic system implies that the detector should be insensitive to the flow of carrier gas and should have a small dead volume.

Sensitivity as expressed in terms of minimum detectable amount refers to the amount of analyte which gives a detector signal equal to twice the noise level.

Linear range of a detector is the range over which it exhibits a constant response for the unit amount of sample.

Response time is the time required by the detector to give a certain portion (usually 63%) of the final response.

Response of a detector is considered selective
if its response (relative molar response or response per
unit mass) to a particular class of compound is signifi-
cantly different from its response to others.[12]

Over 30 detectors have been developed for
analyzing the column effluents since the introduction of
gas chromatography.[13-14] Of these only six are commonly
used: thermal conductivity (TCD), flame ionization (FID), flame
photometric (FPD), thermionic (TID), electrolytic conduc-
tivity (ED), and electron capture detector (ECD). Even
though rugged universal detectors like the thermal conduc-
tivity (TCD) and flame ionization detector (FID) are most
commonly used in routine analysis, use of others has been
on the increase partly due to the complexity of the mix-
tures currently analyzed and partly due to the much higher
response of the selective detectors for certain classes of
compounds, especially the ones containing Cl, Br, I, P, S
and N.[15]

The present study deals with certain operational
and mechanistic aspects of one of these selective detec-
tors, namely the electron capture detector (ECD). Because
of its marked sensitivity toward certain compounds the use
of the ECD is widespread. It finds application in residue
analysis of agricultural chemicals, drugs, certain bio-
chemicals, microbial metabolites, and organometallic com-
pounds.[16-26] Numerous environmental controversies relating
to DDT, the PCBs, the freons and the chlorination of water

have arisen primarily due to the marked sensitivity of
the ECD to halogen compounds.[27-31]

Despite its widespread use, and extensive mech-
anistic studies by different groups, the ECD has barely
changed in its basic configuration since it was first
described by Lovelock.[32] It is essentially a simple ion
chamber with two electrodes and an internal ionization
source (see schematic of a commercial ECD on page 49).
In its basic form the ECD resembles other members of the
family of ionization detectors using nuclear radiation as
the source of ionizing species, which includes the ioniza-
tion cross section detector, electron mobility detector,
argon ionization detector, and helium ionization detector.[33-35]

Various detector configurations have been inves-
tigated, starting with the coaxial design which evolved
from the argon ionization detector.[36-39] Other common
configurations include the parallel plate (with two flat
electrodes of equal size), the concentric tube (with
cylindrical electrodes), and the pin-cup design (with a
cylindrical and a point electrode).[40-44]

Except for one, all commercially available ECDs
employ radioactive isotopes as ionization sources, the
exception being the one manufactured by Beckman Instru-
ments, Inc., Fullerton, California, which produces primary
electrons by rare gas discharge.[45] Generally, a β emitter
is used as the source of primary particles, because the

ion current obtained is higher than that from γ, and less noisy than the one obtained with α radiation.[46-48] Usually a metal impregnated with a radioactive isotope is either attached to, or itself serves as, the cathode.

Titanium tritide, scandium tritide, and gold foil plated with ^{63}Ni are the most commonly used sources of primary electrons; various other isotopes such as ^{85}Kr, ^{90}Sr, ^{99}Te, ^{147}Pm, and ^{241}Am have also been tried. The choice between ^{3}H and ^{63}Ni is usually determined by temperature requirement and cost. ^{3}H-Ti and ^{3}H-Sc, though better sources because of weaker (17.6-18.9 Kev compared to 67 Kev for ^{63}Ni)[49] but denser radiation, can be used safely up to 225° and 300° respectively,[50] while ^{63}Ni-Au can be safely used to 400°.[38] ^{147}Pm-Au foils have been reported to be as stable as ^{63}Ni-Au foils with comparable performance at a lower cost.[51]

B.   MECHANISM OF RESPONSE

The particles emitted by the radioactive source in the detector produce secondary electrons by collisional ionization of the carrier gas molecules. Commonly used carrier gases are N_2 and Ar-CH_4 (95%:5% respectively).

$$N_2 \xrightarrow{\beta} N_2^+ + e^- + energy \qquad \text{1}$$

$$N_2^+ + N_2 \longrightarrow N_4^+ \qquad \text{2}$$

$$Ar \xrightarrow{\beta} Ar^+ + e^- + energy \qquad \text{3}$$

$$Ar^\circ + e^- \xrightarrow{\text{applied potential}} Ar^* \qquad \text{4}$$

$$Ar^* + CH_4 \longrightarrow Ar^0 + e^- + CH_4^+ + energy \underline{\qquad} 5$$

$$p^+ + e^- \longrightarrow neutrals \underline{\qquad\qquad\qquad} 6$$
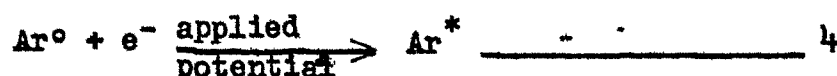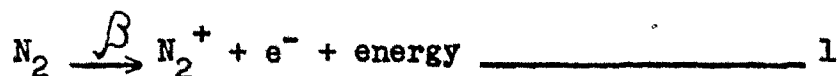
p^+ represents cations produced by collisional ionization (Eq. 1 and 3) and subsequent reactions (Eq. 2 and 5). With N_2 as the carrier gas the predominant species are believed to be N_2^+, N_4^+, and with Ar–CH_4, Ar^+, ArH^+, $ArCH^+$, $ArCH_2^+$, $ArCH_3^+$, $ArCH_4^+$, etc. Due to the presence of impurities in the carrier gas H^+, $H^+(H_2O)_n$, NO^+, NH_4^+, O_2^-, etc. are also often present.[52,53]

The ionization due to β radiation is confined to 2 mm from a ^3H source; for ^{63}Ni the β ionization region extends to 6–8 mm from the foil at ambient pressure (54–56). These figures, however, are not universally accepted.[57]

N_2 and Ar with 5% CH_4 are used as carrier gases. Pure argon readily gives metastables (with relatively long life times - of the order of 10^{-6} s),[58] which leads to undesirable ionization of solute molecules;[59] therefore, small amounts of CH_4 are added as a quench gas. Methane also helps to lower the energy of secondary electrons to thermal levels.[54,60]

Rapid lowering of energy of the secondary electrons is necessary to enhance the electron capture process. It has been reported that the "thermalization" of the secondary electrons produced by ionization of monoatomic or diatomic gases occurs in fractions of a microsecond in the presence

of n-hexane,[61] whereas in the absence of a quench gas it can take up to 50 ms.[54]

/ When a constant (DC) or intermittent (pulsed) potential is applied to the polarizing electrode, a background current (commonly referred to as the 'standing current' in EC literature) is obtained by collection of the thermal electrons.

When an electron capturing species AB enters the detector cell, the following reactions may occur:

$$AB + e^- \longrightarrow AB^{-} + energy \underline{\qquad\qquad} 7$$
$$AB + e^- \longrightarrow A^{\cdot} + B^{-} \pm energy \underline{\qquad} 8$$
$$AB + e^- \longrightarrow A^{-} + B^{\cdot} \pm energy \underline{\qquad} 9$$
$$AB^{-} + P^{+} \longrightarrow neutrals + energy \underline{\qquad} 10$$
$$B^{-} + P^{+} \longrightarrow neutrals + energy \underline{\qquad} 11$$
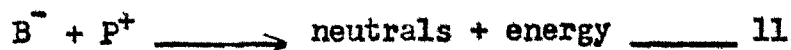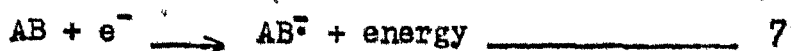
The solute molecule may absorb electrons (absorption, capture, and attachment are used interchangeably in the literature and likewise in this dissertation ; furthermore, the term electron capture in this text has no relation to the same term used in the nuclear chemistry) to form a radical anion (Eq. 7) or a radical and a negative ion (Eq. 8). The energy evolved in the first (nondissociative) reaction is thought to arise from the electron affinity of the molecule and is either liberated as radiation or shared with other molecules in collisions. In dissociative capture (Eq. 8), the absorption of a thermal electron leads to formation of a

radical and an anion. The net result in either case is substitution of an electron by a negative ion of greater mass. The detector signal is generated by a net decrease in the standing current, which occurs because of the much greater recombination rate of negative ion with positive ions. Recombination of ions occurs 10^5-10^8 times faster than the recombination of free electrons and positive ions.[62]

The kinetics of electron capture reactions have been studied extensively in pulsed mode by Wentworth and co-workers.[54,60,63-65] Using steady state approximation and assuming that, with Ar-10% methane and constant pulsed conditions (with a long pulse interval), the electron energy is close to thermal, Wentworth and coworkers have advanced four mechanisms for electron attachment processes, which occur principally in the field-free period.[63]

$$e^- + AB \longrightarrow AB^- \qquad \text{Mechanism I}$$

$$e^- + AB \longrightarrow A^\bullet + B^- \qquad \text{Mechanism II}$$

$$e^- + AB \longrightarrow AB^- \begin{cases} \longrightarrow A^\bullet + B^- & E_a > \Delta E \qquad \text{Mechanism III} \\ \longrightarrow A^- + B^\bullet & E_a = \Delta E \qquad \text{Mechanism IV} \end{cases}$$
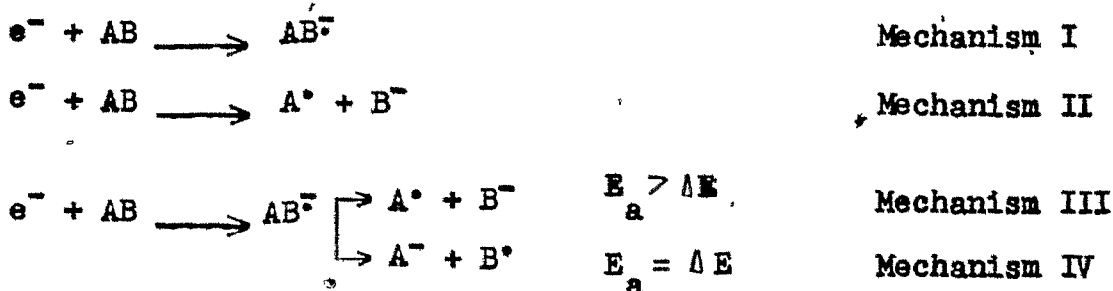
Mechanism I depicts a pure, nondissociative electron capture resulting in the formation of a radical anion. In such a case the total change in the internal energy is equal to the electron affinity of the solute molecule. Aromatic hydrocarbons and carbonyl compounds were reported to follow this mechanism.

Aliphatic halides (except fluorides) were
reported to follow Mechanism II, whereas aromatic chlorides, bromides, and iodides follow Mechanism III. Mechanisms III and IV assume the formation of an intermediate radical ion whereas Mechanism II leads straight to the dissociation of the parent molecule. It was reported that II and III can be differentiated on the basis of the observed activation energy and overall change in internal energy (bond dissociation energy minus electron affinity of the radical forming negative ion). The activation energy for III was reported to be lower than that for II.

Differentiation between III and IV is based on activation energy (E_a) and the overall change in energy (ΔE). In III, $E_a > \Delta E$ whereas in IV, $E_a = \Delta E$. Acetic anhydride, benzyl acetate and ethyl acetate were reported to give acetate ion according to Mechanism IV.[60] These mechanisms are based only on variations in response with changes in detector temperature and may not necessarily describe the exact kinetics of the electron capture process plus ensuing reactions.

In nondissociative reactions the cross-section for electron capture decreases with the increase in electron energy, which leads to a decrease in response with an increase in temperature. In dissociative capture reactions the energy required for dissociation of the molecule is greater than that released in its formation (an endothermic process); thus the probability of electron attachment (and

in turn response) increases with an increase in temperature.

C.   MOLECULAR STRUCTURE AND RESPONSE

For certain classes of compounds the ECD is by far the most sensitive detector available today. Considerable effort has been directed toward developing a general, empirical relationship between the structure of a given molecule and the magnitude of its response. Some of the rules developed so far are as follows.

In the case of halogen-containing compounds, response (commonly referred to in terms of the electron capture coefficient) is inversely proportional to the electronegativity and bond energy. Response decreases for the series I > Br > Cl > F (66). According to Lovelock and Gregory, the degree of electron attachment of an electrophore is independent of the nature of the hydrocarbon moiety; however, specific hydrocarbon and other structures adjacent to an electrophore may change the attachment coefficient. The absorption due to a halogen substituent is low when the latter is adjacent to an ethylenic double bond or to a benzene ring; by contrast this absorption is high when halogen is in an allylic or benzylic position and its increase exceeds direct proportionality to the number of halogens.[67]

The relative contribution of chloro, nitro, and amino substituents on aromatic rings and the influence of

the position of these substituents on the response of
an ECD have been studied by Zielinski and Fishbein.[68-70]
According to these authors the response increases with
increase in number of chlorine atoms. Response of dich-
lorobenzenes increases in the order p < o < m. Zielinski
et al. have also tried to correlate structure and response
of various pesticides by assigning response factors to
different structural components of the molecules.

Zitko and coworkers have studied the ECD response
of various chlorinated biphenyls.[71] According to these
authors the response increases with increase in chlorine
atom number. Response of decachlorobiphenyl was found to
be 500 times that of 4-chloro biphenyl. It was observed
that most of the increase occurred from mono to trichloro
biphenyl, and an increase by a factor of only 2-3 per chlorine
atom was reported from tetra to decachloro biphenyl.

In case of organophosphate pesticides with phosphate
and thiophosphate groups the response changes in the follow-
ing order.[72]

$$\underset{\displaystyle P - S}{\overset{\displaystyle S}{\|}} > \underset{\displaystyle P - S}{\overset{\displaystyle O}{\|}} > \underset{\displaystyle P - O}{\overset{\displaystyle S}{\|}} > \underset{\displaystyle P - O}{\overset{\displaystyle O}{\|}}$$

Dawson has observed that the response of alkyl
lead is affected by the chain length and the number of
hydrocarbon chains. Tetraethyl lead gives a response that
is ten times higher than the response of dimethyl diethyl
lead.[73]

Correlation between electron capture response and structure for divalent sulphur compounds has been reported by Satouchi and Kojima.[74] The electron affinities of disulphides with allyl and phenyl groups were found to be higher than those of aklyl disulphides; trisulphides gave values similar to the allyl and phenyl disulphides. Phenyl disulphides and trisulphides showed nondissociative capture while nondissociative and dissociative capture was observed at low and high temperatures for allyl disulphides.

In order to take advantage of the remarkable sensitivity of the ECD, derivatization techniques have been developed for compounds which normally do not respond in the ECD. This has opened a new area for study of extremely important compounds present in minute traces in biological fluids. A detailed review of the subject has been presented by Cummins.[75] Common practice has been to synthesize perfluoro alkyl derivatives to obtain greater sensitivity and volatility; however, Landowne and Lipsky have suggested that in the case of haloacetate the sensitivity was due to the carbonyl group.[76] This observation was supported in their detailed study by Martin and Rowland.[77]

A theoretical limit for the electron capture rate constant has been developed on the basis of collision-limited electron interaction. This limit was approached within a factor of two by some strongly electron-capturing compounds.[78]

Despite the efforts of many scientists, a comprehensive scheme to establish a relationship between response and structure of a compound has, as yet, not been derived. Efforts in this direction are hampered by the fact that the response factor changes significantly even with slight changes in operational parameters which are extremely difficult to control. This has led to large discrepancies in the published results.

Lovelock, in his recent paper on theory and practice of the ECD, has pointed out that the common error in calculation of response factors stems from failure to recognize the fact that the electron-molecule reaction is of second order. Small changes in either flow rate of carrier gas or ionization current can lead to significant change in the proportion of the molecules ionized, thus changing the detector response. This problem, according to him, can be overcome by operating the detector in the pseudo-first order region.[79]

D.   OPERATING PARAMETERS AND RESPONSE

Numerous problems and controversies in day-to-day operation and the ECD literature arise from the fact that even though the ECD appears to be a very simple device, there are many small variables which can change its performance significantly. Some of these variables are polarizing potential, detector temperature, and the nature and flow rate of the carrier gas.

Polarizing Potential

A polarizing potential is applied to collect the secondary electrons present in the detector chamber to obtain the 'standing current'. This potential can be constant (DC) or intermittent (pulsed). With an increasing DC potential, an increase in standing current is observed until a saturation current is obtained; from then on no further increase in current occurs up to a fairly high voltage. It has been observed that the maximum response occurs at a certain fraction of the full standing current, which may vary from 20-90% depending on detector geometry. In other words, the response increases with increase in standing current up to a certain point, after which it begins to fall again. This effect is observed because in DC mode the electrons are accelerated toward the anode resulting in a decrease in residence time of the electrons in the cell, which in turn affects the attachment process. Choice of DC potential is governed by detector geometry and compound type, as a result it is generally recommended that response profiles for various compounds should be checked.[80-82]

Lovelock in 1963 reported various effects which can grossly distort the results obtained from an ECD operating with a DC potential. These include space charges and contact potentials. Under normal conditions, the concentration of positive ions in the detector cell is several thousand times higher than the concentration of electrons, which gives rise

to a potential opposite to the applied potential and interferes with the collection of secondary electrons.[83,84]

According to various studies conducted by Lovelock an ECD does not work exclusively as an ECD in the DC mode; rather, results obtained may in part be due to its response as an ionization cross section detector, electron mobility detector and/or argon ionization detector.[83,85]

The pulsed mode of operation was introduced by Lovelock to overcome some of the problems associated with the DC mode. Because for all practical purposes the rate of formation of secondary electrons is constant, the electron concentration rises linearly with time until a potential pulse of sufficient width and amplitude drives the electrons to the anode. In practice, due to recombination and other processes, the electron concentration reaches a maximum value. Thus in pulsed ECD the standing current (the sum of current collected over a period of time) decreases with increase in pulse interval but average electron concentration increases. In other words, within certain limits the average electron population in the cell is proportional to the pulse interval and inversely proportional to frequency.[83]

It has been reported that for some strongly electron-capturing compounds response in the pulse mode is four times that in the DC mode;[86] however, for certain compounds whose capture cross section increases with an increase in electron energy, the response is greater in the DC mode.[87]

The pulsed mode operation is preferred by many researchers in physiocochemical studies of the detector, but the DC mode is more commonly used in routine analysis, because satisfactory operation in pulsed mode requires a much cleaner system.[88]

Detector Temperature

Detector temperature is the operational parameter most stressed in the literature. The choice of detector temperature is governed by two factors: the first is the chromatographic requirement (which depends upon the temperature at which the solute elutes through the column with no decomposition) - this sets the lower limit for detector temperature; the second is the maximum temperature authorized for the radioactive source, which sets the upper limit.

The kinetic studies of Wentworth and coworkers have shown that, depending upon the capture mechanism, an increase in temperature may lead to an increase or decrease in electron capture coefficient. As a result, the response of certain substances can vary as much as 5000-fold within common gas chromatographic temperature limits. According to Wentworth and Chen, for 1.0% precision in results the detector cell temperature should be controlled to within $\pm 0.3°$.[63]

Zlatkis and Pettit have studied the effect of detector temperature on the EC response of various derivatives of various alcohols and amines and observed that the

response can vary by a factor of 5 depending upon the temperature of the detector.[89,90]

During their study of operational parameters, Devaux and Guiochon observed a large increase in the 'standing current' with an increase in temperature;[91,92] however, only slight or no increase in standing current with an increase in temperature was observed by Simmonds et al.[93]

Carrier Gas Flow Rate and Pressure

The most controversial parameter is perhaps the carrier gas flow rate. Effects of flow rate have been studied in detail by Devaux and Guiochon.[91,92,94] On the basis of their extensive studies they concluded that, although the electron capture detector is a concentration-sensitive detector (according to Halasz's classification[95]), its response is dependent on the flow rate in an even more complex manner. It was recommended that the flow rate through the detector should be optimized in terms of standing current and response, and should be held constant with a scavenger flow. The effect of flow rate on the 'standing current' has been disputed by van de Wiel and Tommasen.[96] Their studies have revealed that the effect observed by Guiochon and Devaux is mainly due to the electron capturing impurities (oxygen, etc.) in the carrier gas.

The only study relating to the effect of pressure on the ECD has been conducted by Scolnick.[97] In that study Scolnick observed that the 'standing current' increases

with an increase in pressure; however, the effect of
pressure on response was not studied.

E. SOME IMPORTANT DEVELOPMENTS

Even though the electron capture detector has
changed little in its basic configuration, some noteworthy
improvements in its operation, and mechanistic understanding,
have been made, which need to be mentioned separately.

Wentworth Correction

For a reasonable calibration the peak (observed as
a reduction in the standing current) should be considerably
smaller than the standing current. Under normal operation,
the linear range is not much larger than 10-20% of the
standing current and the response is linear over two decades
only.

Lovelock in his early papers proposed that capture
of electrons bears resemblance to the adsorption of light
and thus Beer's law should be applicable to electron capture
response.[98,99]

$$I = I_o^{-Ecx}$$

where I_o = the initial standing current

I = cell current

c = concentration of the solute

E = electron capture coefficient of the solute

x = constant related to cell volume

19

However, application of this expression did
not improve the linearity of response appreciably.

From the kinetic studies of the electron capture
process, in pulsed mode, Wentworth and coworkers derived
the following expression.[54,63]

$$\frac{I_o - I_c}{I_c} = ka \text{ , wherein}$$

$$I_o - I_c = R \quad \text{and}$$

$$\frac{R}{I_c} = ka \quad ; \text{ thus}$$

$$\frac{R}{I_c} \propto a$$

where K   = capture coefficient of the capturing species

a   = concentration of the capturing species

R   = response

I_o = initial cell current

I_c = cell current after introduction of the
capturing species

Thus the response measured relative to cell current
is proportional to the solute concentration.

Fennimore et al. constructed an analogue device
which expressed the response relative to the cell current.
It was reported that under suitable conditions (long pulse

period of 1000-2000 us and with weakly capturing species)
response was linear to as high as 98% of the detector
saturation current, giving a linear dynamic range of
1×10^5. [100,101]

The Constant Current System

The use of Wentworth's correction gave the ECD a
linear range somewhat comparable to that of the other GC
detectors; however, the long pulse interval required for
satisfactory operation of the system put extremely stringent
condition on the cleanliness of the detector, which could
not be easily met in normal day-to-day operation. Another
approach for obtaining a linear response was adopted by
Maggs et al. [102]

In regular pulsed operation the pulse characteris-
tics (pulse width, interval and amplitude) are held constant.
The detector signal is observed as a reduction in the result-
ing standing current. In the system developed by Maggs et al.,
the signal is obtained as a change in frequency at a constant
current. The basis of this system lies in the fact that the
electron concentration in the cell is inversely proportional
to the pulsing frequency and since both electron input
(which depends only on the strength of radioactive source)
and output (which is regulated by the cell current held at
a constant level) are constant, the remaining electrons must
be removed by solute molecules and by the small, constant
contribution of the carrier gas cations.

Thus $\quad [e^-][\text{solute}] = \text{constant}$

and $\quad [e^-] \propto \frac{1}{f}$

therefore $\quad$ solute $\propto$ f

where f is the pulse frequency and $[e^-]$ is the concentration of free secondary electrons in the cell.

The linear range for such a system was reported to be 5×10^4.

Under certain conditions (high intensity radio-active source, intensely electron capturing substances and slow flow rates) the constant current system has been observed to give nonlinear response at the lower end of the calibration curve, leading to an S-shaped curve. Sullivan and Burgett developed a kinetic model and showed that the non-linearity occurs because of a high degree of ionization of the solute molecules (up to 90%) in small concentrations.[103] This effect can be overcome, to a degree, by using a high flow rate.

The ECD as a Gas Phase Coulometer

Gas phase coulometry using the ECD was described by Lovelock et al. in 1971.[104] It was pointed out that if the peak area (detector signal) is measured in electron moles (Faradays) and the injected amount is measured in moles, the F/M ratio reflects the electron/molecule ratio, and when this ratio approaches 1, the ECD functions as a gas-phase coulometer in which all substances with large enough electron affinity yield the same molar response. Under these condi-

tions the ECD functions as a mass-sensitive (actually mole-sensitive) device whose response is independent of temperature and carrier gas flow rate. In recent studies such an ECD has been used for absolute determination of strongly electron capturing species.[105,106]

The Effect of Oxygen and Water

The effect that the presence of oxygen and water, in the carrier gas, exerts on the response of an ECD has been studied by a number of research groups. Considerable information has been obtained about the ions present in plasma chromatography and atmospheric pressure ionization mass spectrometry under conditions somewhat similar to those in the ECD, by Karasek and coworkers and Horning and coworkers respectively.[52,109] The presence of oxygen influences the availability of free electrons to the electron capturing species. Oxygen reacts with free electrons to form ion-molecule complexes of the form $(H_2O)_n\ O_2^-$.[107] It has been reported that the electron capture coefficient of oxygen is temperature dependent, high at low temperatures and low at high temperatures. The situation is complicated by the recent finding of Horning et al. that O_2^- may be involved in exchange mechanisms with halides of the solute molecules.[108]

In a comprehensive paper concerning the effect of oxygen on the electron capture detector, van de Wiel and Tommassen showed that the controversies involving the effect of temperature and flow rate on standing current and response

were caused by different levels of contaminants (primarily oxygen) in the carrier gases used by different research groups. They pointed out that in a pure (i.e. free of oxygen and other electron absorbing species) system, the electron concentration is virtually independent of temperature and carrier gas flow rate. With oxygen present the electron concentration decreases and since oxygen is involved in charge transfer, its presence may lead to an increase in response with an increase in temperature.

F.   SOME RECENT DEVELOPMENTS

During the past year some notable developments in electron capture detection have arisen. One such development resulted in the use of the electron capture detector with liquid chromatography. In the system developed by Willmott and Dolphin,[110] the column effluent is completely vaporized and led into the electron capture cell, which is constantly swept by 30 ml/min of N_2. A minimum detectable limit of $< 10^{-10}$ g for Aldrin and a linear range of ~ 500 were obtained.

In order to eliminate the disadvantages associated with the use of radioactive foils (easy contamination, temperature limitation, reactions occurring on metallic foils and licensing requirements) an electron capture detector, which uses photoionization to produce thermal electrons (lyman- α resonance line of hydrogen with triethylamine)

has been developed by Wentworth et al. The detector
was operated in the DC mode and a sensitivity of 50 pg
for carbon tetrachloride was obtained. [111]

Another important development has been reported by
Lovelock, a coulometric ECD which destroyed strongly
electron capturing compounds was used as a 'solute switch'
for obtaining better signal:noise ratio by coherent switching
and synchronous demodulation. An improvement by a factor of
10 in signal:noise ratio was obtained. [112]

G.   THESIS OBJECTIVES

The brief review of literature presented above
shows that considerable progress has been made in under-
standing the ECD; however, a quick look at the problems
associated with its operation reveals that the detector
is far from being domesticated. Detailed studies of
Wentworth and collaborators have indicated various reactions
occurring or supposedly occurring inside the ECD. The
occurrence of these reactions has been deduced from the
data obtained under various experimental conditions; how-
ever, no direct evidence of intermediates or products
originating from electron capture reactions under true ECD
conditions is available. In a corona discharge, with
solutes at high concentrations, electron initiated chain
reactions lead to a variety of products, some typically of
higher molecular weight than the starting material. Products
obtained from chlorobenzene included such compounds as

biphenyl, o-chlorobiphenyl, m-chlorobiphenyl, and p-chlorobiphenyl.[113] Such condensation products can be ruled out under true ECD conditions simply on the basis of collision frequencies. One would expect substances of lower molecular weight, if any, but no such information is available and, furthermore, few data are available on the effect of such parameters as voltage, temperature, carrier gas, flow rate, and pressure on electron capture reactions, and the contribution made by intermediates and products in terms of EC response. A study of these parameters in relation to response and electron capture reactions leading to neutral products form the bulk of this dissertation. Need of such information arises for a variety of reasons:

First, the elegant technique of coulometric EC with two detectors in series[104] calls for compounds whose reaction products have little or no EC response. When 'absolute' calculations are attempted,[106,114] an ultimate ratio (most likely 1:1) between the capturing molecules and the capture electrons needs to be assumed; and electron absorbing products should again be absent.

Second, the calculation of molecular electron affinities from electron capture response,[115] and the calculation of ultimate detection limits,[115a] may be influenced by strongly electron-capturing reaction products. The coulometric response has been generally assumed to represent a natural

limit for the electron capture process; greater than coulometric response has been postulated for compounds which give electron-capturing products.[104]

Finally, from an analytical point of view, it was interesting to consider the possibility of using product(s) as a means of identification of the parent compound.

This study was therefore designed for investigating whether neutral products are formed in an ECD, and if so, for observing the effect of various parameters, e.g. applied potential, concentration of solute molecules, pressure and flow rate of carrier gas, cell temperature, and presence of other reacting species, on the formation of these products and in some cases, on the response of the detector. During the course of the study some other interesting observations were made and a part of this work deals with those observations and their implications.

EXPERIMENTAL

A.   APPARATUS

The major portion of this study was conducted
using a benchtop gas chromatograph (Tracor, Model 550)
equipped with two ^{63}Ni electron capture detectors and a
dual channel electrometer. The initial part of the
study, however, was conducted with a Microtek 220 gas
chromatograph equipped with an electron capture detector
and two flame ionization detectors (at the University of
Missouri, Columbia). The polarization potential was ob-
tained from a DC/pulse power supply provided with the gas
chromatograph and a Keithley 0 to $\pm$1200 V power supply
(Model 240A). During the course of study many different
models of strip chart recorders were used.

Nitrogen carrier gas (at U.M.C.) was obtained by
flash-off from a 5000-litre liquid nitrogen tank. This
nitrogen was guaranteed to contain less than 3 ppm oxygen.
For most experiments performed at Dalhousie University
prepurified N_2 (Linde Specialty Gases), containing less
than 5 ppm of oxygen and 5 ppm of water, was used as the
carrier gas. Before entering the chromatograph the carrier
gas was passed through a molecular sieve, an activated
charcoal filter, and a commercial trap (Supelco Carrier Gas
Purifier, Supelco Inc.) to remove oxygen and water. The
flow rate of the carrier gas was regulated by fine metering
valves (Nupro Valves, Model 2SG2).

B.   REAGENTS AND CHROMATOGRAPHIC MATERIALS

A number of halogenated pesticides and other electron capturing compounds of interest were obtained from various chemical supply companies, e.g. Fisher Scientific Co., Dartmouth, N.S., Aldrich Chemical Company, Milwaukee, Wis., U.S.A., New Laboratory Supplies, West Chester, Pa., U.S.A., K & K Laboratories Inc., Plainview, N.Y., U.S.A., and Pfaltz & Bauer Chemicals, Flushing, N.Y., U.S.A.

All organic solvents (hexane, benzene, acetone, methanol and cyclohexane) were of Fisher pesticide grade or equivalent quality. In certain cases, these solvents were distilled in an all-glass still with Clearfit joints (Aldrich Chemical Co.).

Chromatographic materials such as Chromosorb W, silanized glass wool, silicone rubber septums, O-rings and various liquid phases (OV-101, OV-17, SE-30 and Carbowax 20M) were purchased from Chromatographic Supplies Ltd., Brockville, Ont.

Radioactive foils, ^{3}H-Sc and ^{63}Ni, were obtained from United States Radium Corporation, Bloomsburg, Penn., U.S.A., and New England Nuclear Co., New Haven, Conn., U.S.A., respectively.

Column packings were made either by simple coating in a rotary evaporator or by a technique described by Aue et al. for preparation of modified supports.[116]

C.   THE PRELIMINARY SET-UP FOR OBSERVATION OF PRODUCTS

The initial experiments for observation of electron capture products were carried out using a series configuration, such that the components of the effluent from the first detector were separated in the second column before being detected by a second detector. The arrangement used is shown schematically in Figure 1.

The whole system was made gas-tight.   The detectors were made leak-tight by careful grinding of the adjoining surfaces of the top, middle and bottom parts. The tightness of the system was periodically checked by closing a valve located at the end of the flow path and watching the ball of the rotameter drop to zero. This was the only purpose for having a rotameter in the system, since flow measurements were done by bubble flow meter at the exit line of the second detector.

Detector 1 was used in a variety of configurations; e.g. carrier entering from the top or bottom, and positive or negative potential being applied to either the top or bottom electrode with the other serving as the collector.

D.   PRESSURE STUDIES

In order to study the effect of pressure on the response of an EC detector, a very fine metering valve was put at the exit line of the detector and a 1/16" union tee was introduced between the column and the detector, one end of the tee joint being connected to a pressure gauge.

Figure 1

Arrangement of chromatographic columns
and detectors

Col. 1   First column

Col. 2   Second column

EC-1   First EC detector

EC-2   Second EC detector

▽   Fine metering valve
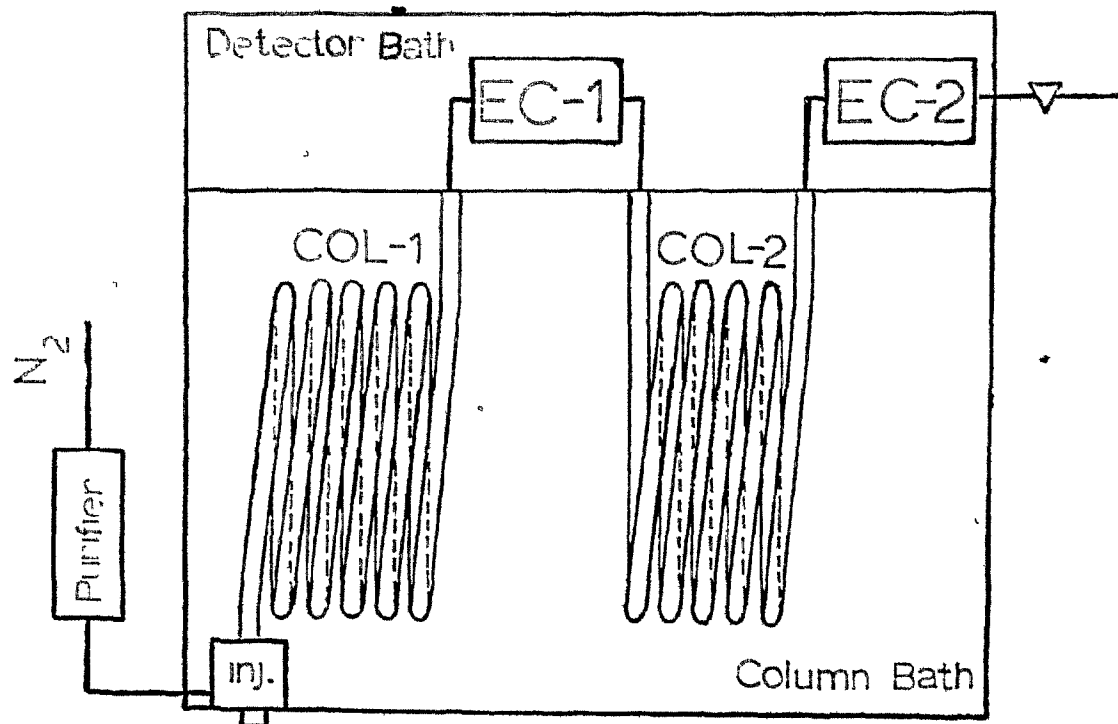
Pressure inside the detector cell was varied by manipulating both the inlet pressure and inlet and exit valves, while maintaining the same total flow, measured at ambient pressure.

Column effluent was introduced from the bottom of the detector, which was polarized with DC or pulsed potential.

Prepurified Nitrogen was used as the carrier gas. Total flow at the exit was 40 ml/min.

E.   ADDITION OF VARIOUS REACTANTS TO THE CARRIER GAS

To observe the effect of various additives on products and product patterns, different additives representing a variety of chemical structures were introduced into the carrier gas stream. The additives used included: hydrogen, carbon dioxide, carbon monoxide, ammonia, water, methane, pentane, hexane, heptane, iso-octane, 2-pentene, methanol and acetonitrile.

The gaseous reactants were added to the carrier gas stream directly before it entered the injection port. The flow of these reactants was controlled by a very fine metering valve with a numerical counter (Matheson Model No. 6800-1006).

The liquid additives were incorporated by making the carrier gas flow through a stainless steel reservoir containing the additive. The amount added was varied by changing the relative amount of carrier gas flowing through

32

Figure 2

Flow system used for addition of various reactants

C.G.	Carrier gas line
A_1	Additive line 1
A_2	Additive line 2
Add. Reser.	Liquid additive reservoir
P_1	Purge line for detector 2
P_2	Purge line for detector 1
▽	Fine metering valve
▼	'on'/'off' valve
I.P.	Injection port

A₂

C.G.

A₁

Rotameter

O₂ Trap

Add Reser.

To I.P

P₂

P₁
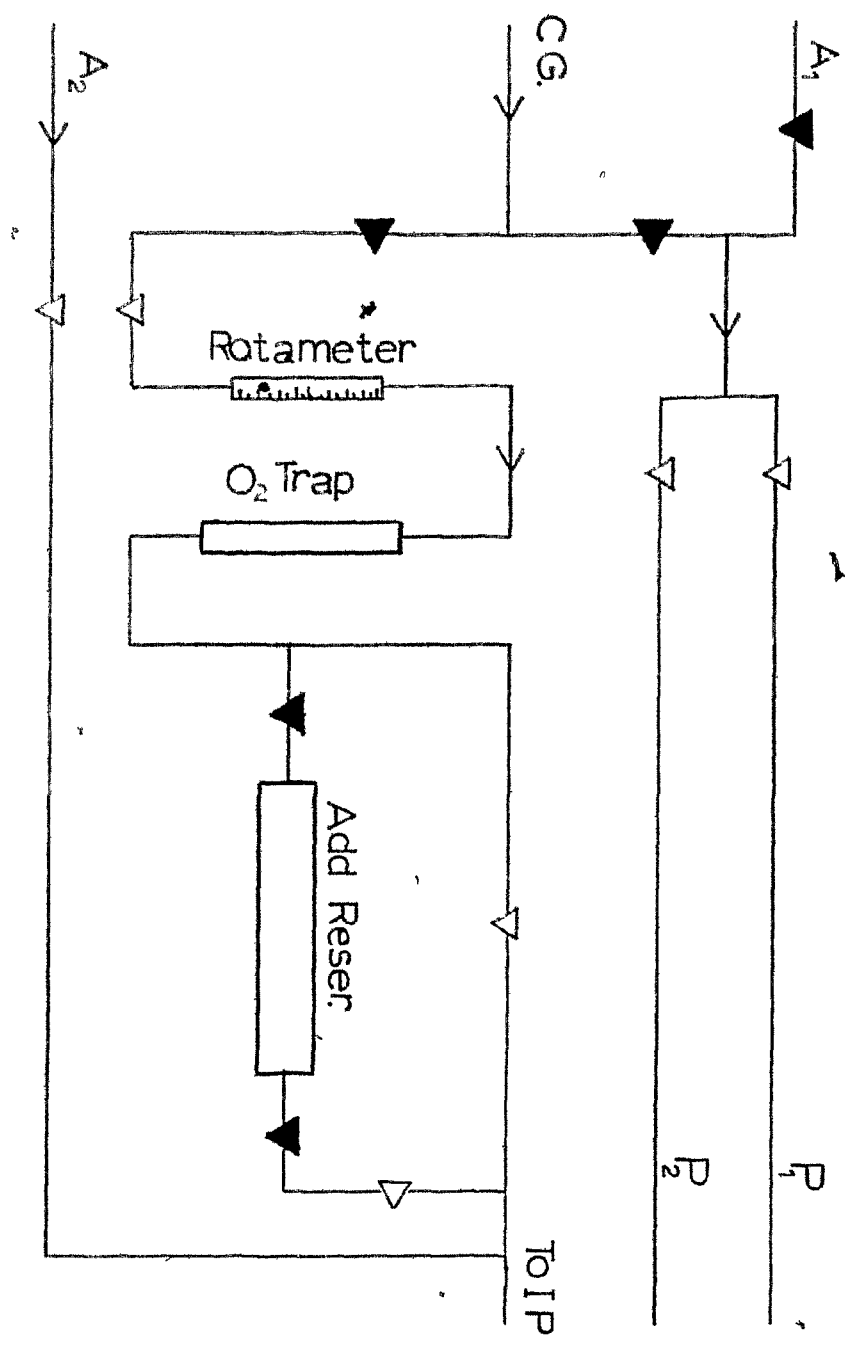
the reservoir and bypass, as shown in Figure 2.

F.   USE OF DIFFERENT CARRIER GASES

In order to observe the effect of different carrier gases on product formation in the EC detector, prepurified helium and argon (in addition to nitrogen), alone and with additives, were used as carrier gases. The same flow systems described earlier for the additives were employed in these experiments.

G.   HIGH RESOLUTION SET-UP

The valve bath provided with the instrument (Tracor 550) was modified into a column bath so that the two columns could be operated at different temperatures. A reactor/detector with a small dead volume was constructed. In order to facilitate the turn 'on'/turn 'off' of the EC reaction, the reactor/detector was made in modified coaxial configuration. Figure 3 shows the schematic of this reactor/detector.

A Tracor ^{63}Ni electron capture detector was used as the second detector. The second column was operated at considerably lower temperature to facilitate the separation of light EC products. Figure 4 depicts the schematic of the whole chromatographic system.

Figure 3

Schematic of EC reactor/detector

a	Anode
b	Quartz tee
c	Detector heating block
d	Cathode
e	Teflon insulation
f	^{63}Ni foil
g	¼" Swagelok union
h	¼" Quartz tube

a

b

c

d

e

f

g

h
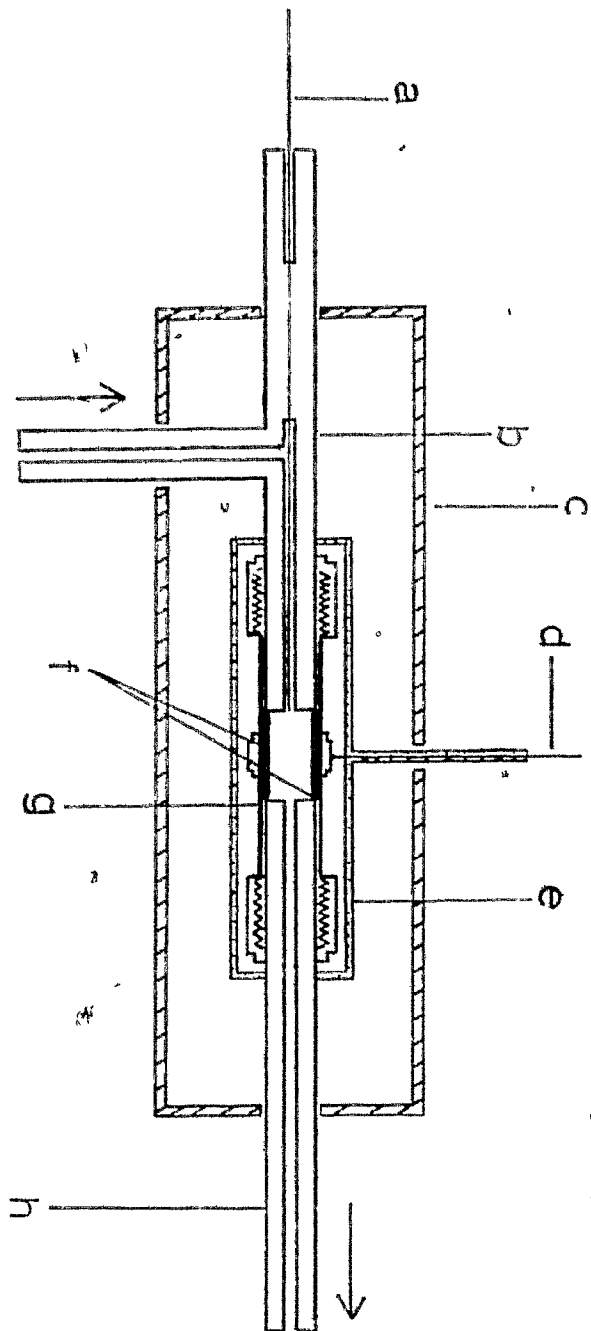
Figure 4

Schematic of the high resolution set-up

I.P.	Injection port
C_1	Column bath 1
C_2	Column bath 2
D_1	EC reactor/detector
D_2	Tracor ^{63}Ni detector
$\triangledown$	Fine metering valve
P_1	Purge line for detector 2
P_2	Purge line for detector 1
T	Heated transfer conduit

N₂

P₂

P₁

P

C₁

T

D₁

L

D₂

C₂
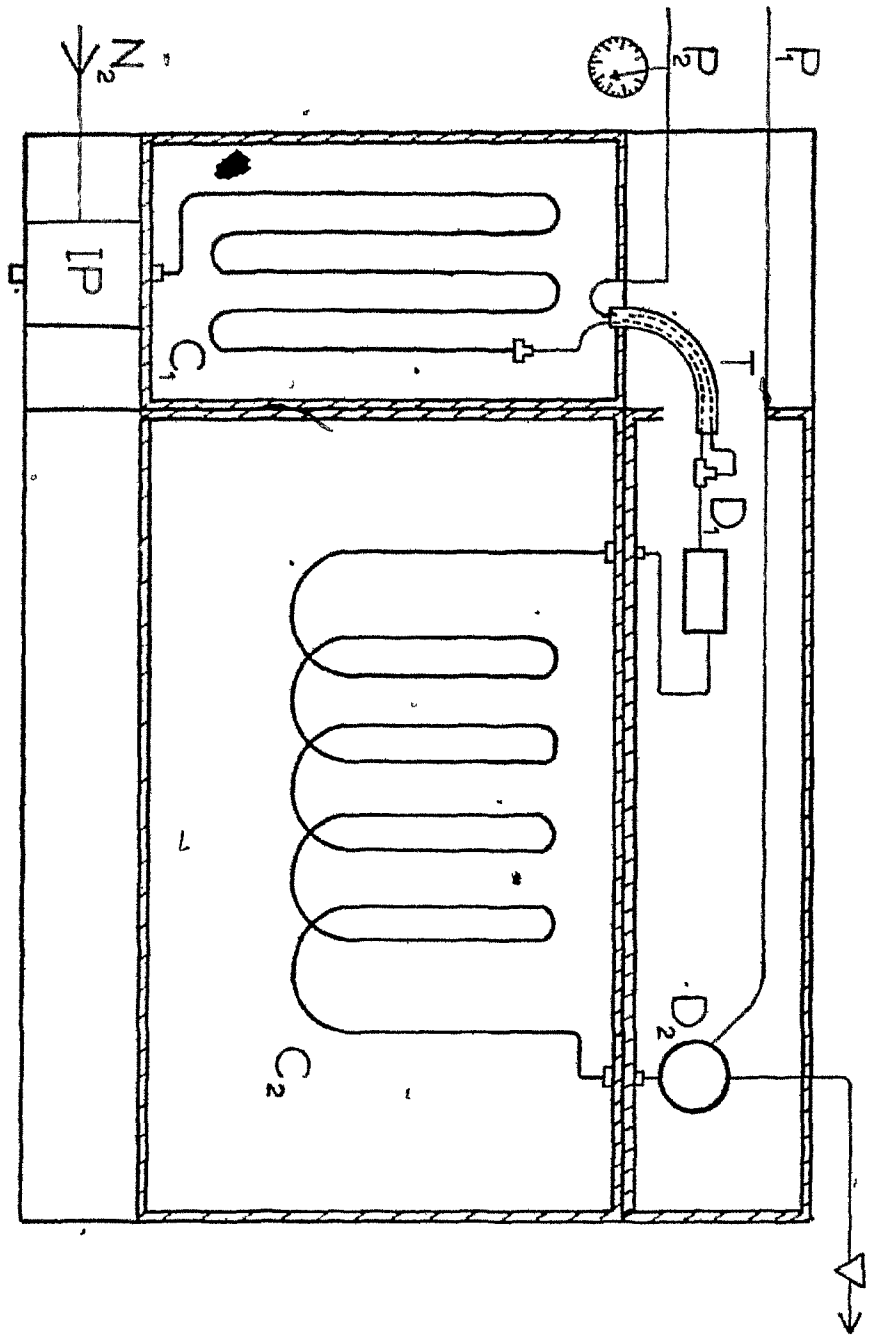
RESULTS AND DISCUSSION

A.   STANDING CURRENT AND RESPONSE

In routine analysis, the efficiency of an ECD is generally thought to be dependent upon the magnitude of the 'standing current' and periodic checks of voltage or pulse width profiles are made to get a measure of its performance. These checks, though a good measure to ascertain the cleanliness of the detector, tend to obscure the fact that the magnitude of the standing current has little relation to the actual concentration of the electrons in the cell and the response of the device.

Since, for a particular carrier gas and radioactive source, the rate of formation of the free electrons is constant, in pulsed mode the electron concentration in the cell should increase with increase in pulse interval until an equilibrium (due to recombination and other processes) is reached. However, the standing current, i.e. the sum of the electrons collected over a period of time, decreases with an increase in pulse interval. Figure 5 depicts this effect of pulse period on electron concentration in the detector cell.

It can be assumed that within certain limits the electron concentration in the cell is proportional to the increase in pulse interval and, since the electron capture process is dependent on the concentration of the electrons

in the cell, the response especially of a weak absorber
should be proportional to the pulse interval. This is
illustrated in Figure 6, which shows that even though the
standing current drops, the response of chlorobenzene (a
weak absorber) increases proportionally with the increase
in pulse interval.

B.   COULOMETRIC OPERATION

In 1971 Lovelock and coworkers reported that for
intensely electron absorbing solutes, under suitable con-
ditions, i.e. high electron concentration and low solute
concentration, an electron capture detector can be operated
as a gas phase coulometer in which 90% or more of the
solute is ionized. Under these conditions all strongly
electron absorbing molecules would be expected to give
equal molar response. Figure 7 shows the calibration curve
of five pesticides; lindane, heptachlor, heptachlor epoxide,
dieldrin and p,p'-DDT. A ratio close to 1:1 was obtained
for peak area (in Faradays) and the injected amount (in
moles) for all compounds except DDT. The F/M ratio for DDT
was significantly off, presumably due to the decomposition
in column and transfer lines.

A coulometric ECD is a mass sensitive device, whose
response would be largely independent of the temperature and
changes in flow rates. Such independence is shown in Figure
8 which shows two chromatograms obtained for two nanograms of

38

Figure 5

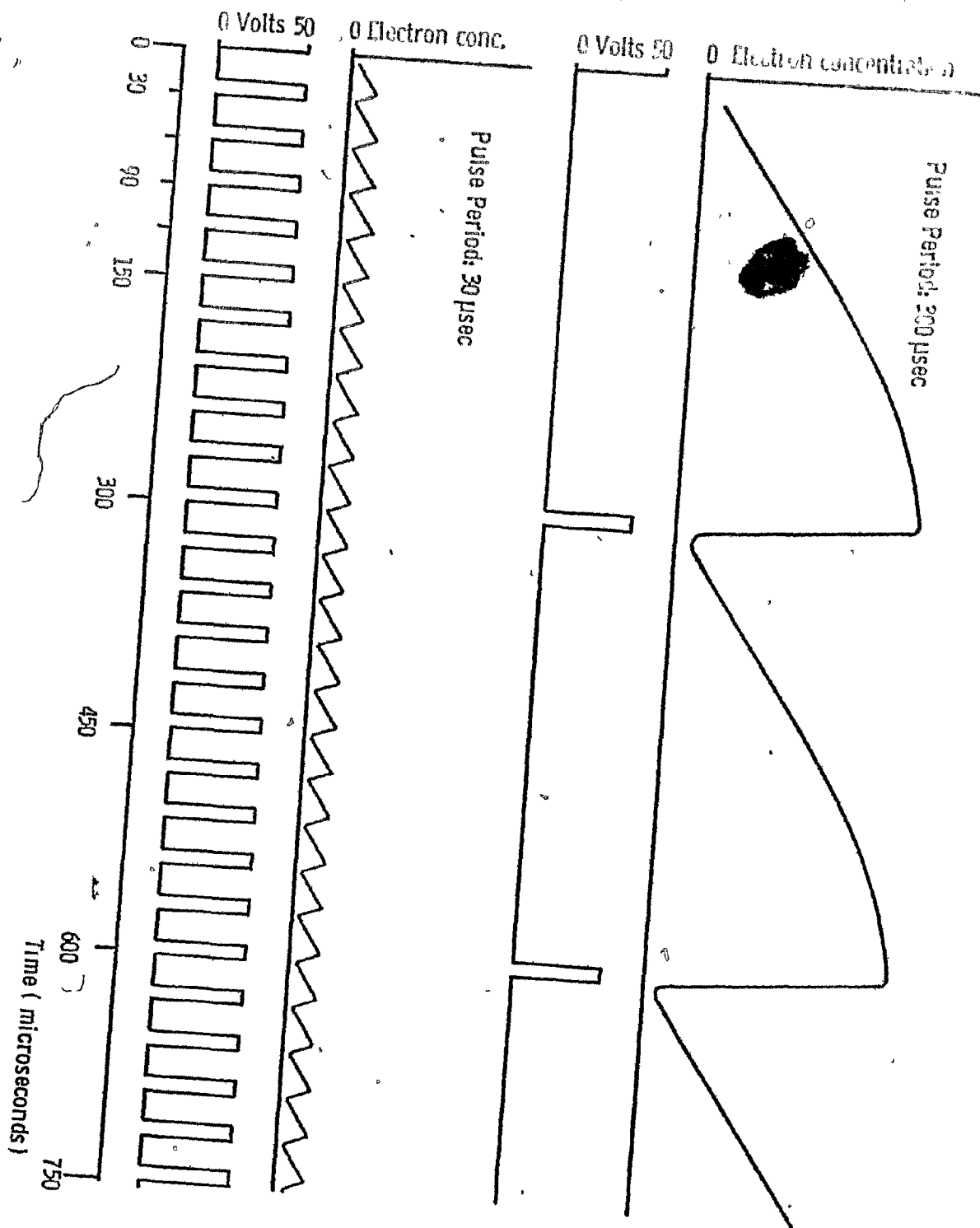Schematic of changes in electron concentration in the detector cell at two different pulse intervals.

0 Volts 50   0 Electron conc.

Pulse Period: 30 μsec

0 Volts 50   0 Electron concentration

Pulse Period: 300 μsec

0 30 90 150 300 450 600 750

Time (microseconds)

Figure 6

Effect of the pulse period ($\simeq$ electron
concentration) on standing current and
response of chlorobenzene. Column
temperature: ambient; pulse width 10 us.
The standing current decreased from ~ 3.4
nA at 30 us pulse period to ~2.7 nA at
300 us.
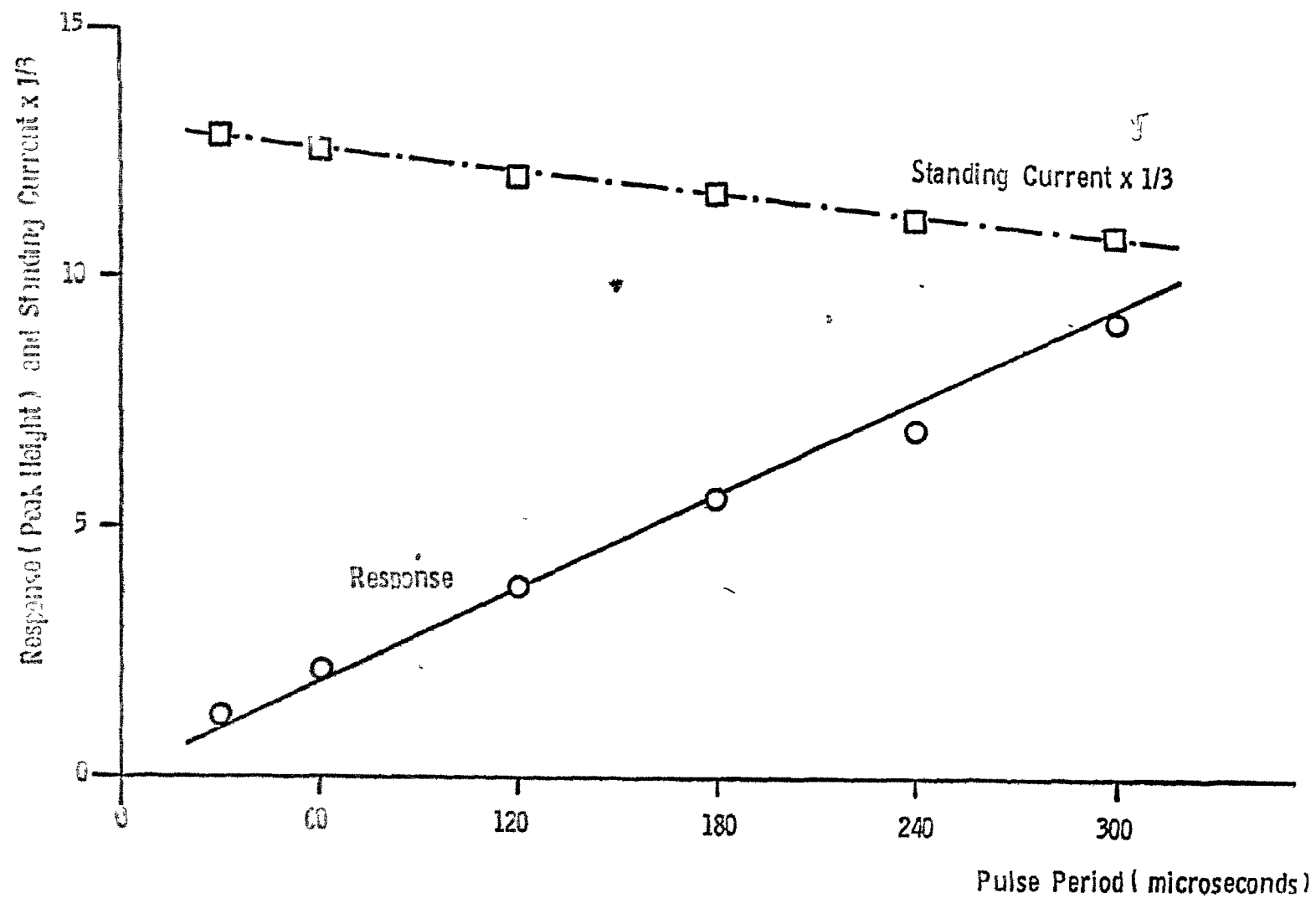
Aroclor 1254 (a mixture of chlorinated biphenyls)
and Halowax 1013 (mixture of chlorinated naphthalenes)
obtained at detector temperatures 100° apart. These
mixtures contain compounds with different degrees of
chlorination and consequently different coefficients of
electron capture. The later peaks with higher number
of chlorine atoms (higher electron affinity) give similar
responses at both temperatures, whereas the response of
the components with low electron affinity increases with
the increase in temperature, pointing towards a dissociative
mechanism of electron attachment.

As stated earlier, under coulometric conditions the
response of the detector is relatively immune to changes in
flow rate. This is illustrated in Figure 9, which shows
three chromatograms at different flow rates obtained by
adding varying amounts, 0, 20 and 57 ml/min of a "scavenger"
gas (i.e. N_2 added to the carrier gas at the exit of the
column) to 6 ml/min of nitrogen flowing through the column.
No significant change in the response of the test compounds,
lindane, heptachlor, heptachlor-epoxide and dieldrin, was
observed. The only exception was the response obtained for
p,p'-DDT; again, the inconsistency in case of DDT can be
attributed to the decomposition of this compound in the
chromatographic system. The cause of the dips in baseline
after the peak is not clear, though it is generally believed
to relate to the development of contact potential in the
detector cell and ionization of solute molecules by metastables.

Figure 7

Calibration curves of five chlorinated
hydrocarbon insecticides. Detector conditions:
Pulse width 8 us, pulse interval 300 us,
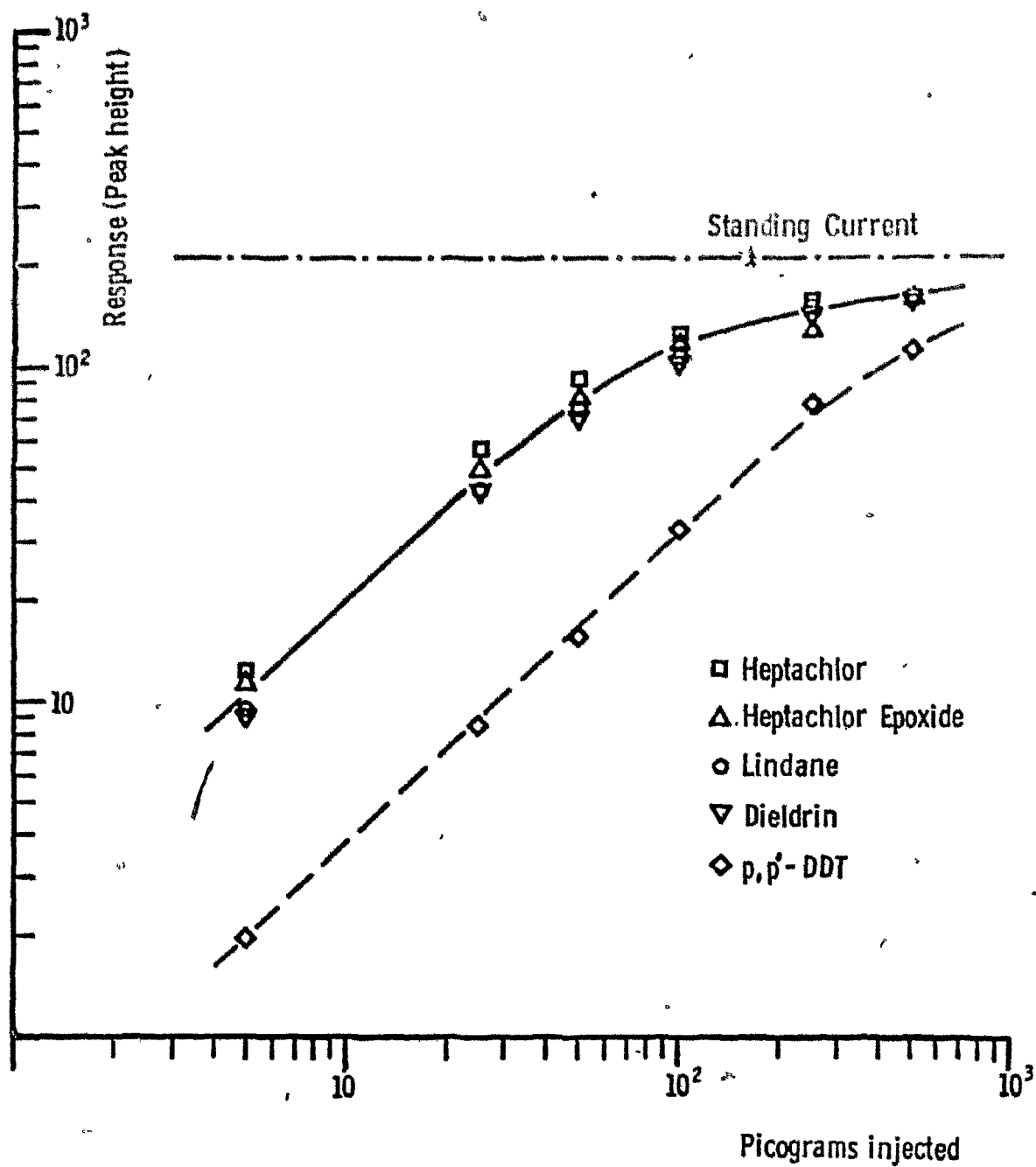temperature 300°, N_2 flow through column
6-7 ml/min.

Response (Peak height)

10^3

10^2

10

Standing Current

□ Heptachlor

△ Heptachlor Epoxide

● Lindane

▽ Dieldrin

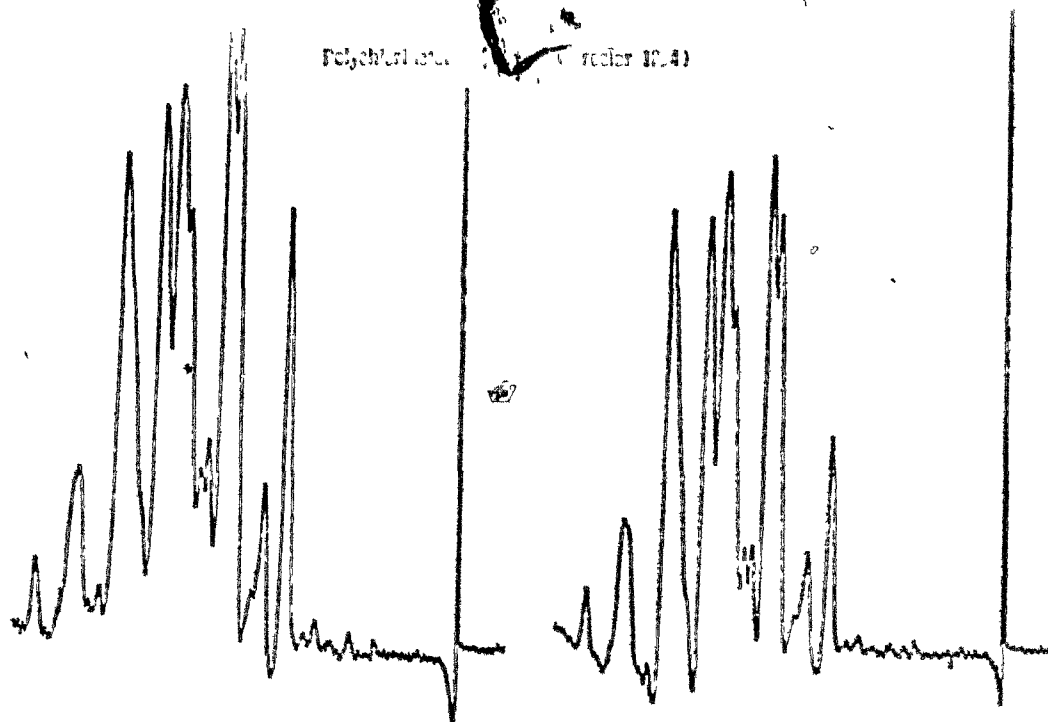◇ p,p'- DDT

10 10^2 10^3

Picograms injected

Figure 8

Chromatography of polychlorinated biphenyls
and naphthalenes at two detector temperatures.
N_2 flow 6-7 ml/min, pulse width 8 us, pulse
interval 300 us, 2 ng of each mixture injected.

Polychlorinated   roclor 1254)

Polychlorinated Naphthalenes (Halowax 1013)

Detector temperature 350°   Detector temperature 250°

°C 200   160   120   °C 200   160   120
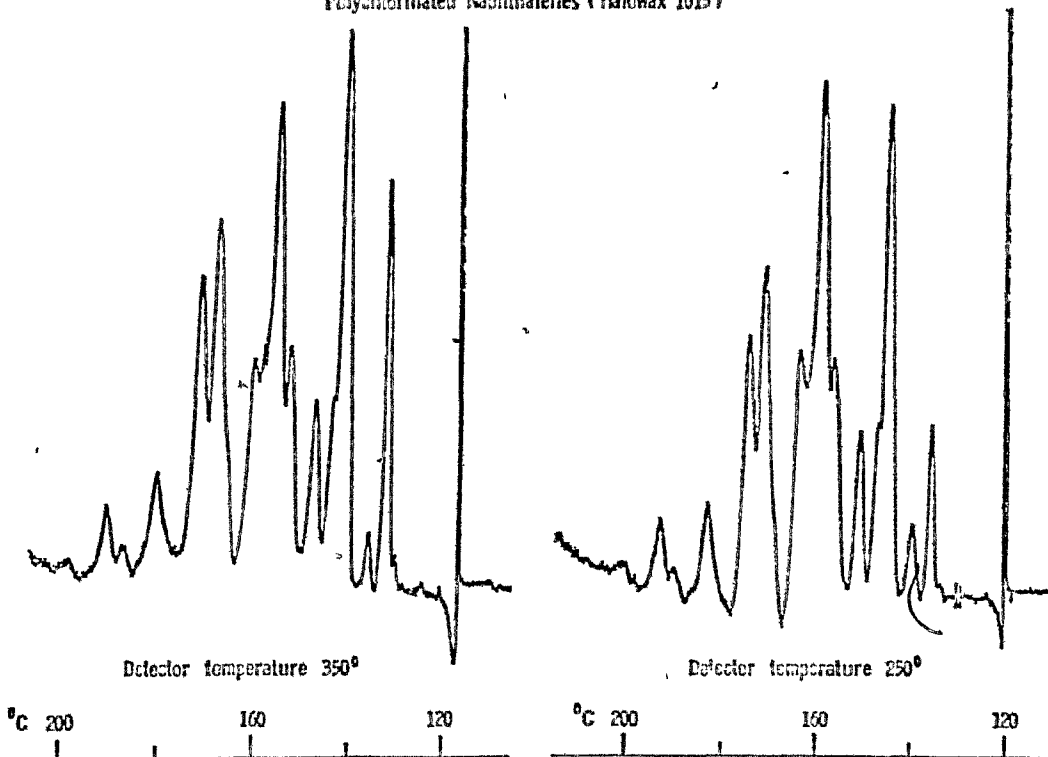
These results indicate the feasibility of
temperature programmed gas chromatography with ECD
even at low concentrations, provided proper care is
taken in the choice of a column and other gas
chromatographic parameters. Temperature programming
with the ECD at relatively high concentrations has
been performed by Bostwick et al. and Kniep and co-
workers.[117-118] By making use of a precolumn, good
results have been obtained in temperature programmed
EC-GC by McCullough and Aue;[119] however, use of a precolumn,
despite its obvious advantages as a vent and peak selecting
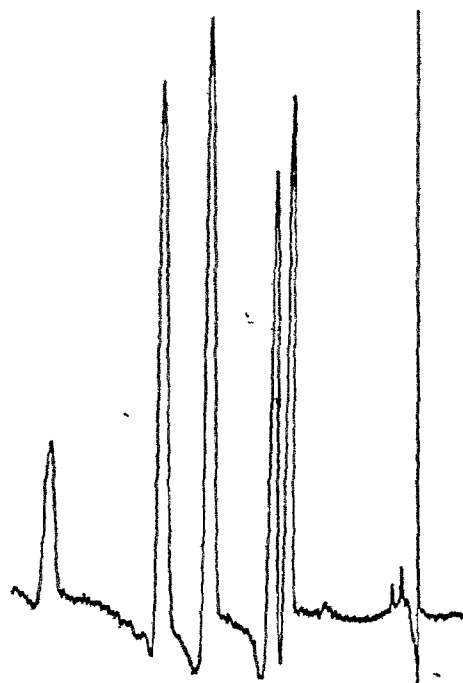device, makes the system somewhat difficult to operate.

Figures 10 and 11 show temperature programmed
chromatograms of some chlorinated hydrocarbon pesticides
at two different concentration levels. Although the re-
sponse of the strongly electron capturing compounds is
relatively insensitive to the changes in detector temper-
ature and flow rate, the response of the weak absorbers in
the column bleed does show a dependence on these parameters.
Thus a decrease in the response to column bleed at a higher
detector temperature would be observed if its components
follow associative electron capture mechanisms. This seems
to be the case for the bleed from a modified support based
on Carbowax 20M.[116] Figure 11 shows that the rise in base-
line at 350° is appreciably smaller than at 250° or 300°.
Thus operation at higher temperature is preferred because

Figure 9

Chromatograms obtained at various flow rates.
Pulse width 8 us, pulse interval 300 us, detector
temperature 350°. Column N_2 flow 6-7 ml/min;
additional scavenger flow as indicated, 50 pg
of each insecticide injected.
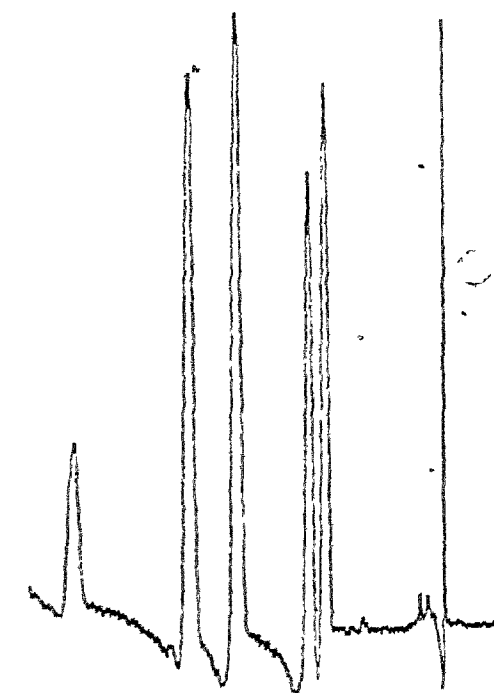
Without Scavenger Flow   Scavenger Flow 20 ml/min.   Scavenger Flow 57 ml/min.

°C 200   160   120   200   160   120   200   160   120

45
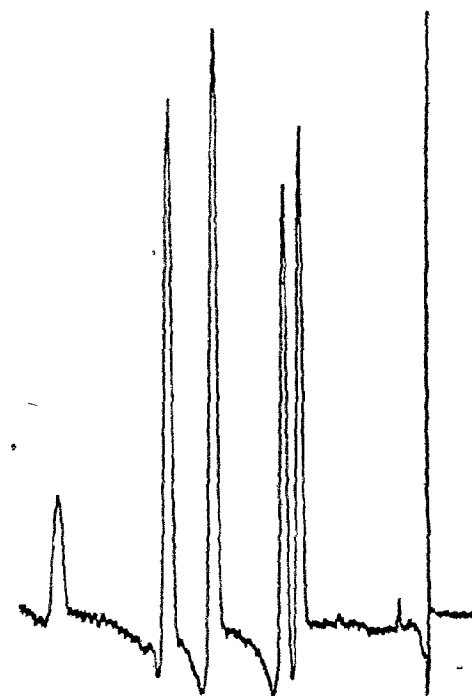
Figure 10

Temperature-programmed separation of small
amounts of chlorinated hydrocarbons, at two
different detector temperatures. 5 pg of
each insecticide injected, other conditions
as in Figure 9.

Detector temperature 350°

°C   200   160   120

Detector temperature 250°

200   160   120

p,p'-DDT

Dieldrin

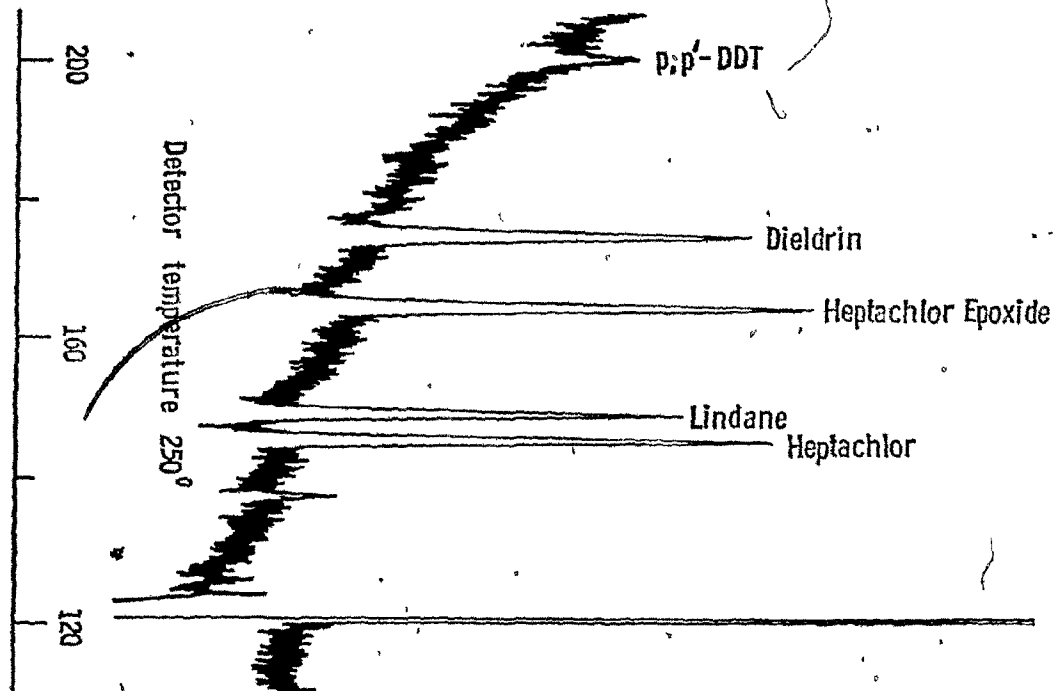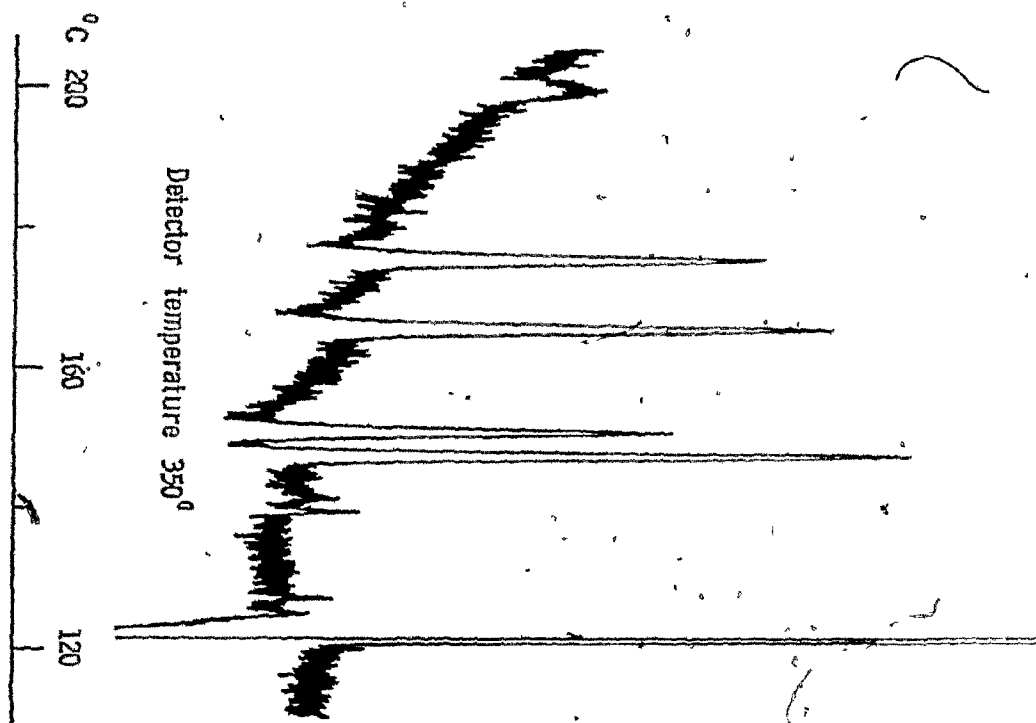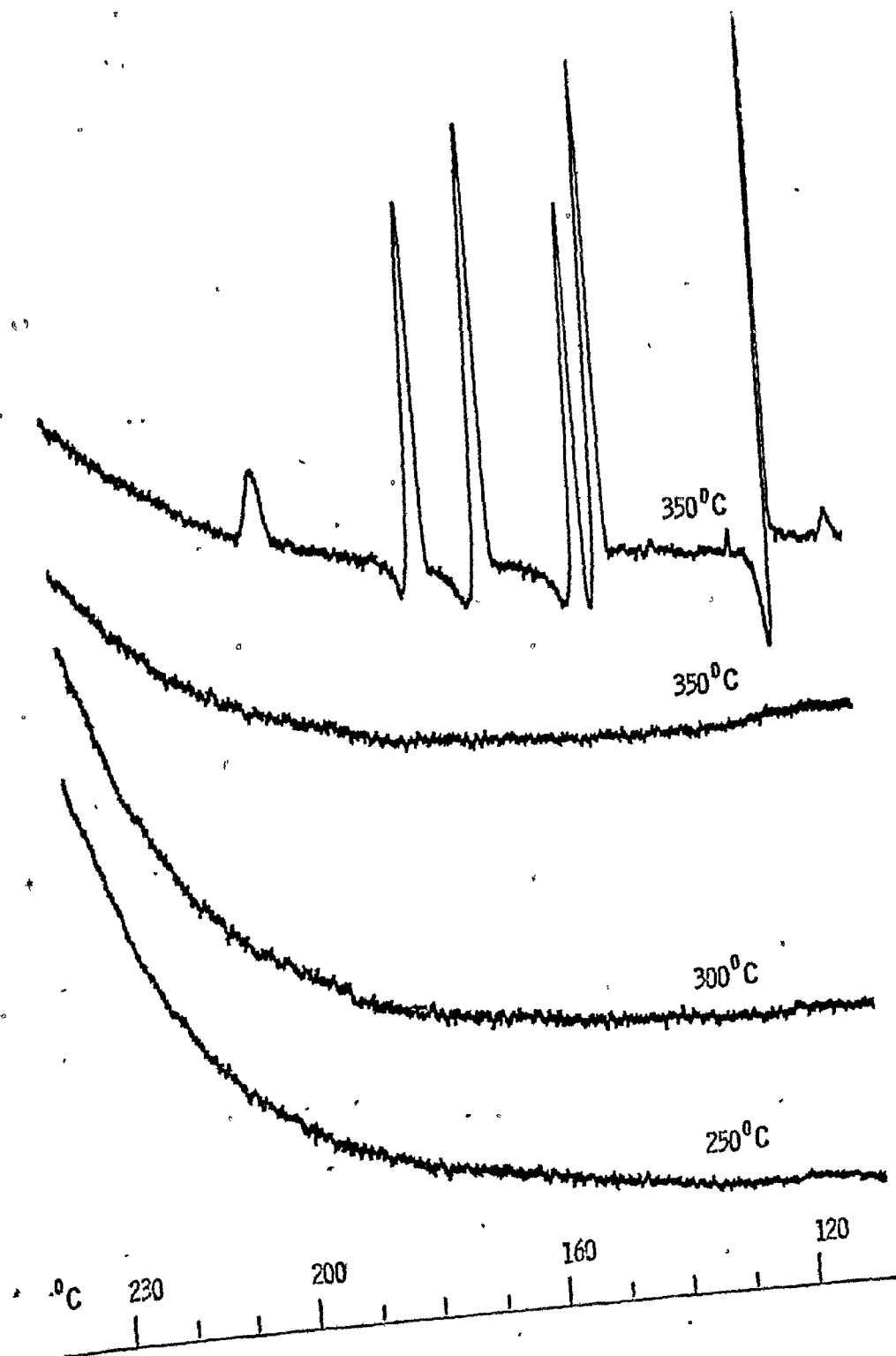Heptachlor Epoxide

Lindane

Heptachlor

46

Figure 11

Baseline stability during temperature
program, measured at different detector
temperatures. 25 pg of each insecticide
injected for the upper trace, other
conditions as in Figure 9.

350°C

350°C

300°C

250°C

°C   230   200   160   120

of this and other reasons such as the effect of
oxygen (low at high temperature) and the decrease in
cell contamination.

C.   ELECTRON CAPTURE PRODUCTS

The term product in this context refers to any
extraneous peak detected only by the second detector,
which tends to decrease when higher voltages are applied
to the first detector (i.e. when the electron capture
reaction is shut off).

All products thus observed had shorter retention
times than their parent compounds. This would be expected
since the predominant EC reactions in case of halogenated
hydrocarbons are assumed to involve loss of halide, halide
ions having been observed directly in plasma chromatography
by Karasek and coworkers.[120,121] Formation of compounds
with higher molecular weight has only been reported to
occur under radically different conditions (high concentra-
tion, glow discharge), and, though unlikely, the possibility
of such products with longer retention times and low EC
response (perhaps originating from column bleed, wall reac-
tions, etc.) cannot be completely ruled out. Similarly,
other neutral products with short retention times and little
EC response may also be formed, but not detected.

The initial study of products from electron capture
reactions was conducted using two commercial ^{63}Ni electron

capture detectors. These detectors are asymmetric
compared to most coaxial and parallel plate designs: the
upper chamber containing the ^{63}Ni foil and polarizing
electrode is separated from the lower chamber, containing
the collecting electrode, by a narrow channel (Fig. 12).
In the conventional configuration, the column effluent
enters through the upper chamber and exits through the
lower chamber.

The two EC detectors were first tested separately
in the normal configuration and under normal conditions,
and were found to be quite similar in terms of the 'base
line' current (standing current) and the response for
selected test compounds: lindane, heptachlor and heptachlor-
epoxide. Figures 13 and 14 show the calibration curves for
lindane with the two detectors.

The instrumental set-up was then changed to the
arrangement shown in Figure 1. In this configuration, the
unreacted solute and products formed in the first electron
capture detector were separated in the second column and
detected by the second detector. Both detectors were
operated in the DC mode. The optimum voltage for the
first detector (EC-1) varied from 30-60 V, depending upon
the column temperature, i.e. column bleed, whereas optimum
voltage for the second detector varied from 10-15 V. The
baseline current of EC-1 was about twice that of EC-2
$(6.4 \times 10^{-9}$ versus 3.6×10^{-9} A). It was also observed that

49

Figure 12

Schematic of Tracor ^{63}Ni electron capture detector.
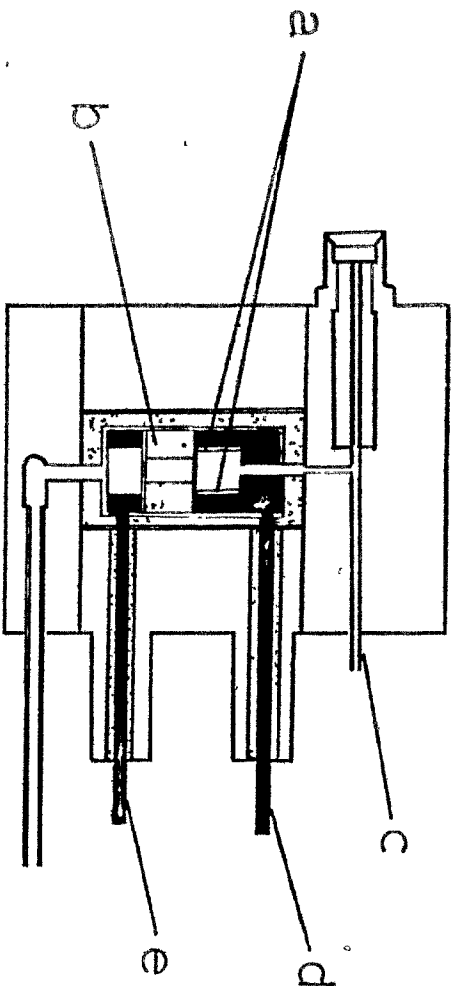
a. ^{63}Ni foil

b. Boron nitride insulator

c. Purge gas line

d. Top electrode

e. Bottom electrode

Figure 13

Calibration curve of lindane, obtained with
EC-1 in normal configuration. Detector
conditions: polarizing potential -15 V DC,
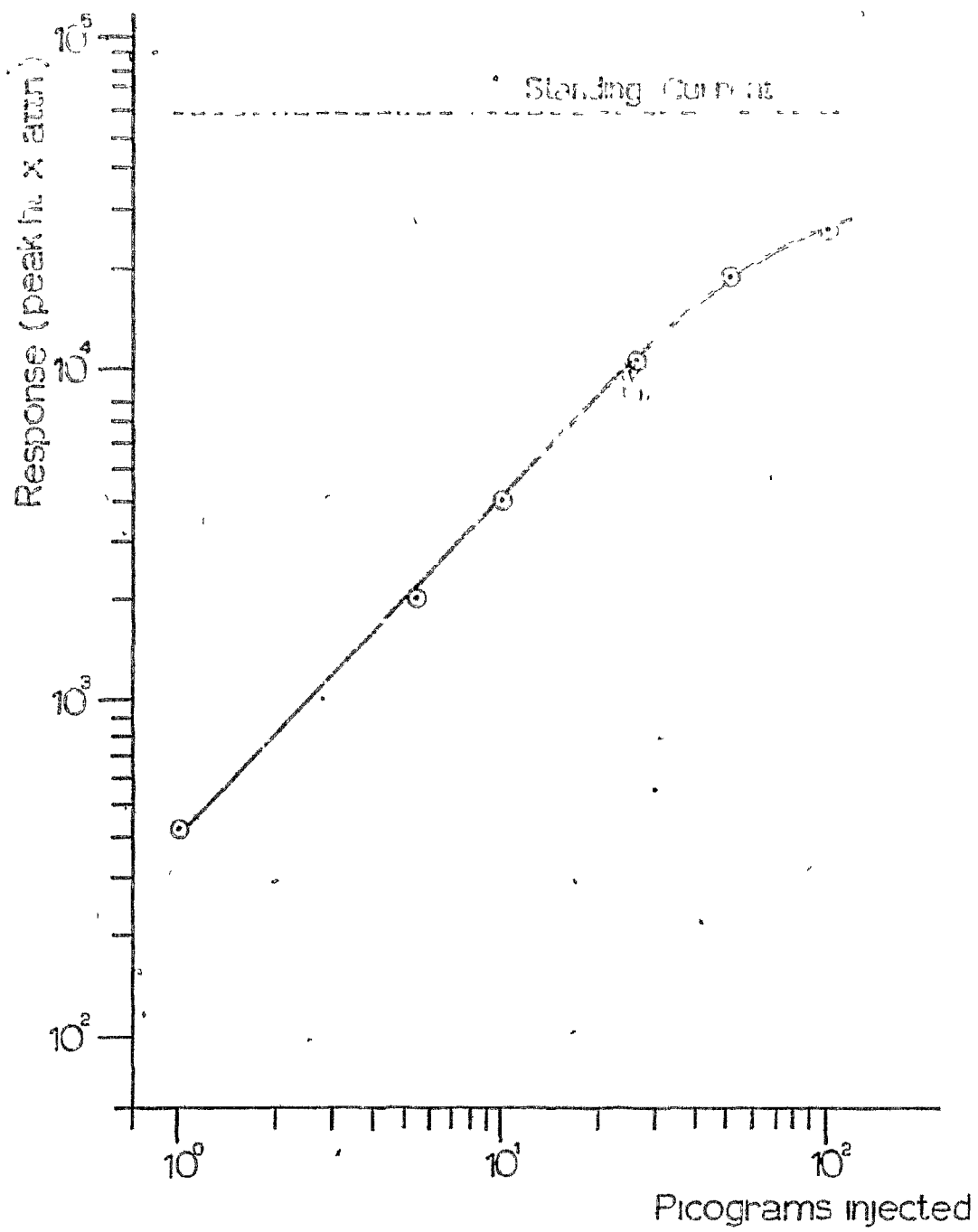temperature 300°, N_2 flow through column
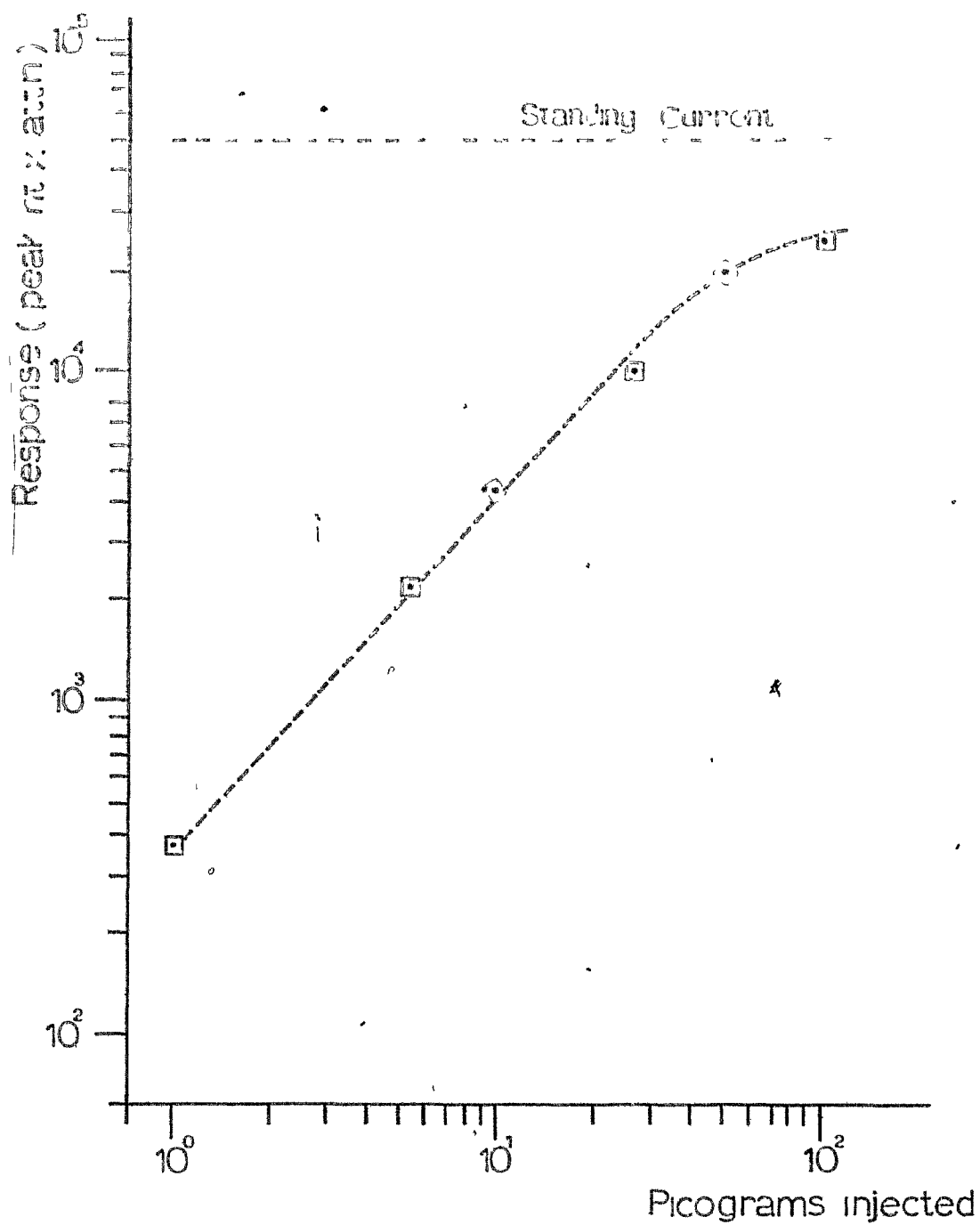30 ml/min.

51

Figure 14

Calibration curve of lindane, obtained with EC-2 in normal configuration. Detector conditions as in Figure 13.

the response of EC-1 was considerably higher than the response of EC-2.

The effect of different parameters such as voltage, flow rate, detector temperature and presence of reactive species, etc. on the electron capture reaction and product formation was studied.

Effect of Voltage

In their pioneering study on gas phase coulometry using an EC detector, Lovelock and Maggs reported that when sufficiently high voltage ($\sim$100 V) was applied to the cathode, the electron capture reaction in the detector was stopped and the solute molecules passed through the detector unscathed.[104] In the same study Lovelock et al. also commented on the improbability of finding an electron capturing product from electron capture reactions. In the present study, it was observed that the magnitude of voltage required for turn off (voltage at which electron capture process stops) varies with the sign of the polarizing potential, the electron capturing species and the geometry of the detector. It was noticed that the turn-off occurs at a much higher voltage (around +1000 V) when positive potential is applied to the upper electrode (Tracor ^{63}Ni ECD), whereas with negative potential it occurs at relatively low potential (-100 V). Little difference was found between this and the other possible configuration in which a field

of this direction can be operated (the other electrode
in each case serves as the collector and is at ground
potential as are the entrance and exit lines) i.e. having
the negative potential at the lower electrode. Similarly,
either of two configurations can be used when the field is
reversed, with the same results. The plot of baseline
current versus voltage also reflects the situation (Fig.
15). With positive potential at the upper electrode the
less mobile cations have a much longer distance to travel
and a higher potential is needed for reaching the saturation
current. It is generally accepted that the movement of
cations and anions at low E/P (Field Strength/Pressure)
ratios is predominantly governed by diffusion.[122]

The effect of field strength on electron capture
reactions in EC-1 can be observed in Figures 16, 17, 18 and
19, which were obtained using two levels of dieldrin and
lindane. The characteristic S-shaped curve for the un-
reacted substances reaching the second detector is shifted
to higher voltages when positive potential is applied to
the upper electrode or negative potential to the lower
electrode, while the other serves as the collector. The
probable reason for this effect is the formation of a
space charge (due to the slow-moving cations) which opposes
the applied field, effectively lowering its strength and
thus impeding the fast removal of thermal electrons from
the cell.

Figure 15

Voltage profile EC-1

_____   Negative potential applied to
the top electrode

- - - -   Positive potential applied to
the top electrode

Detector temperature 290°

Note: The voltage profile measured with positive
potential applied to the top electrode is
an S-shaped curve; however, its upper part
could not be recorded in this case because
of electrical insulation problems at the
high temperature involved.

Cell Current (μ amps)

2 4 6

10⁰

10¹

Applied Potential (volts)

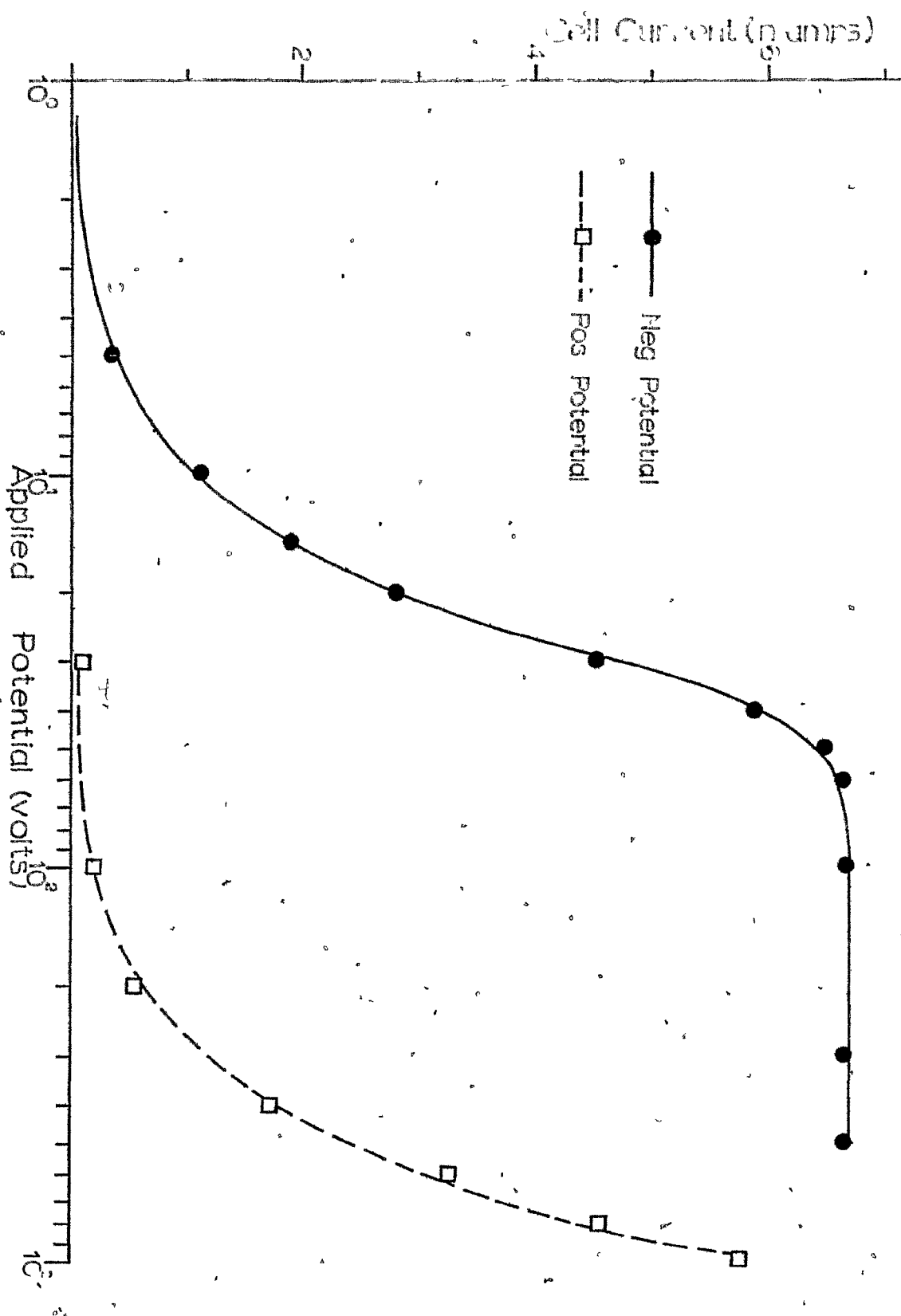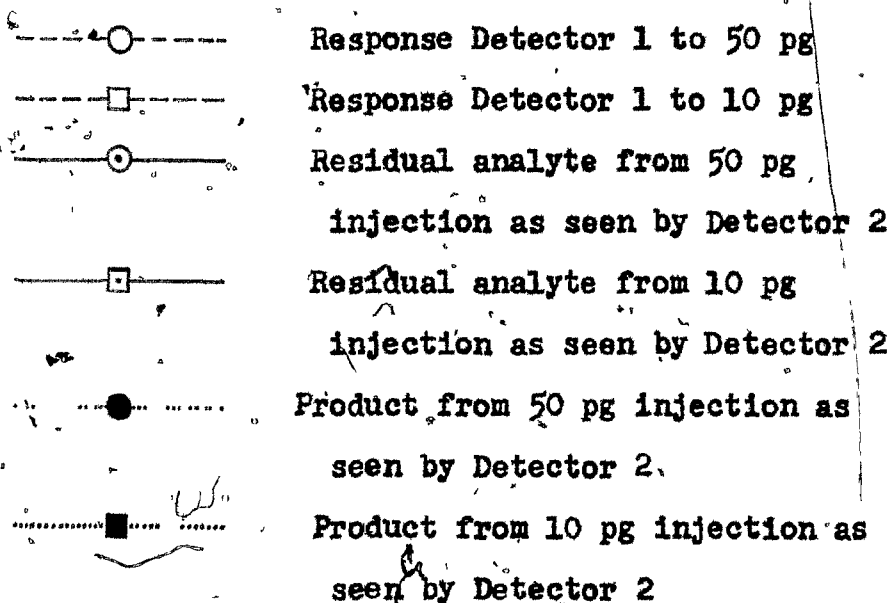10²

10³

Neg Potential

Pos Potential

Figure 16

Effects of voltage change in Detector 1 on
response of dieldrin in Detector 1; and
response of residual dieldrin and its product
(formed in Detector 1) as seen by Detector 2;
measured with 10 pg and 50 pg amounts per
injection. Negative voltage applied to upper
electrode in Detector 1; gas chromatographic
effluent enters from top. Column temperature
200°.

Response Detector 1 to 50 pg

Response Detector 1 to 10 pg

Residual analyte from 50 pg
injection as seen by Detector 2

Residual analyte from 10 pg
injection as seen by Detector 2

Product from 50 pg injection as
seen by Detector 2.

Product from 10 pg injection as
seen by Detector 2

Dieldrin

Amperes Peak Height ^{R}

DET1 Dieldrin 50pg

10pg

DET 2
Dieldrin 50

Dieldrin 10

Prod 50

Prod 10

PLT1
Sig Current

10^n

10^n

10^{10}

10^n

10^{-12}

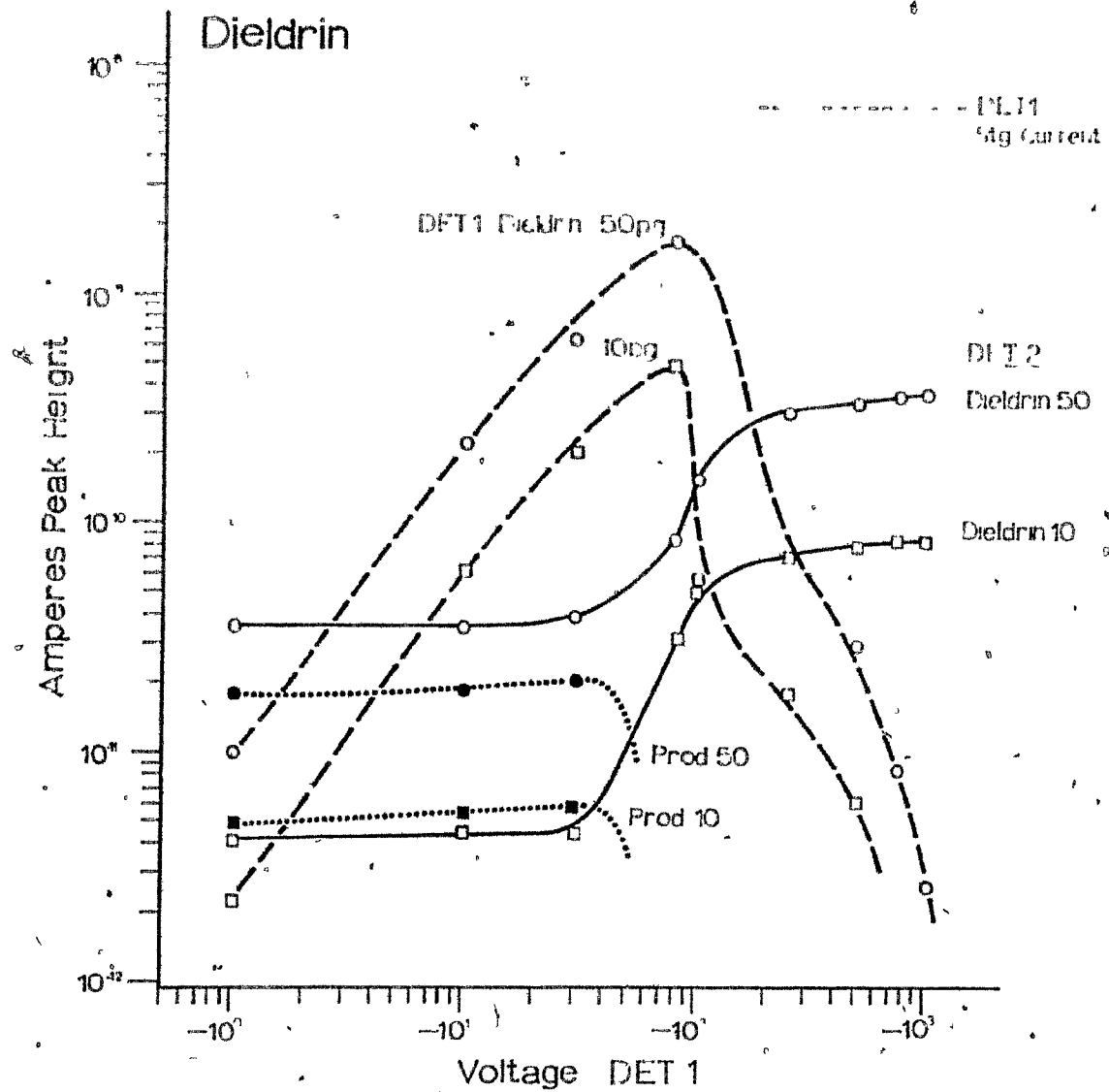-10^n -10^1 -10^1 -10^3

Voltage   DET 1

56

Figure 17

.Effects of voltage change in Detector 1 on
response of residual dieldrin and its product
(formed in Detector 1) as seen by Detector 2.
Positive voltage applied to upper electrode.
Other conditions as given in Figure 16.

Note: Shown is the beginning of two S-shaped curves
for residual dieldrin. The remaining part of
the S-curve could not be recorded due to
electrical insulation problem at the high
temperature involved.

Dieldrin

DET 2

Amperes Peak Height

Dieldrin-50

Dieldrin-0

Prod -50

Prod -10

10^9

10^{10}

10^{11}

10^{12}

$+10^0$ $+10^1$ $+10^2$ $+10^3$
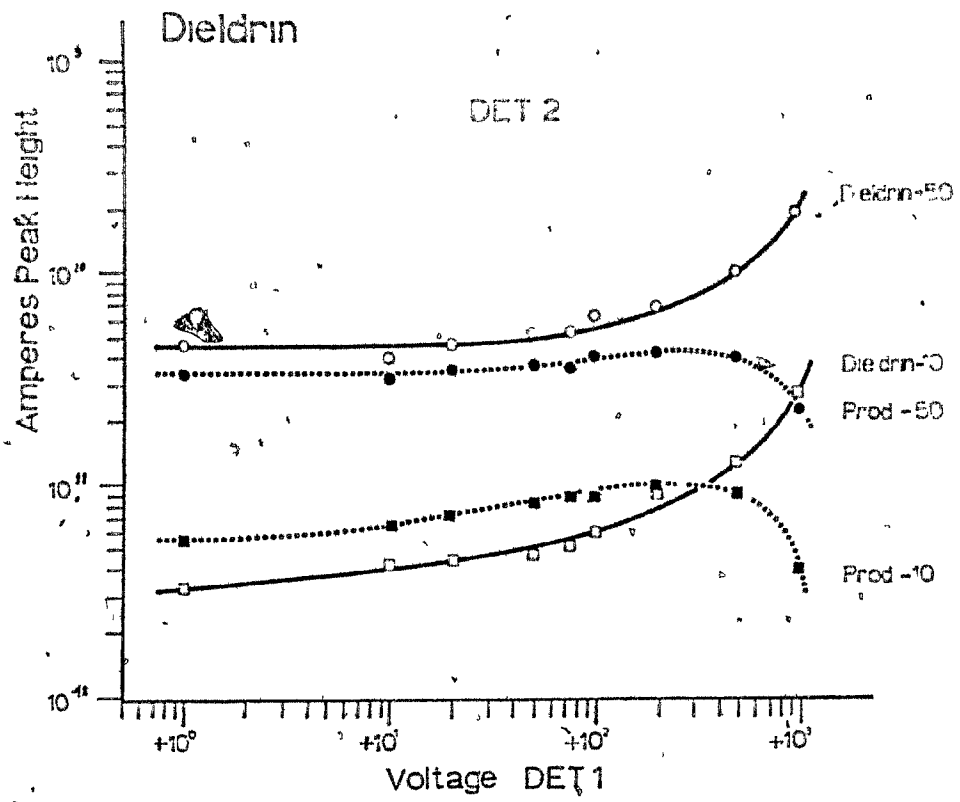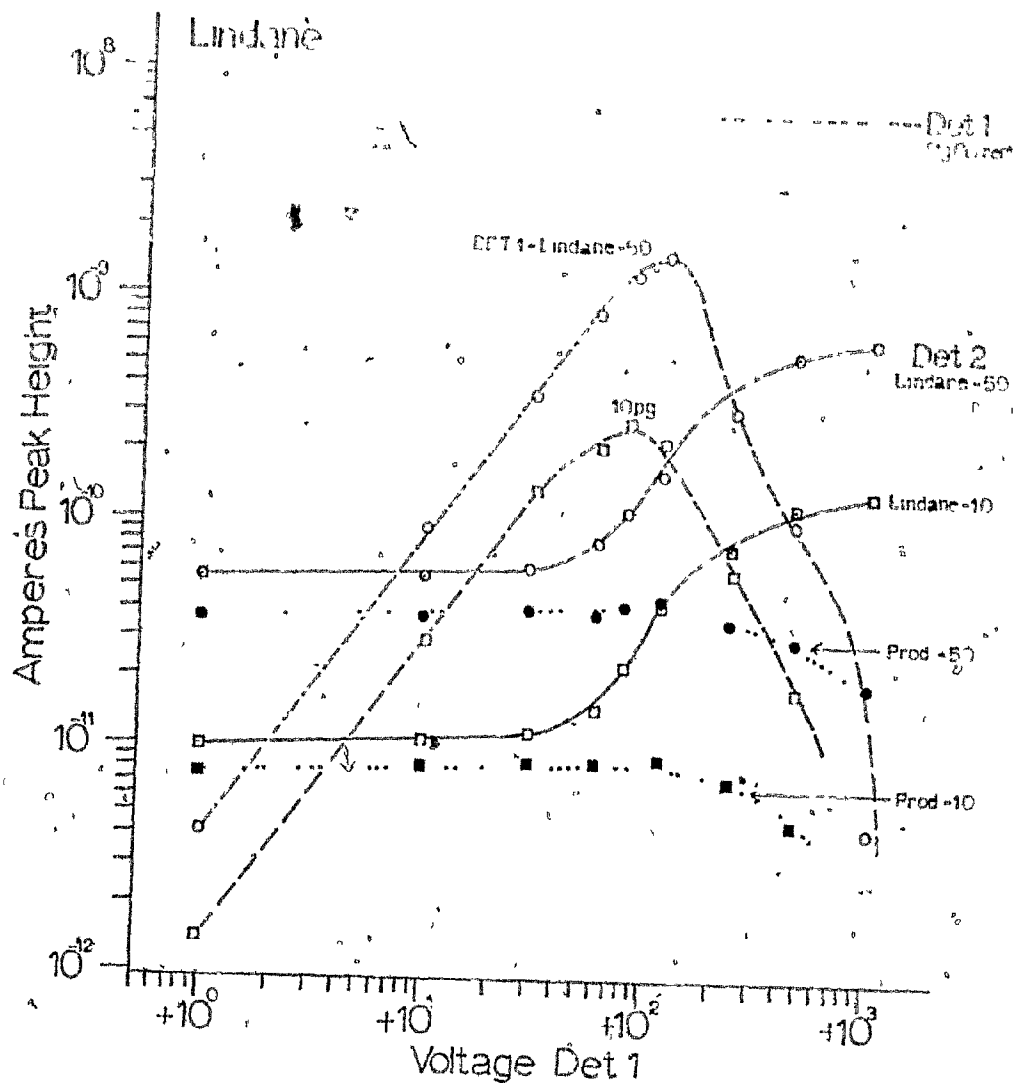
Voltage   DET 1

Figure 18

Effects of voltage changes in Detector 1 on the
response of lindane in Detector 1; and response
of residual lindane and its product (formed in
EC-1) as seen by EC-2. Chromatographic and other
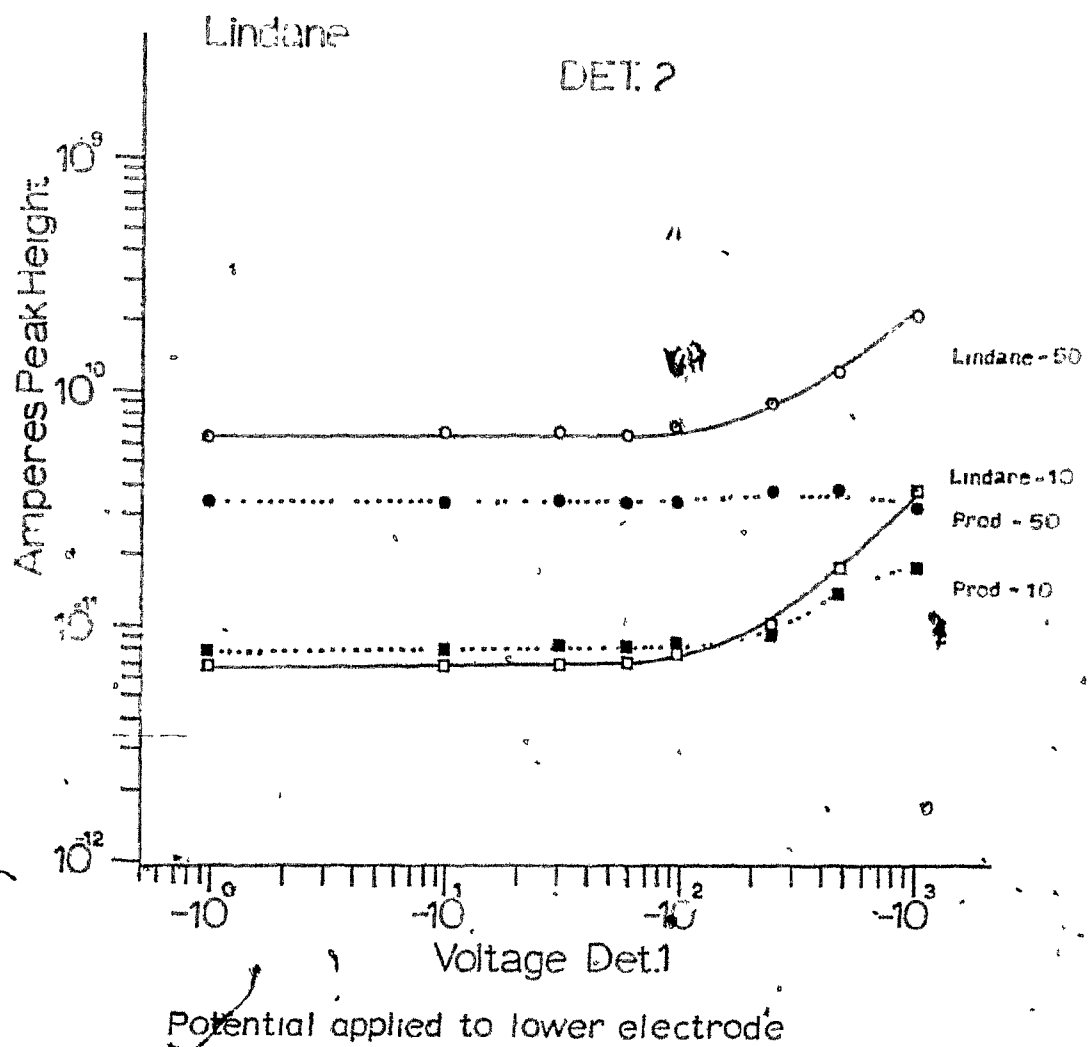conditions as in Figure 16.

Lindane

10^8

10^9

10^{10}

10^{11}

10^{12}

Amperes Peak Height

DET 1-Lindane-50

10pg

Det 1

Det 2
Lindane-50

Lindane-10

Prod -50

Prod -10

$+10^0$ $+10^1$ $+10^2$ $+10^3$

Voltage Det 1

Potential applied to lower electrode

58

Figure 19

Effects of voltage changes in Detector 1
on response of residual lindane and its
products (formed in Detector 1) as seen by
Detector 2. Negative voltage applied to
the lower electrode. Other conditions as
given in Figure 16.

Note: Shown is the beginning of two
S-shaped curves for residual dieldrin.
The remaining part of the S-curve could
not be recorded due to electrical insulation
problem at the high temperature involved.

Lindane   DET. 2

Amperes Peak Height

10^9

10^0

10^{12}

Lindane – 50
Lindane – 10
Prod – 50
Prod – 10

-10^0 -10^1 -10^2 -10^3

Voltage Det.1

Potential applied to lower electrode

Little difference was observed between these
characteristic curves and those for other compounds
tested in this manner (1,1,2,2-tetrachloroethane,
hexachloroethane, bromobenzene, benzyl chloride,
o-chloronitrobenzene, m-chloronitrobenzene, p-chloronitro-
benzene, 2,3,5,6-tetrachloronitrobenzene, hexachlorobenzene,
lindane (γ-hexachlorocyclohexane), heptachlor, aldrin,
heptachlor-epoxide, dieldrin, decachlorobiphenyl, and
methyl parathion.

Large differences, however, were noticed in the
tendency of compounds to form electron capturing products,
which could be detected by the second detector.

Compounds which do not respond well in the electron
capture detector gave less pronounced profiles, e.g. Figure
20 shows the profile for benzyl chloride. It indicates that
most of the compounds with small electron capture coefficient
go through an ECD largely unharmed, and only a small fraction
of the molecules is ionized in the detector. As expected, no
EC responding products were obtained for this and similar
compounds (chlorobenzene, bromobenzene, etc.).

Figure 21 shows the voltage profile for hexachloro-
ethane, which was found to be one of the best-responding sub-
stances. It can be observed that the first detector is re-
markably efficient in breaking down the compound at low
voltages. Calculations based on the S-curve of the second
detector (corrected for nonlinearity) reveal that more than
99% of the compound is consumed in the first detector.

60

Figure 20

Voltage profile for benzyl chloride, using 500
and 20 pg injections. Column temperature 95°.
No products observed.

Benzyl Chloride

Amperes Peak Height vs. Voltage DET 1

DET 1 — [CH₂Cl] 500pg

20pg

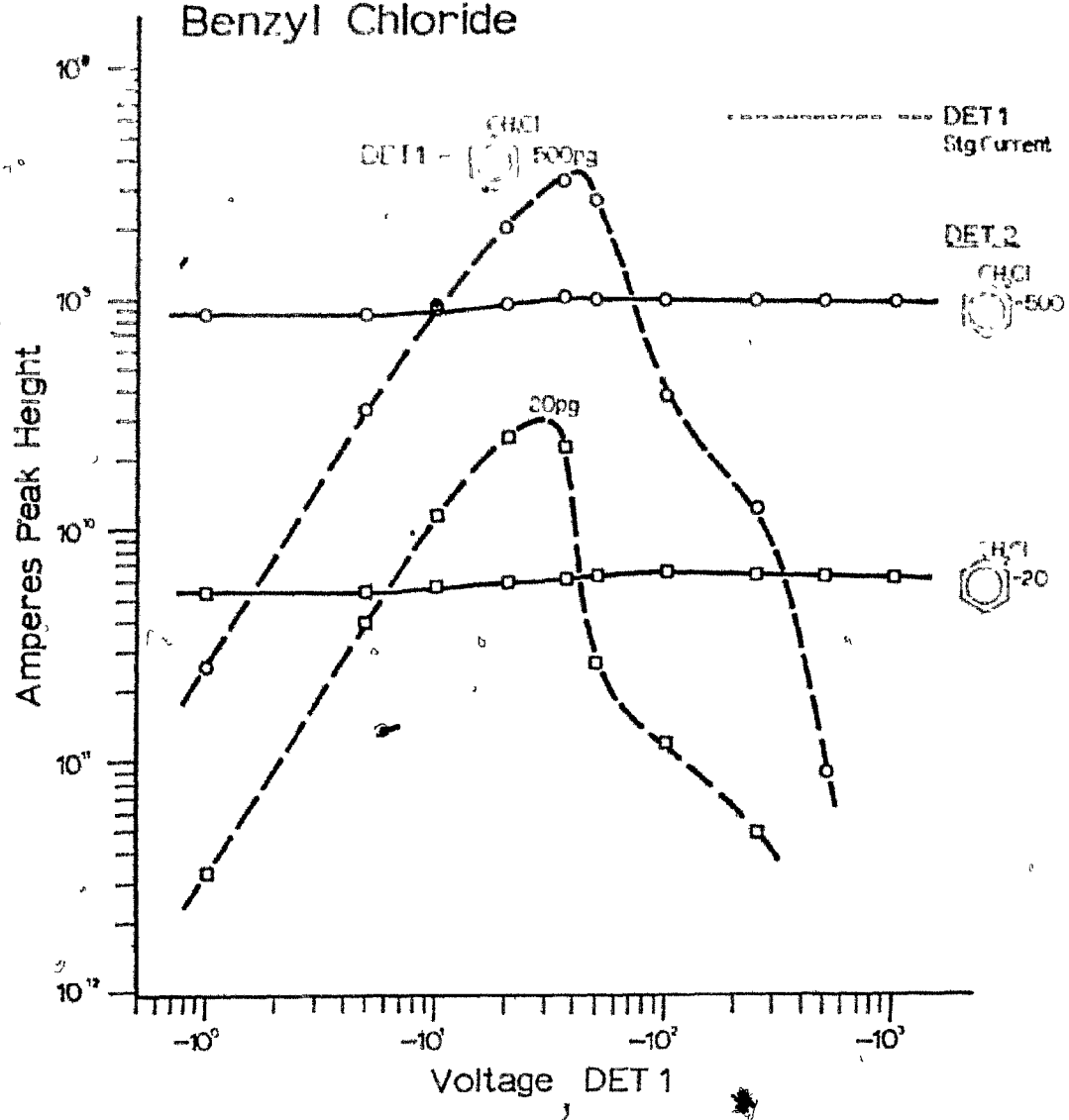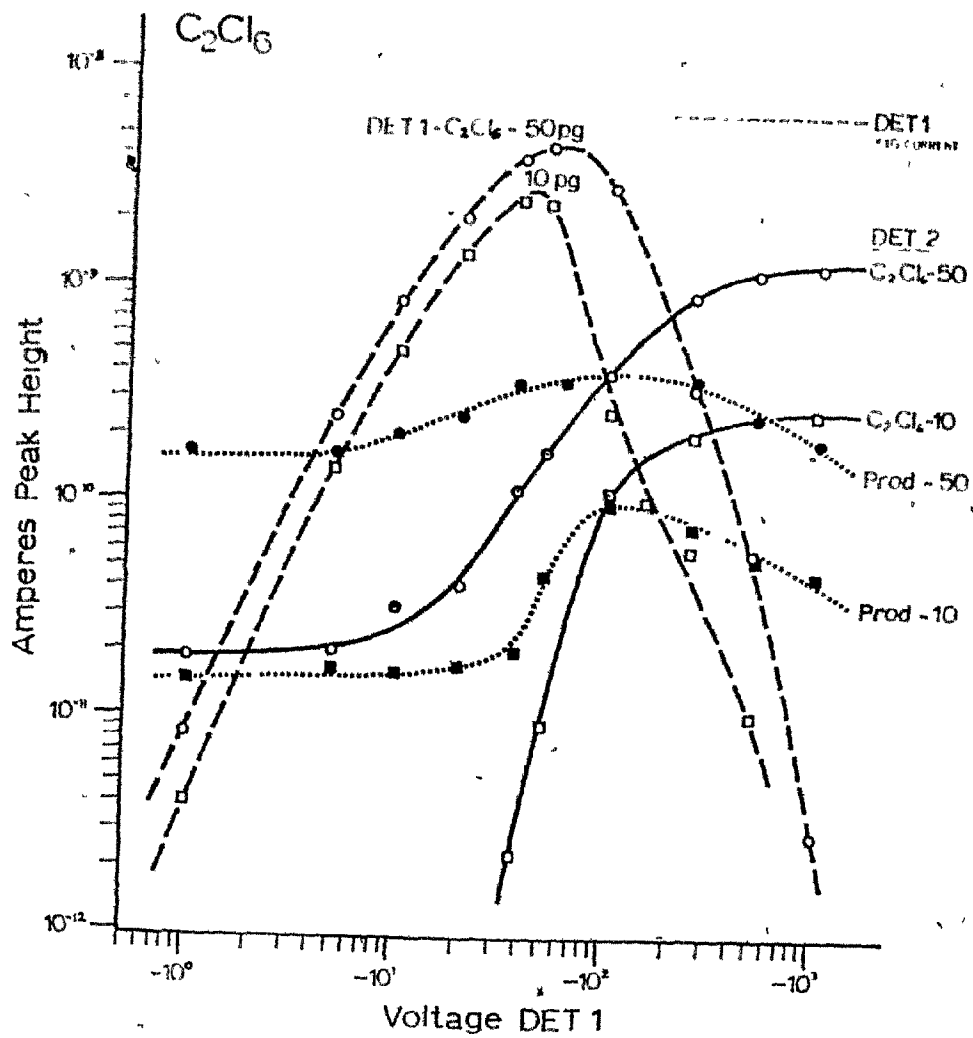DET 1 Stg Current

DET 2

[CH₂Cl]-500

[CH₂Cl]-20

61

Figure 21

Plot of voltage change versus response of
hexachloroethane similar to the one shown
in Figure 16. Column temperature 90°.
Column effluent enters in EC-1 from the bottom.

C_2Cl_6

DET 1-C_2Cl_6 - 50pg

10 pg

DET 1

DET 2
C_2Cl_6-50

C_2Cl_6-10

Prod - 50

Prod - 10

Amperes Peak Height

Voltage DET 1

Chromatograms obtained at different voltages (V_1) for this compound in the two detectors are shown in Figure 22. The chromatograms are arranged side-by-side (rather than reproducing the original dual-channel tracings) for clearer illustration. It should be noticed, perhaps, that the 50 pg of hexachloroethane are way beyond the linear range of the first detector, but this excessive amount had to be used in order to pick up both the compound and its products throughout the entire voltage range. Figure 21 also shows that maximum of product is obtained in the middle voltage ranges, which could be attributed to consumption of this product in the first detector after its formation from the parent compound. Failure to turn off the reaction for this compound could be due to the large cross-section of electron capture for this molecule. The possibility of product formation by the interaction of cations and solute molecules, cannot be completely ruled out.

These chromatograms (Fig. 22) and voltage profiles (Fig. 21) seem to indicate that, in the DC mode, the maximum of reaction and the maximum response do not coincide.

Assuming that at low voltages the decrease in response and the baseline current (resulting from the collection of free electrons) are related, a rough estimate of the extent of reaction at lower voltages can be made by multiplying the response by a correction factor f where

$$f = \frac{\text{baseline current at high voltage (at plateau)}}{\text{baseline current at low voltage}}$$
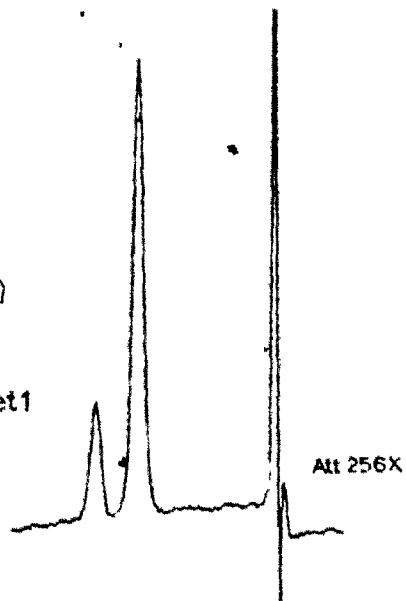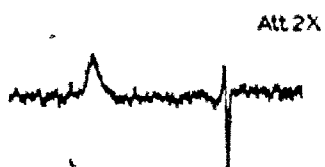
63

Figure 22

Chromatograms obtained from 50 pg hexachloroethane as seen by two detectors. Simultaneously obtained chromatograms are placed side by side. Voltage in Detector 1: 0, -36, or -1000 V, voltage in Detector 2: constant (optimum).
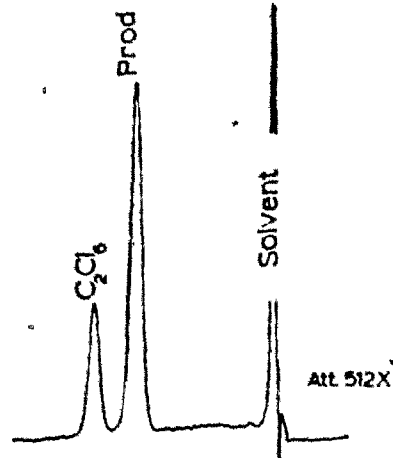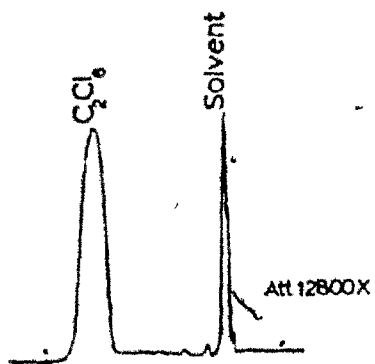
DETECTOR 1

DETECTOR 2

Polar Voltage Det 1

Att 2X

0 Volts

Att 256X

C_2Cl_6

Solvent

Prod

36 Volts

C_2Cl_6

Solvent

Att 12800X

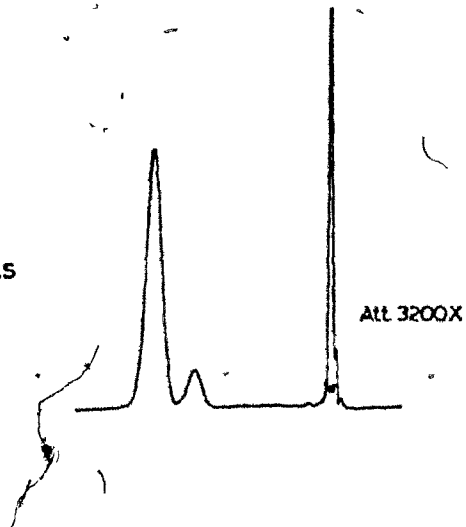Att 512X

1000 Volts

Att 64X

Att 3200X

Figure 23 shows the response profile of 1 pg of hexachloroethane at different voltages; the dotted line corresponds to the extrapolated response corrected for the decrease in the standing current at low voltages. The extrapolated response increases to a maximum and then shows a decrease indicating that either the simple extrapolation does not hold at very low voltage or that the electron affinity of hexachloroethane is higher for free electrons with kinetic energy somewhat higher than thermal or the presence of other electron capturing species.

Another attempt was made to speculate on the extent of reaction at different voltages. The S-curve obtained from the second detector was used in calculating the analyte consumed in the first detector and, from these data, a rough estimate of the response of the first detector was made. No corrections were made to account for the response of products in the first detector; with this in mind, aldrin, a compound with low responding products, was chosen. No attempt was made to account for such phenomena as the change in cross section of solute with the change in electron energy and neutralization of the negative ions at the anode, etc.

The data from the S-curve were corrected for non-linearity of response and used in calculating the amount of analyte consumed. This amount was then corrected for efficiency of charge collection (f) and multiplied by an empirical constant, equating the highest responses from measured and

65

Figure 23

Measured response of 1 pg hexachloroethane, with calculated (corrected) response.
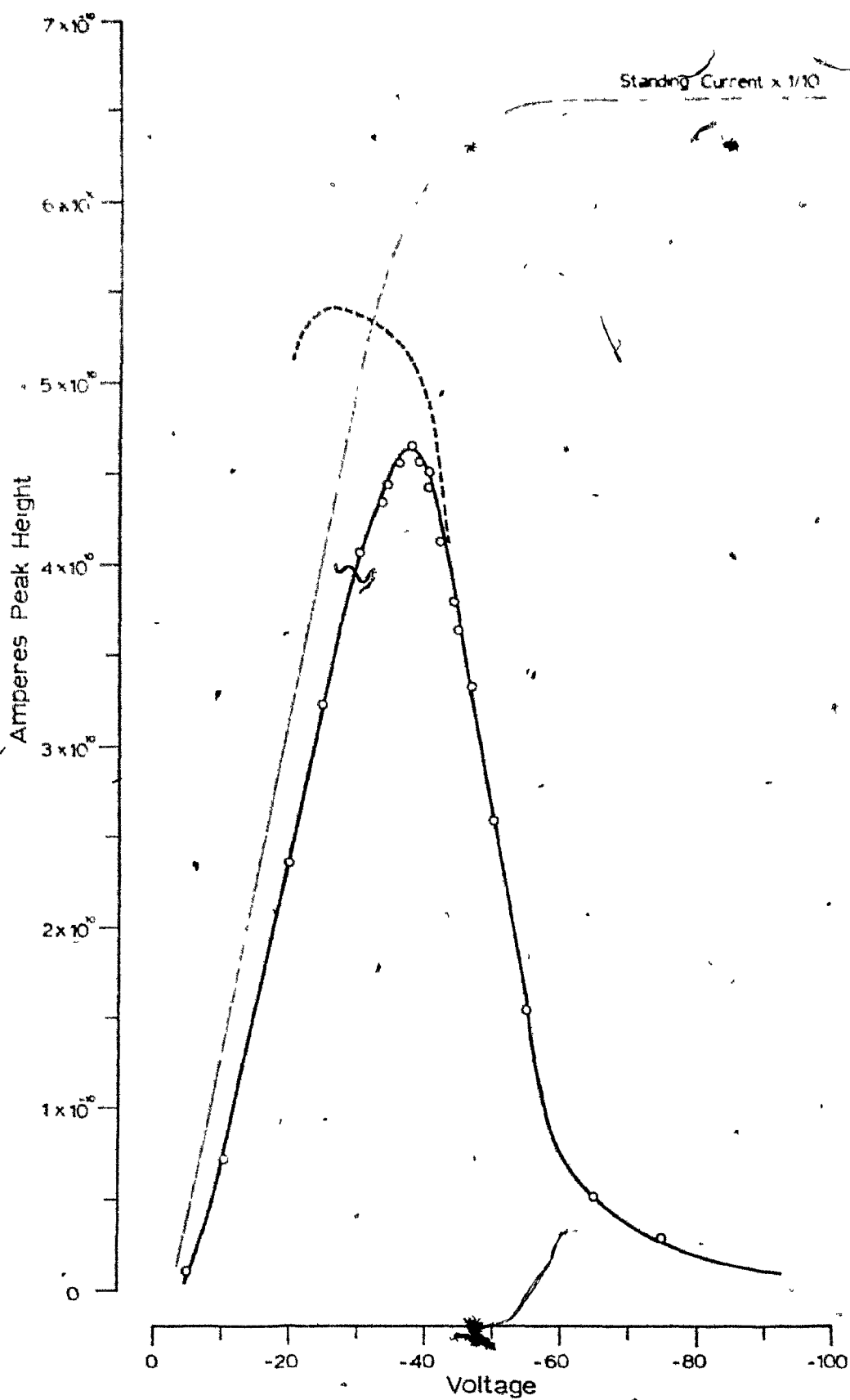
calculated voltage profiles to account for the sensitivity difference between the two detectors. The values thus obtained bore resemblance, particularly in the position of maxima, to the response actually measured in the EC-1. Figure 24 shows these results. The discrepancy between the measured and calculated response at high voltages could, for instance, result from the decrease in the observed response due to collection of anions at these voltages.

Effect of Various Additives

In an attempt to gain insight into the processes occurring in the electron capture cell, various additives were added to the carrier gas stream and their effect on the products and product pattern (number and relative size of the product peaks) was recorded. Initially N_2 was used as the carrier gas, later Ar and He were also tried. Five compounds, 2,3,5,6-tetrachloronitrobenzene, pentachloronitrobenzene, hexachlorobenzene, lindane and δ-hexachlorocyclohexane, were used as the test compounds.

Gaseous additives were added to the carrier gas stream through a fine metering valve with numerical counter whereas the liquid additives were added by saturating part or whole of the carrier gas stream. Results obtained are summarized in Table 1 (on page 71).

When Argon was used as the carrier gas results were similar to those obtained with nitrogen, except that the small molecular peaks were more abundant in the case of Argon.

Figure 24

  Plot similar to the one shown in Figure 16,

  but using 50 pg injections of aldrin. The

  response of Detector 1 was calculated (●--●)

 from the amount of aldrin consumed in Detector 1,

  ____ minus (⊙--⊙), and standing current in

  Detector 1. Column temperature 200°.

Aldrin
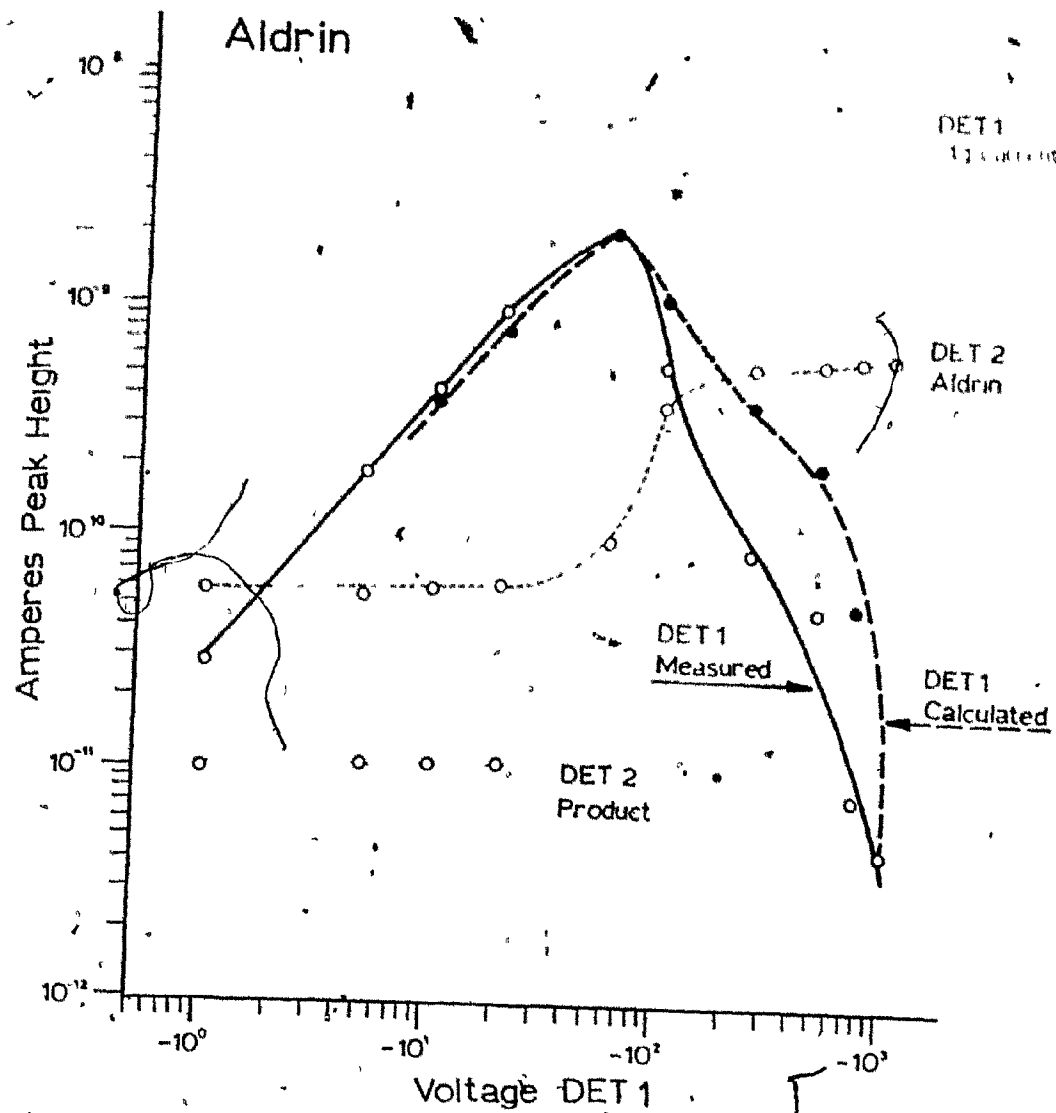
Figures 25 and 26 show the chromatograms obtained for pentachloronitrobenzene with N_2, N_2/iso-octane, Ar (methane was added to the EC-II to retain sensitivity), and Ar/iso-octane.

The best product patterns were obtained with Ar/iso-octane. The amount of iso-octane added varied from 200-400 ug/min (calculation based on the saturation of carrier gas); amounts at the upper limit gave better results.

These results, along with the results from the voltage study, seem to indicate that the electron capture process depends primarily on the ease of electron absorption, which in turn is dependent upon the electron energy; generally, the closer it is to thermal, the greater is the capture cross-section for large and complex solute molecules. This may be the reason for increased breakdown of the compound and product in presence of large molecules such as iso-octane, which are more effective in 'cooling' the electrons through inelastic collisions. Furthermore, large molecules may facilitate the fast release of energy from the solute molecular anions and radicals and thus prevent them from disintegrating into very small non-detectable fragments.

Figure 25

Chromatograms obtained from the second
detector for 200 pg of pentachloronitrobenzene
injected into the first column with N_2 vs
N_2/iso-octane as the carrier gas. Chromato-
graphic conditions: column temperature (1) 190°,
column temperature (2) 115°. Flow rate 30 ml/min.
Second detector operated in pulse mode with pulse
width 10 us and pulse interval 300 us.

Nitrogen / iso-octane
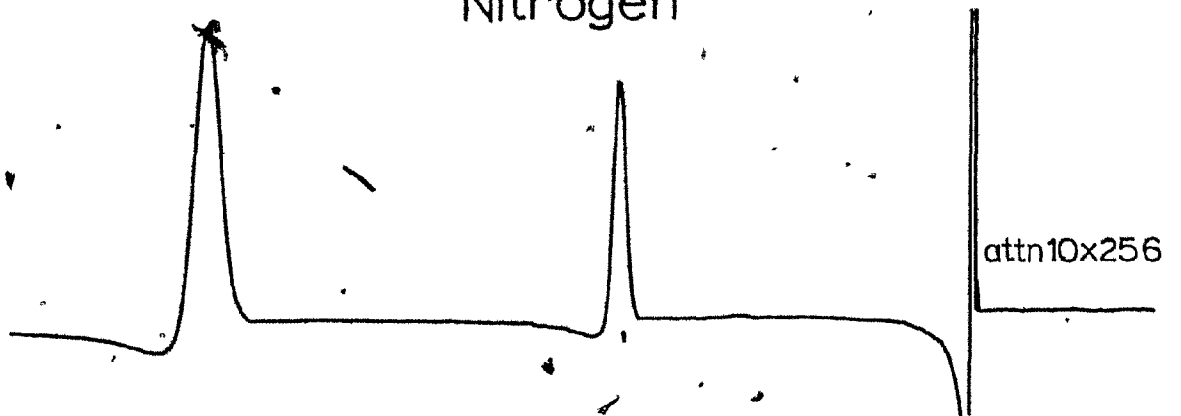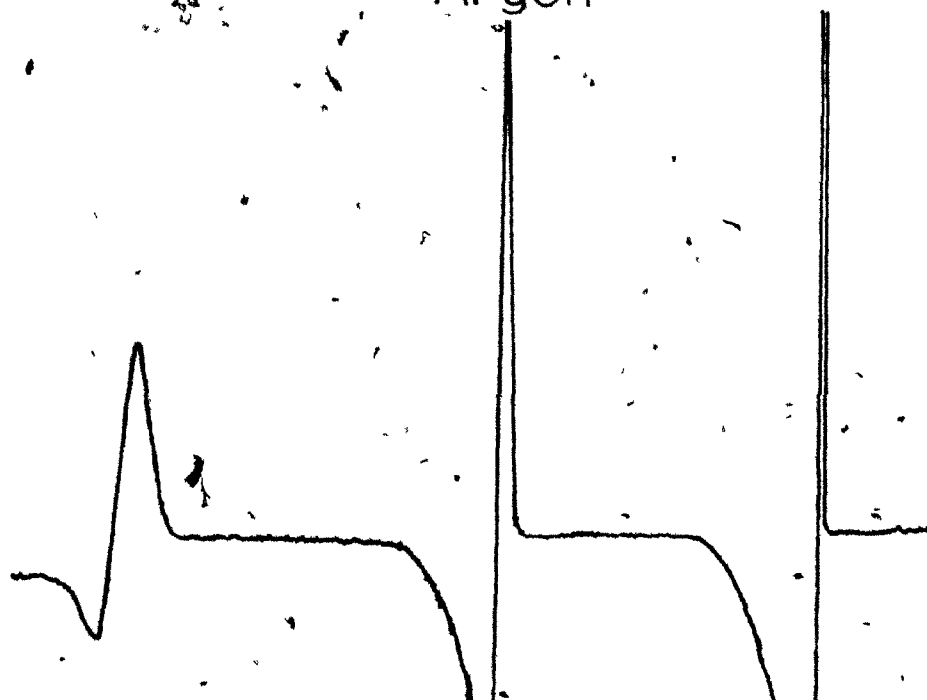
attn,10×128

Nitrogen

attn10×256
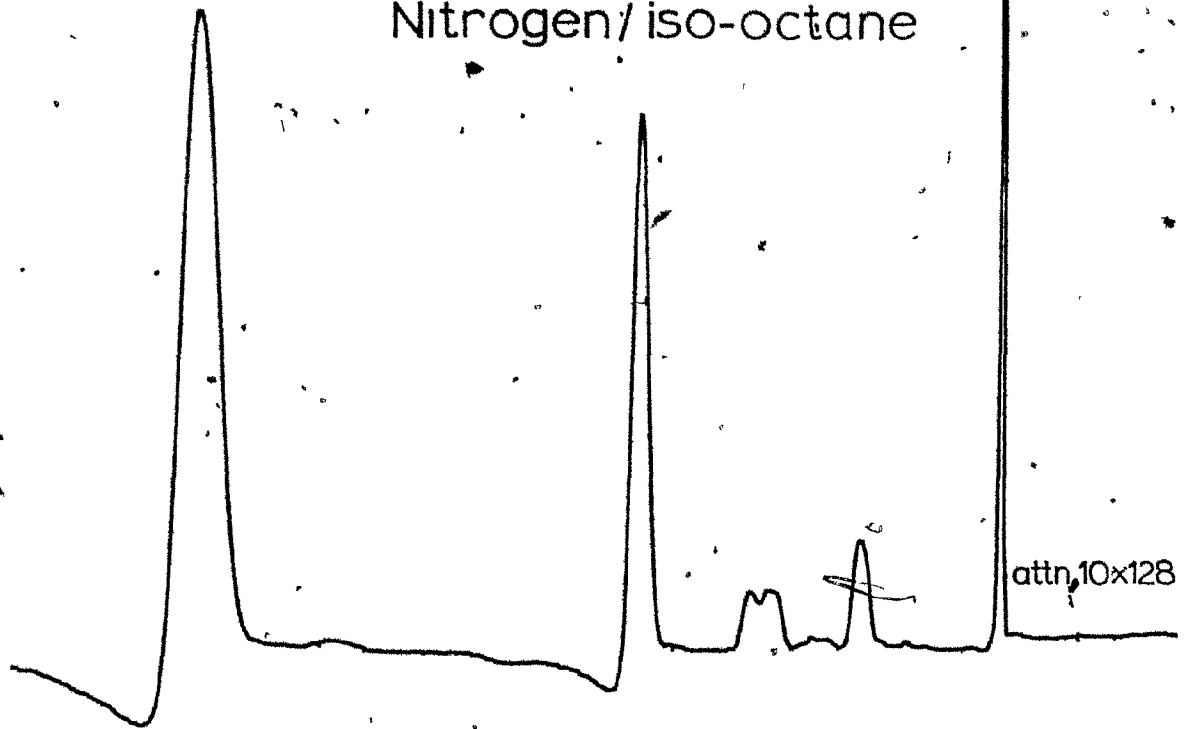
Figure 26

Chromatograms obtained from the second detector
for 200 pg of pentachloronitrobenzene with
Ar vs Ar/iso-octane as the carrier gas.
Chromatographic conditions as for Figure 25.
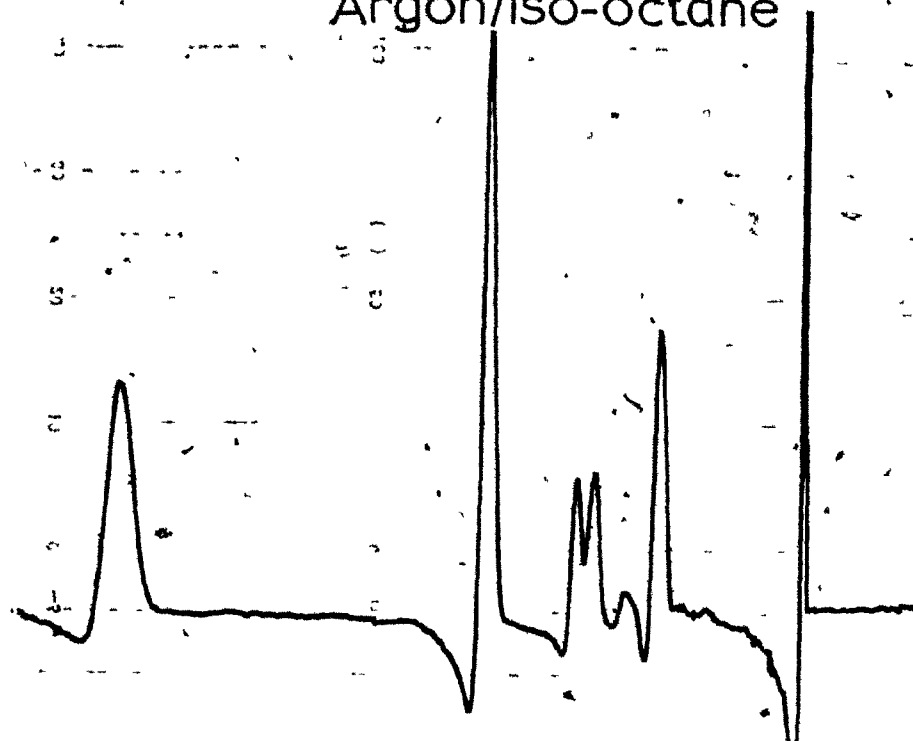
Argon

Argon/iso-octane

TABLE 1

Effect of Additives on the Electron Capture Products

Additive	Observations
Hydrogen	No changes in products or product patterns observed when added in small amounts ($< 1\%$), but large numbers of extraneous peaks, un-related to electron capture processes, were obtained, especially in case of hexachlorobenzene, lindane and δ-hexachlorocyclo-hexane, when H_2 was added in large quantities.
Water	No noticeable changes were observed. Very large amounts affected the detector response.
Carbon monoxide	No significant change in products or product patterns at low concentrations, response of EC-II was very low at higher concentrations.
Carbon dioxide	Same as for CO.
Ammonia	Response of EC-II was very low, no observation could be made.
Methane	Some changes in product patterns were noticed; a slight increase in smaller molecular weight products with lower retention times was observed.
n-Pentane	A somewhat greater increase in smaller molecular weight products than observed for methane.
n-Hexane	Same as for C_5H_{12}.
Hexanes	Same.
n-Heptane	Same.
Iso-Octane	Significantly larger product peaks were obtained for all test compounds.

TABLE 1 - continued

| Additive	Observations
2-Pentene	Same results as for CH_4 at low concentrations. Response of EC-II was significantly lower at higher concentrations.
Methanol	Same as for 2-pentene.
Acetonitrile	Same as for 2-pentene.

Effect of Temperature

In order to observe the effect of temperature on the electron capture process and product formation in the case of strong electron absorbers, the temperature of the detector/reactor (EC-1) was varied over a hundred degrees, i.e. 200-300°C. Three test compounds, 2,3,5,6-tetrachloronitrobenzene, pentachloronitrobenzene, and hexachlorobenzene, were injected into the gas chromatograph; the products and unreacted compound were then monitored by the second detector.

No significant change in the relative or absolute amount of product peaks and the parent compound peak was observed for any of the three test compounds. This was expected, since temperature has had little influence on EC response under normal analytical conditions. (It should be noted, though, that EC response was reported to show strong temperature dependence under conditions employed by Wentworth et al for physicochemical studies.[52,54] Figure 27 shows the chromatograms of products and unreacted tetrachloronitrobenzene observed in the second detector for two different temperatures of the first detector.

Figure 27

Chromatograms of products and unconsumed 2,3,5,6-
tetrachloronitrobenzene obtained in Detector 2,
with detector 1 at two different temperatures.
100 pg of the compound was injected. Carrier gas
N_2/iso-octane.

Compound   Products   B   280°

Compound   Products   A   210°
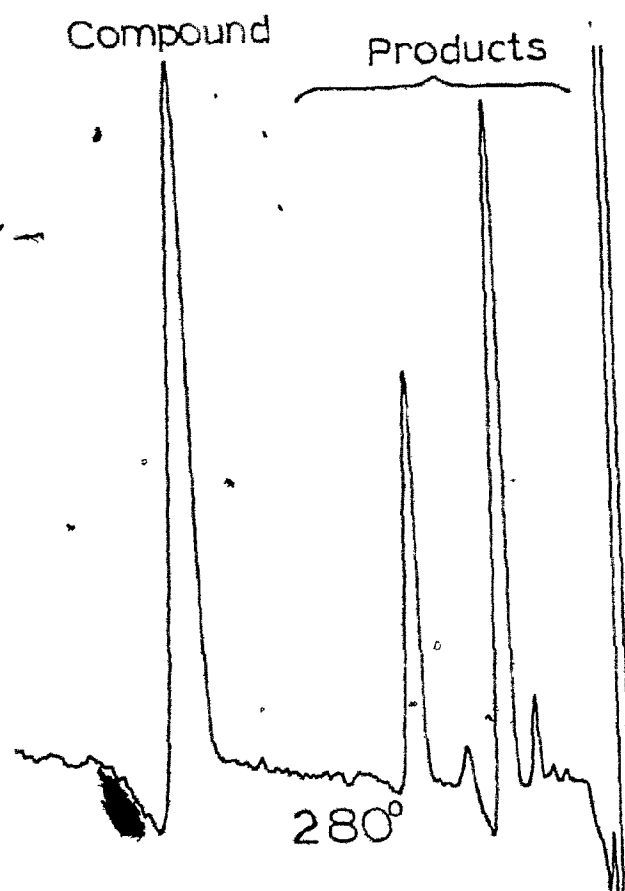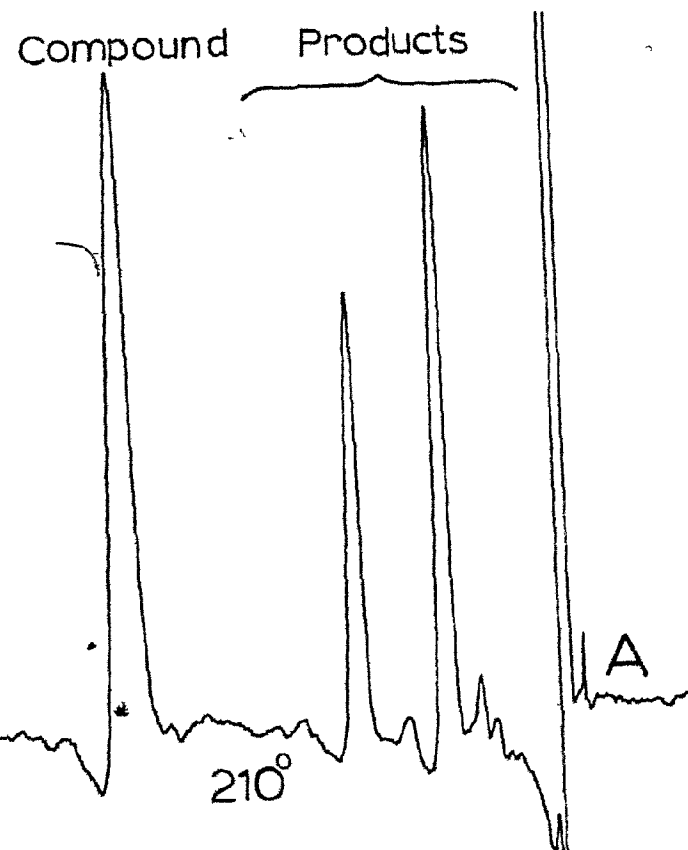
D. ## HIGH RESOLUTION SET-UP AND TENTATIVE IDENTIFICATION OF PRODUCTS

A limited attempt was made to identify some of the product peaks resulting from electron capturing reactions for a few selected compounds, viz. tetrachloronitrobenzene, pentachloronitrobenzene, hexachlorobenzene, 2,4,6-trichloronitrobenzene, tetrachlorobenzenes, chloronitrobenzene, hexachloroethane and tetrachloroethane. The attempt had to be limited because of the numerous problems associated with identification of unknown substances by retention time data only, which was further complicated by the rigid requirements of EC-GC. Thus the identifications are at best tentative. Positive identification of the products would require elaborate structural analysis techniques, which in the author's opinion is rather difficult considering the fact that the amount of sample (products) available is a few picograms at best, which is well below the detection capability of most analysis techniques. The only technique that could possibly be used directly is atmospheric ionization mass-spectrometry with extensive signal conditioning by computers as used by Horning and coworkers.[123]

A high resolution set-up shown in Figure 4 was constructed. The first column was placed in a separate isothermal column bath, so that the second column could be operated at a considerably lower temperature to facilitate the separation of more volatile products. Special effort

was made to reduce the dead volume of the system to
minimize the peak spreading; towards this end the Tracor
^{63}Ni EC detector was replaced by a modified coaxial ^{63}Ni EC
reactor/detector of our own design.

Argon doped with iso-octane was used as the carrier
gas. Standard compounds suspected to be identical to the
products were injected and their retention time in the second
column was compared to that of the products resulting from EC
reactions. This approach required some speculation as to the
identity of the products and the mechanism of their formation.
It was assumed that products are formed, either by dissocia-
tion of the molecular radical anion in the gas phase or by
dissociation of these anions on the cell wall. Products re-
sulting from neutralization may be too small to be detected
by the second detector. Dissociation of chlorinated hydro-
carbon ions is believed to result in the formation of halide
ions and radicals. Chloride ions have been observed in some-
what similar conditions by Karasek and coworkers in plasma
chromatography.[120] Recently Horning's group has observed
phenoxy ions under conditions close to plasma chromatography
with compounds such as hexachlorobenzene and pentachloro-
nitrobenzene when very small amounts of oxygen were present.

The identification of products was further compli-
cated by non-availability of a number of compounds of interest.
Results based on retention time data only are summarized as
follows in Table 2. These results, though error prone, seem

to indicate that the products in most cases are formed by loss of halogen(s) and the nitro group. In the case of aromatics, the ring stays intact. Loss of the nitro group is quite surprising; available data from plasma chromatography and atmospheric ionization mass-spectrometry do not show this loss. Figures 28 and 29 show the chromatograms obtained for tetrachloronitrobenzene and pentachloronitrobenzene, respectively. The retention time of the major product peaks obtained from 2,3,5,6-tetrachloronitrobenzene and separated in the second column corresponds to that of 1,2, 4,5-tetrachlorobenzene; similarly, the retention time of the major product peak in case of pentachloronitrobenzene corresponds to pentachlorobenzene. For pentachloronitrobenzene the other product peaks (P_1, P_2 and P_3) correspond to the product peaks (P_1', P_2' and P_3') obtained for pentachlorobenzene. This seems to support the assumption that the major product for pentachloronitrobenzene is pentachlorobenzene; similar results were obtained for tetrachloronitrobenzene-tetrachlorobenzene and trichloronitrobenzene-trichlorobenzene. In the case of 2,4,6-trinitrotoluene parent molecules were consumed in the first detector but no electron capturing products were observed (Fig. 30). This observation also seems to support the view that the nitro group is in fact removed with relative ease in the electron capture reaction.

The reactions which are possibly involved in electron capture product formation in the case of nitro and halo com-

Figure 28

      Chromatograms of tetrachloronitrobenzene and

      tetrachlorobenzene obtained in (----) Detector 1.

      Chromatograms of products and unconsumed parent

      compound obtained in (_____) the second detector.

      Chromatographic conditions as in Figure 25.

      Carrier gas Ar/iso-octane. p, p_1 and p_1' are

      product peaks.

      Note: Dark arrow marks passage of parent compound

              through Detector 1, i.e. it indicates

              beginning of retention time scale for

              column 2.
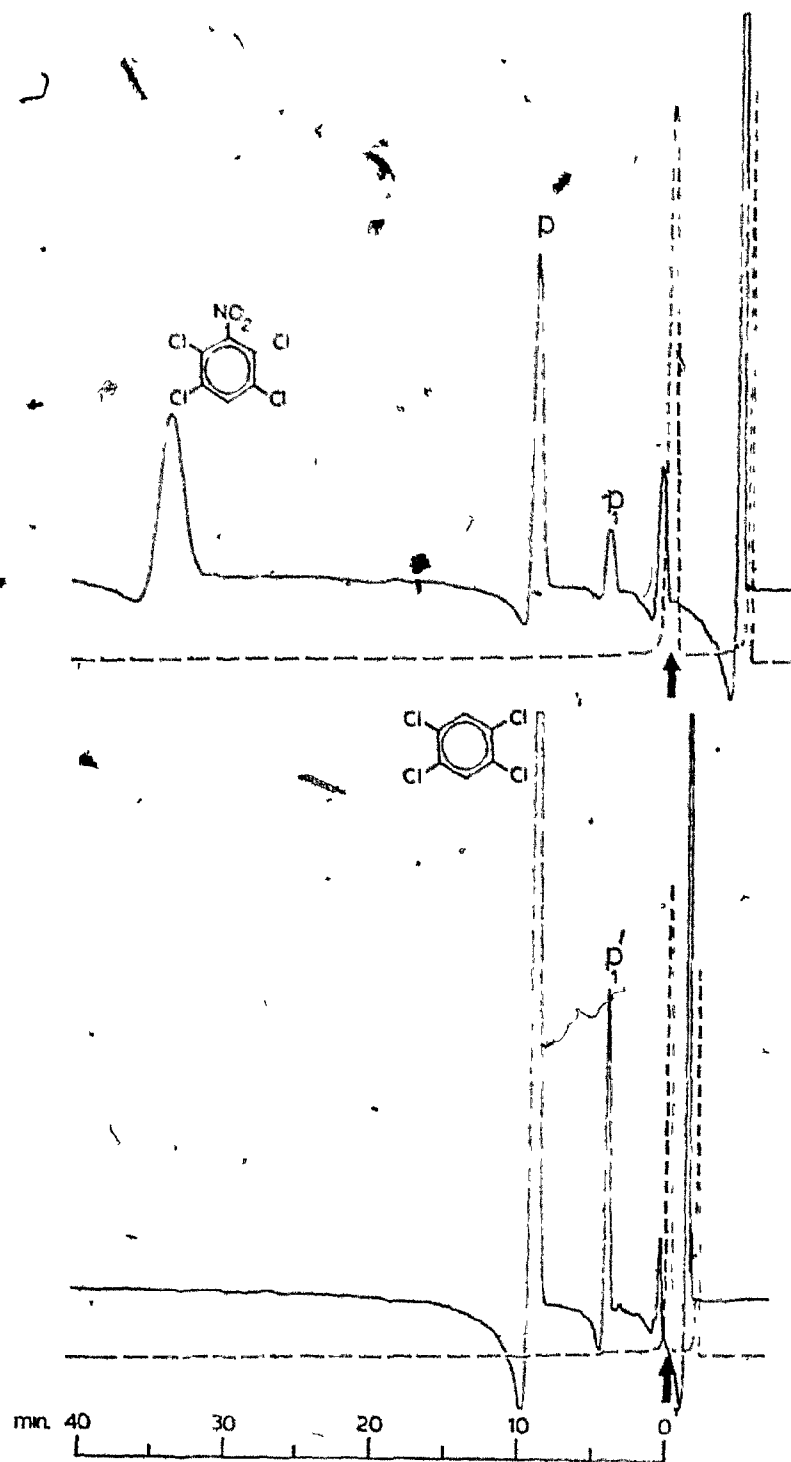
min. 40   30   20   10   0

Figure 29

Chromatograms similar to those in Figure 28,
obtained for pentachloronitrobenzene and pen-
tachlorobenzene. Chromatographic conditions as
in Figure 25, carrier gas Ar/iso-octane. P, P_1, P_2,
P_3, P_1', P_2' and P_3' are product peaks.

Note: Dark arrow marks passage of parent compound
through Detector 1, it indicates the
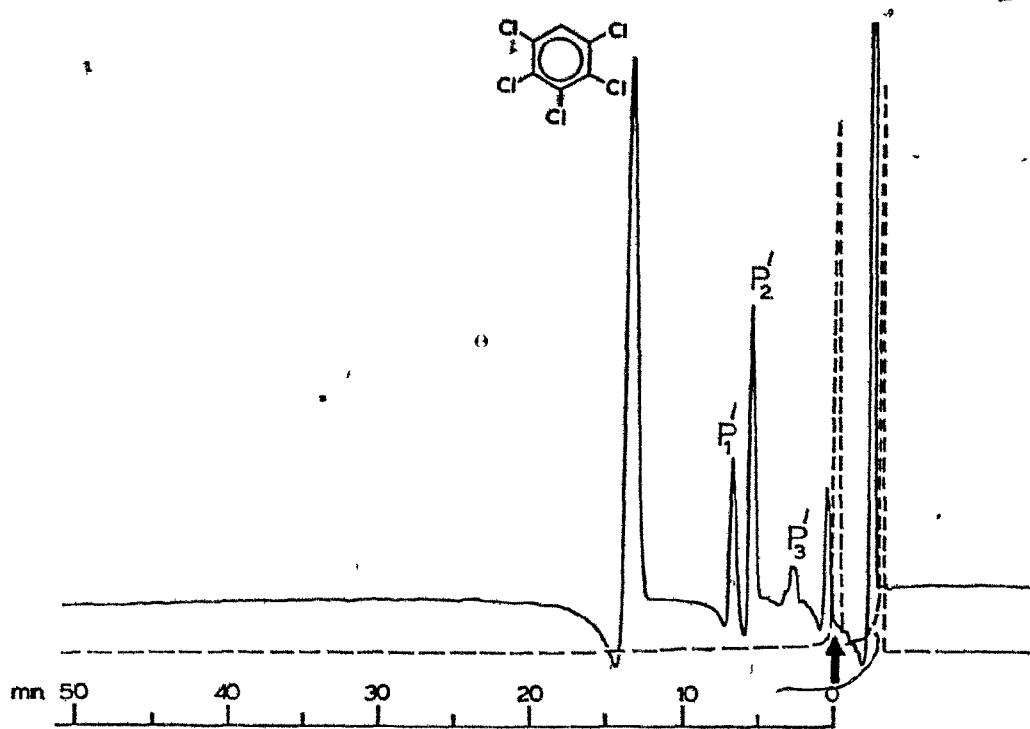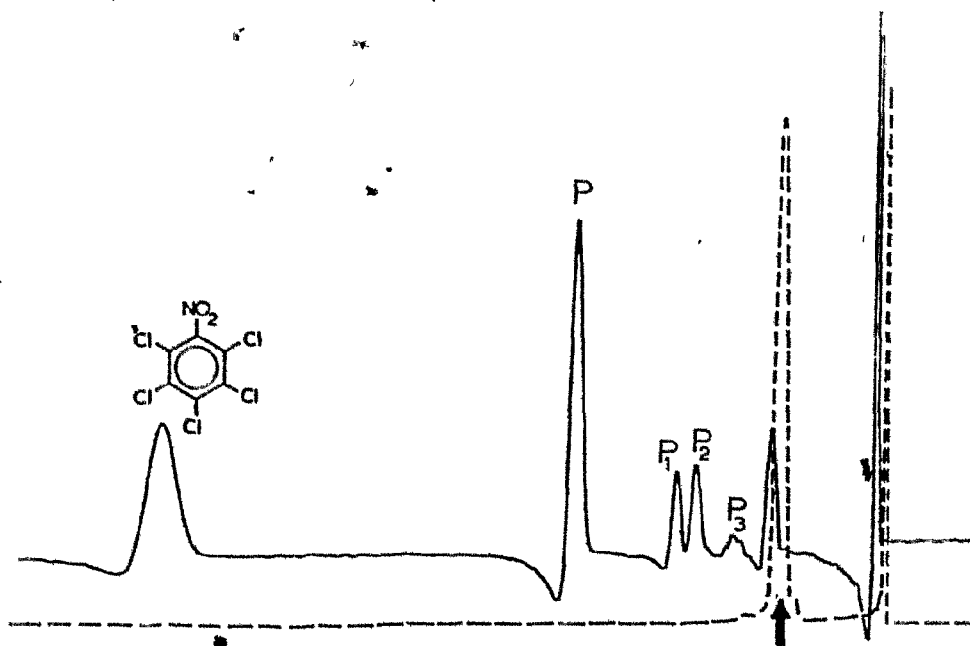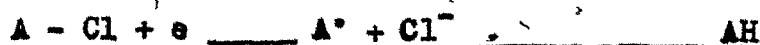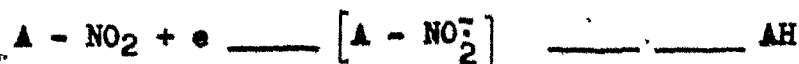beginning of retention time scale for
column 2.

TABLE 2

Possible Electron Capture Products*

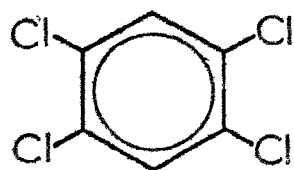| Compound	Possible Products
2,3,5,6-tetrachloronitrobenzene	1,2,4,5-tetrachloro-benzene, 1,2,4-trichlorobenzene, Chlorobenzene
Pentachloronitrobenzene	Pentachlorobenzene, 1,2,3,4-tetrachloro-benzene, 1,2,3,5-tetrachloro-benzene, 1,2,3-trichlorobenzene, Chlorobenzene
Hexachlorobenzene	Pentachlorobenzene, Chlorobenzene
1,2,4,5-tetrachlorobenzene	1,2,4-trichlorobenzene, Chlorobenzene
1,2,3,4-tetrachlorobenzene	1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, Chlorobenzene
1,2,3,5-tetrachlorobenzene	1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene
Hexachloroethane	Tetrachloroethane, Tetrachloroethylene
Chloronitrobenzene	Chlorobenzene

* Compounds whose retention time corresponds to that of
product peaks.

pounds may be summarized as follows:

$$A - NO_2 + e \underline{\hspace{1cm}} \left[A - NO_2^- \right] \underline{\hspace{2cm}} AH$$

$$A - Cl + e \underline{\hspace{1cm}} A^\cdot + Cl^- \underline{\hspace{2cm}} AH$$

On the basis of such 'product spectrum', identification of compounds even at ultra trace levels seems possible. Identification of the isomers at trace levels, even with elaborate techniques such as GC-mass spectrometry, is rather difficult. Complex mixtures could also be identified by their distinctive product patterns; Figure 31 shows the chromatograms of Aroclor 1254 (mixture of chlorinated biphenyls) with and without undergoing electron capture reactions. Hydrogen required for the formation of these products is obtained either from the traces present in the carrier gas or the column bleed or both.

In addition to the identification of products the other main objective of the high resolution set-up was to explore the feasibility of finger printing compounds of environmental interest. Encouraging results were obtained for a few selected compounds. Figures 32 and 33 show such fingerprints obtained for the isomers of hexachlorocyclohexane and tetrachlorobenzene. Peaks in the 'product spectrum' of tetrachlorobenzenes had retention times similar to 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene and 1,3,5-trichlorobenzene. As would be expected 1,2,4,5-tetrachlorobenzene gave just one trichlorobenzene, 1,2,3,4-tetrachlorobenzene gave two trichlorobenzenes, and 1,2,3,5-tetrachlorobenzene gave three trichlorobenzenes.

1,2,4,5-tetrachlorobenzene   − Cl →   1,2,4-trichlorobenzene
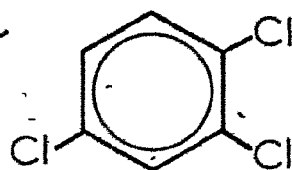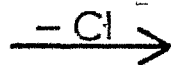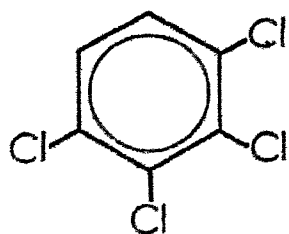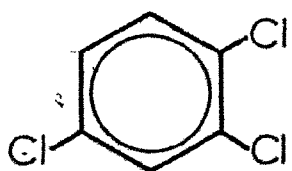
1,2,3,4-tetrachlorobenzene   − Cl →   1,2,4-trichlorobenzene   1,2,3-trichlorobenzene
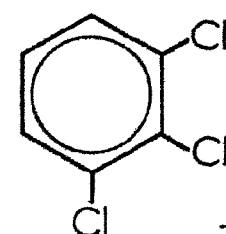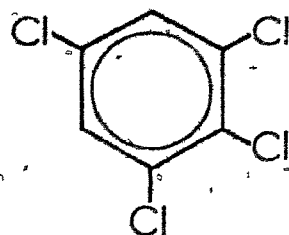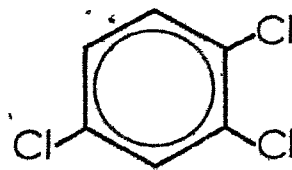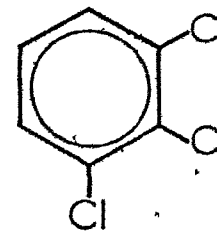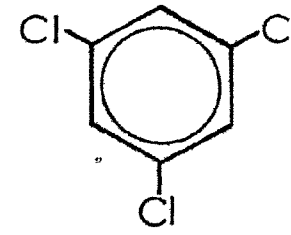
1,2,3,5-tetrachlorobenzene   − Cl →   1,2,4-trichlorobenzene   1,2,3-trichlorobenzene   1,3,5-trichlorobenzene

Figure 30

Chromatograms of 150 pg 2,4,6-trinitrotoluene
from the second detector, with the reactor 'on'
and 'off'. No products observed. Column
temperatures 200° and 135°. Carrier gas
Ar/iso-octane.

Trinitrotoluene

Reactor Off

attn 10 x 128

Reactor On

attn 10 x 128

84
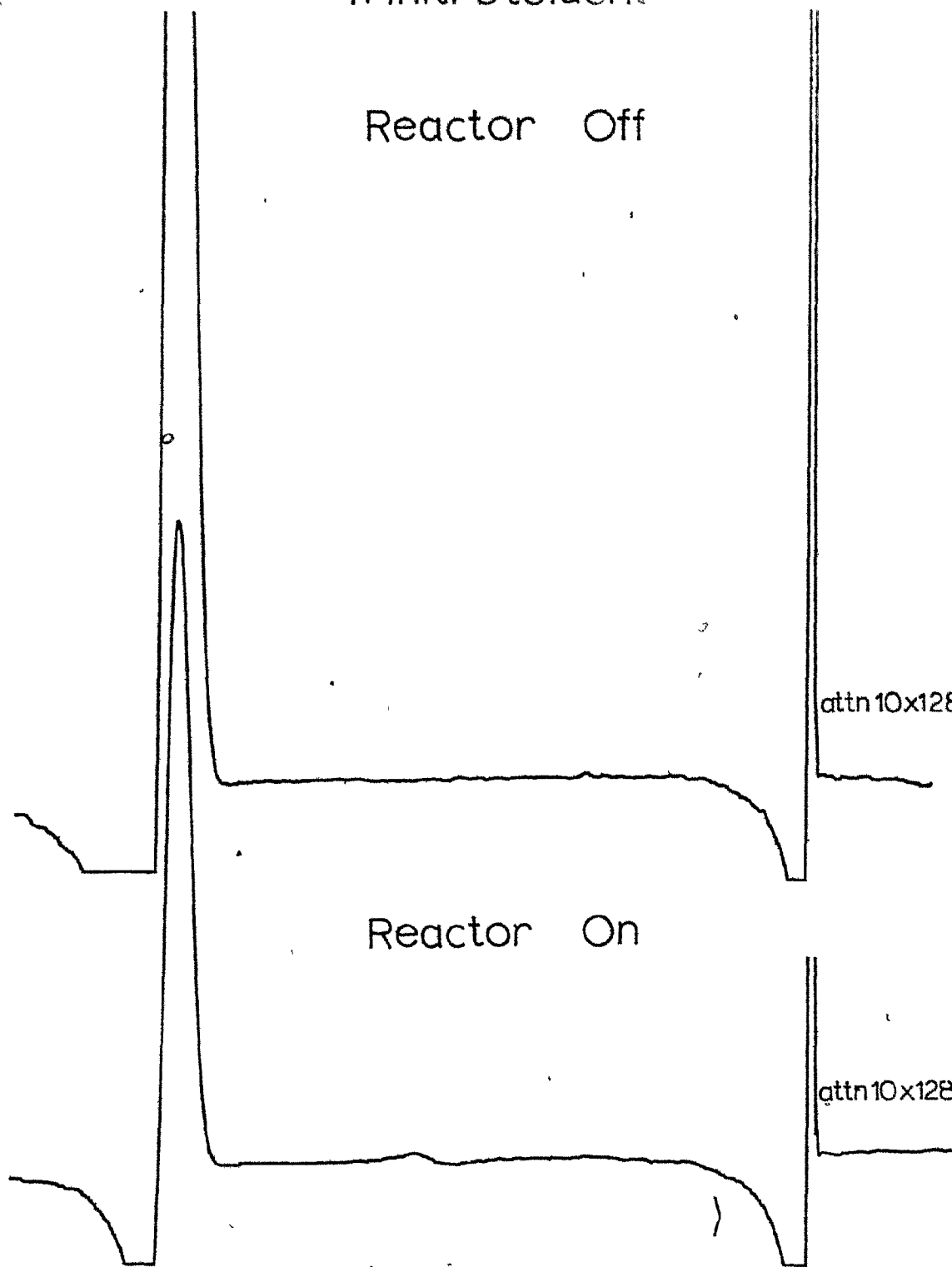
Figure 31

Chromatograms of 2 ng of Aroclor 1254 from
the second detector. Upper trace obtained with
the reactor (EC-1) 'on' and lower one with the
reactor 'off'. Column temperatures 200° and 135°.
Carrier gas Ar/iso-octane.

The early peaks seen only in the upper trace are
products.

AROCLOR 1254
Reactor "On"

AROCLOR 1254
Reactor "Off"

hrs. 3

2

1

0

A

B
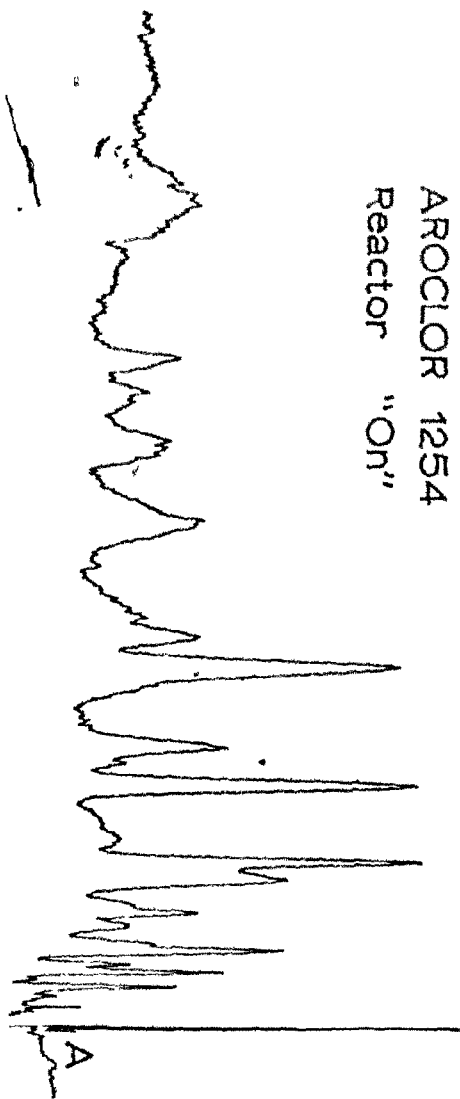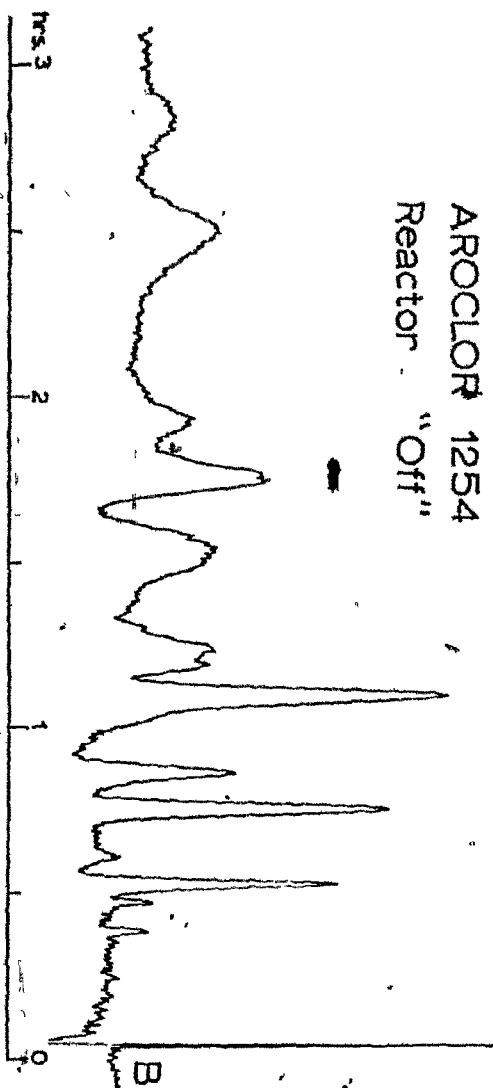
Figure 32

Chromatograms obtained for 200 pg of
hexachlorocyclohexane isomers and their
electron capture products. Chromatographic
conditions as in Figure 25.
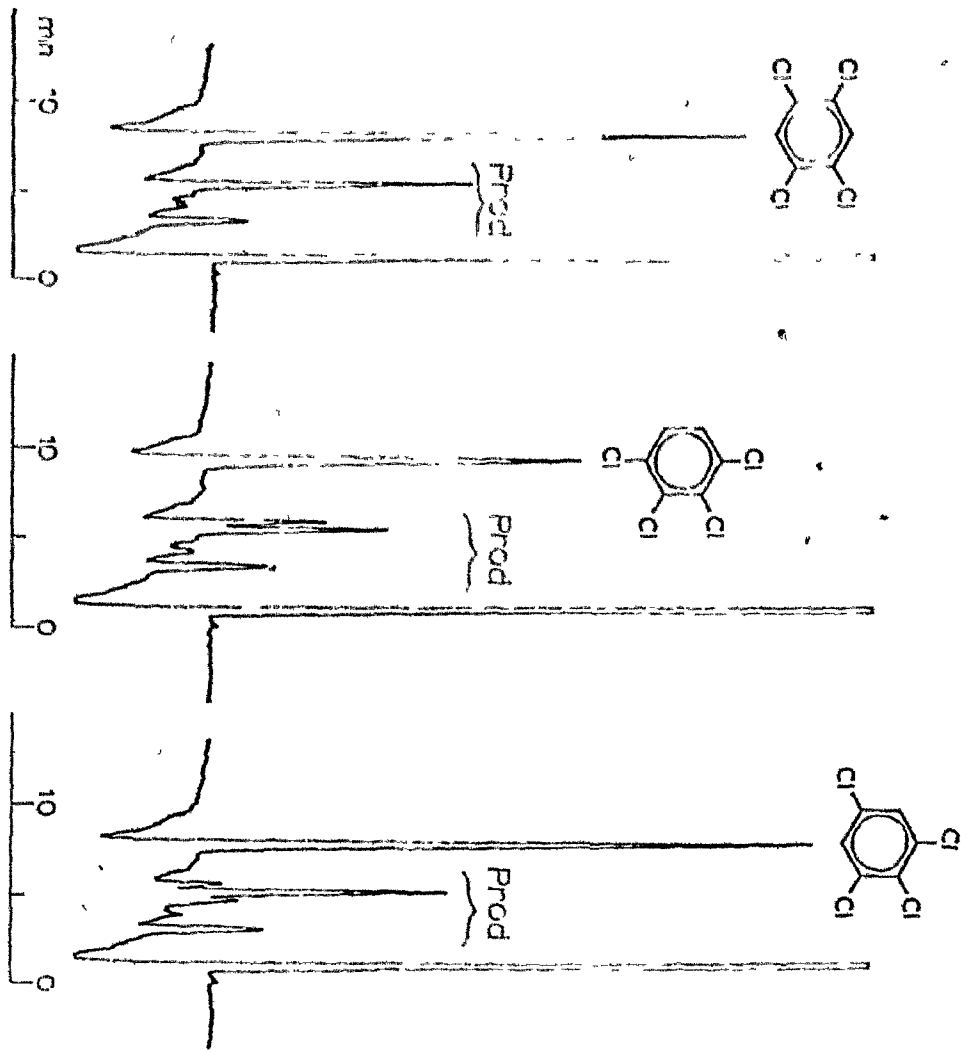
Figure 33

Chromatograms of tetrachlorobenzene isomers
and their products obtained in the second
detector. 250 pg of the compounds injected
into the first column. Chromatographic
conditions: 1st column temperature 170°, 2nd
column temperature 105°. Other conditions as
in Figure 25.
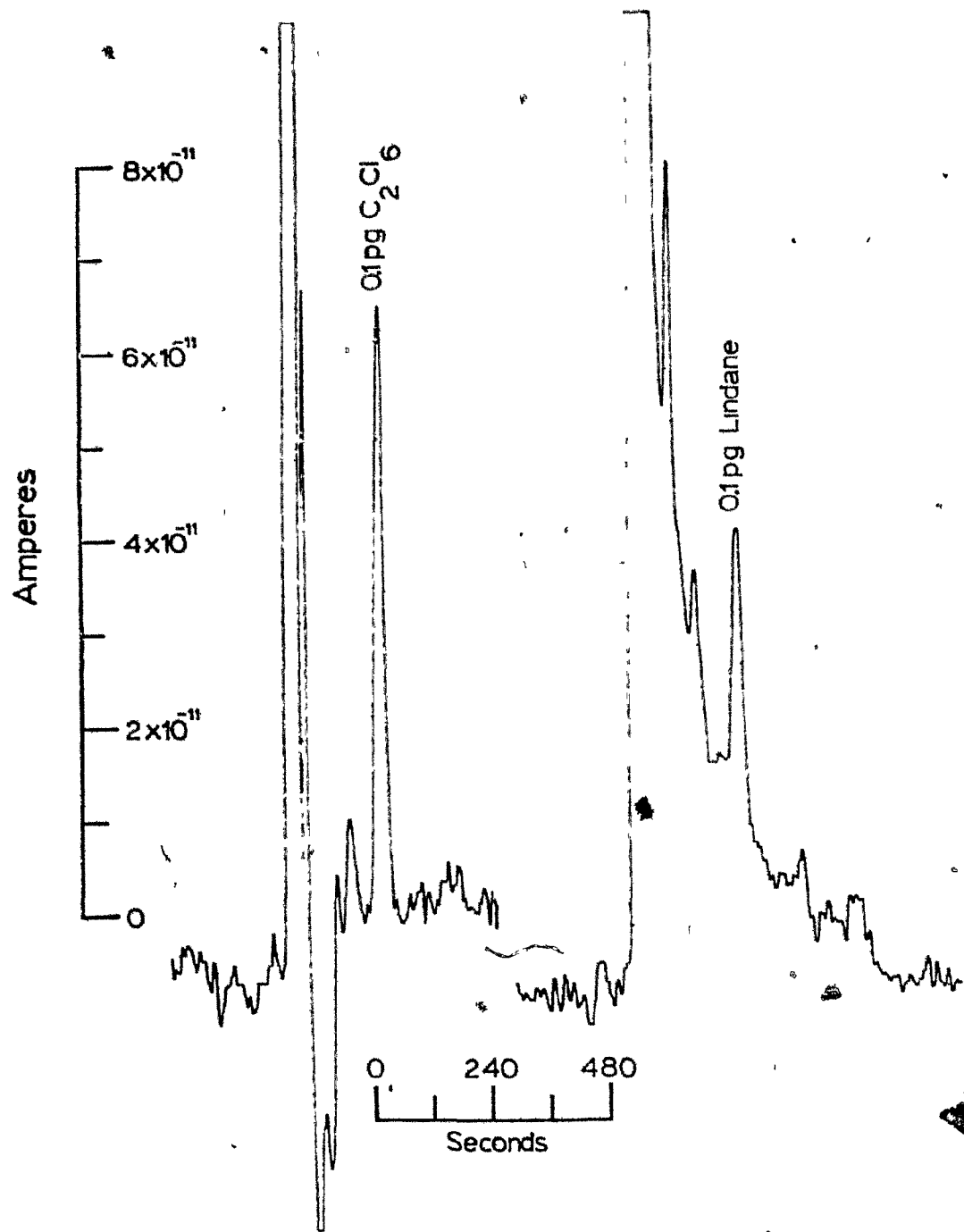
E.   <u>HYPERCOULOMETRIC RESPONSE AND EFFECT OF PRESSURE</u>

During the preliminary product studies, it was observed that at optimum voltage, the response of the first detector was often quite high. At low concentrations calculations of electrons/molecule (Faradays/mole) ratios showed that these values were well beyond the assumed limit of $1.^{104}$ Values as high as 40 were found for certain compounds in small amounts. Measurements of e/m ratios (Faraday peak area/moles injected) at low concentrations are, of course, prone to a number of errors, some of which are difficult to avoid.

Too high an e/m ratio could arise from faulty and/or impure standard solutions, improper calculations, and faulty instruments (primarily electrometers and recorders). None of these should be excessive.

Too low an e/m value could be caused by all of the above plus decomposition in injection port, column or transfer lines, an all too common problem which is rather difficult to diagnose and remedy. Thus, though the accuracy of measurement may not be too high, results should, if anything, tend toward the low side.

Special efforts were made to minimize the problems mentioned above; standards were prepared by other graduate students in the group; electrometers and recorders of three different makes were employed, and the calculations were thoroughly rechecked. Consistently high e/m values were

still obtained. Table 3 shows the ratios obtained for various compounds at different levels of concentration.

The sensitivity of an EC detector under these conditions was found to be very high, as illustrated in Figure 34 with two typical peaks for 0.1 pg of hexachloroethane and lindane. The minimum detectable amount of the former was found to be 1×10^{-14} g (an injection of 20 fg (femtogram) of C_2Cl_6 gave a peak four times higher than the noise); however, the response was found to be linear only up to about 10 pg levels, as shown in Figure 35.

A close examination of the set-up pointed out that since the first detector was located before the second column the 'hypercoulometric' response of this detector is somehow related to the elevated pressure inside the detector cell. As a convention, electron capture detectors operate at ambient pressure. It is not uncommon, however, that an ECD operates under some slight overpressure - be it that the exit line offers some impedance to the flow or be it that such resistance is deliberately introduced to prevent back diffusion of atmospheric oxygen.

To the author's knowledge there has been no mention of the effect of pressure on the response of an ECD. The only study related to pressure is that of Scolnick, in which the effect of pressure on standing current is described.[97] It was reported that the standing current increases with an increase in pressure. The measurements were made in a concentric ^{3}H ECD with pressure ranging from 1 to 1.3 atmospheres.

Table 3

RELATIVE EC RESPONSE

Compound		e/m Ratios		
Amount Injected	1 ng	100 pg	10 pg	1 pg
Tetrachloroethylene	-	0.7	3.6	6.5
1,1,2,2-tetrachloroethane	-	1.3	2.2	-
1,1,2,2-tetrabromoethane	-	4.0	12.0	14.0
Hexachloroethane	-	-	16.0	25.0
Hexabromoethane	-	4.7	17.0	26.0
Octachloropropane*				
3-chloro-1,2-propanediol	0.04	-	-	-
1,4-dibromobutane	-	0.1	-	-
1,2,3,4-tetrabromobutane	-	-	12.0	13.0
Pentachloroethyl ether	-	9.5	22.0	24.0
Diethyl fumarate	0.003	-	-	-
Octachlorocyclopentene	-	2.5	4.0	-
Chlorocyclohexane	0.025	-	-	-
Bromocyclohexane	0.04	-	-	-
α-hexachlorocyclohexane	-	-	5.0	7.0
β-hexachlorocyclohexane	-	2.5	6.2	7.6
γ-hexachlorocyclohexane (Lindane)	-	-	13.0	17.0
δ-hexachlorocyclohexane	-	3.6	14.0	21.0
Nitrobenzene	0.02	-	-	-
Chlorobenzene	0.03	-	-	-
Bromobenzene	0.06	0.07	-	-

Table 3 continued

Compound	e/m Ratios			
Amount Injected	1 ng	100 pg	10 pg	1 pg
Benzyl chloride	0.08	0.15	-	-
m-dinitrobenzene	-	0.65	0.8	-
o-dinitrobenzene	-	0.7	0.8	-
o-chlorophenol	0.01	-	-	-
p-bromophenol	0.02	-	-	-
o-nitroaniline	0.09	0.13	-	-
o-fluoronitrobenzene	-	0.5	0.8	-
o-chloronitrobenzene	-	1.6	3.5	3.8
m-chloronitrobenzene	-	1.5	2.8	3.0
p-chloronitrobenzene	-	1.0	1.6	2.0
o-bromonitrobenzene	-	1.5	5.5	8.5
o-iodonitrobenzene	-	4.0	8.0	8.0
4-chloro-2-nitroaniline	-	2.2	3.6	4.0
2,5-dichloroaniline	0.03	0.04	-	-
2,6-dichloro-4-nitroaniline (Dichloran)	-	4.0	5.0	4.7
2,3,5,6-tetrachloronitrobenzene (Tecnazene)	-	3.0	19.0	32.0
Pentachloronitrobenzene (Quintozene)	-	4.2	13.0	25.0
Hexachlorobenzene	-	-	7.0	11.0
Hexabromobenzene	-	8.0	9.0	14.0
2,4,6-trinitrotoluene	-	-	5.8	5.9

Table 3 continued

Compound	e/m Ratios			
Amount Injected	1 ng	100 pg	10 pg	1 pg
a,a,a',a',2,3,5,6-octachloro-p-xylene*	-	2.0	-	-
Heptachlor	-	-	11.0	15.0
Aldrin	-	-	14.0	17.0
Heptachlor Epoxide	-	-	16.0	17.0
Dieldrin	-	7.4	13.0	15.0
p,p'-DDT*	-	3.4	3.0	-
Decachlorobiphenyl	-	4.3	7.4	-
Methyl parathion	-	-	1.5	2.3
Tetraethyl Lead	-	0.5	-	-

* Extensive decomposition obvious from chromatogram.

Amperes

8×10^{-11}

6×10^{-11}

4×10^{-11}

2×10^{-11}

0

0.1pg C_2Cl_6

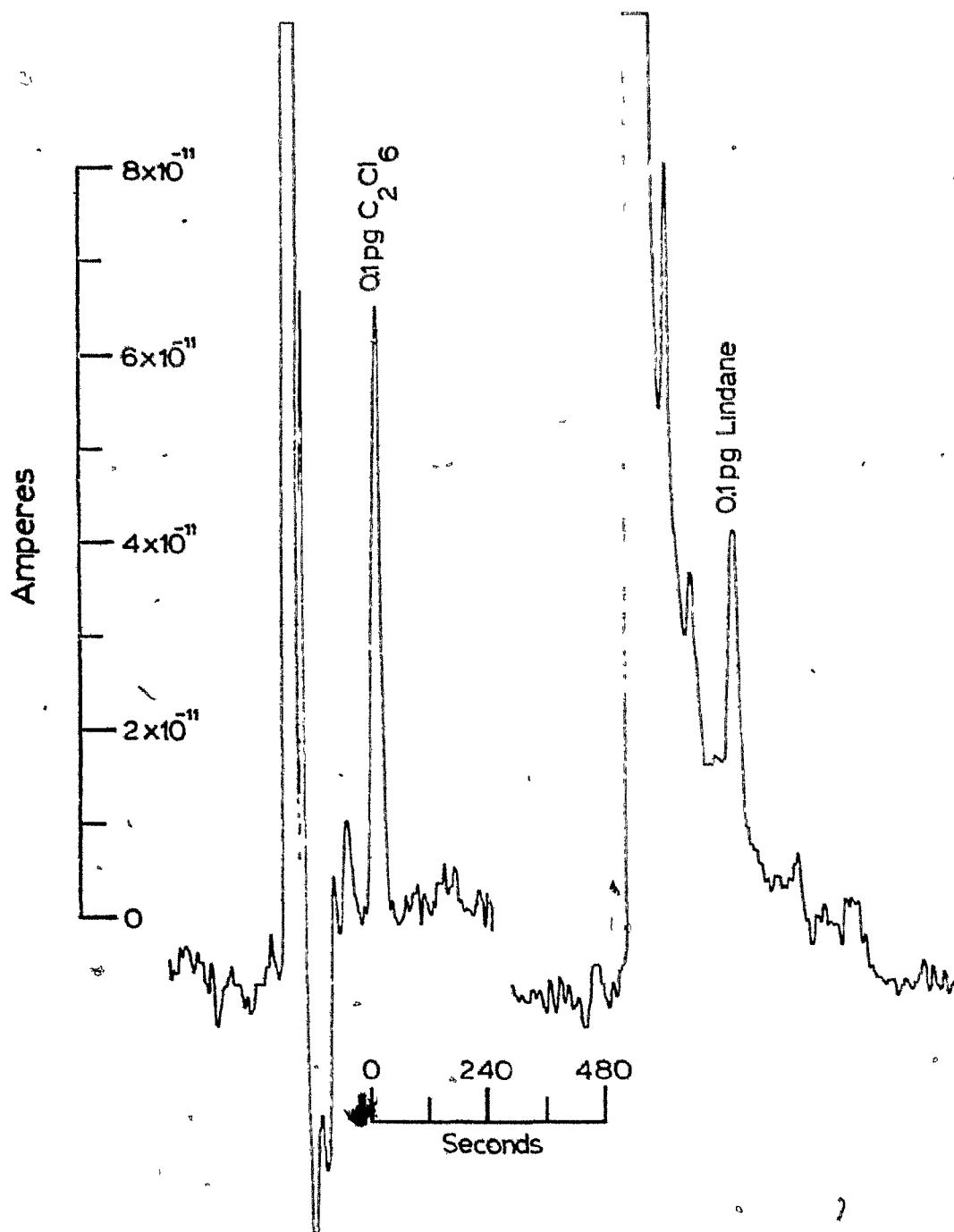0.1pg Lindane

0   240   480

Seconds

92

Figure 34

Chromatograms of two test compounds at the
0.1 pg level. Column temperatures:
hexachloroethane, 90°; lindane, 190°.

93
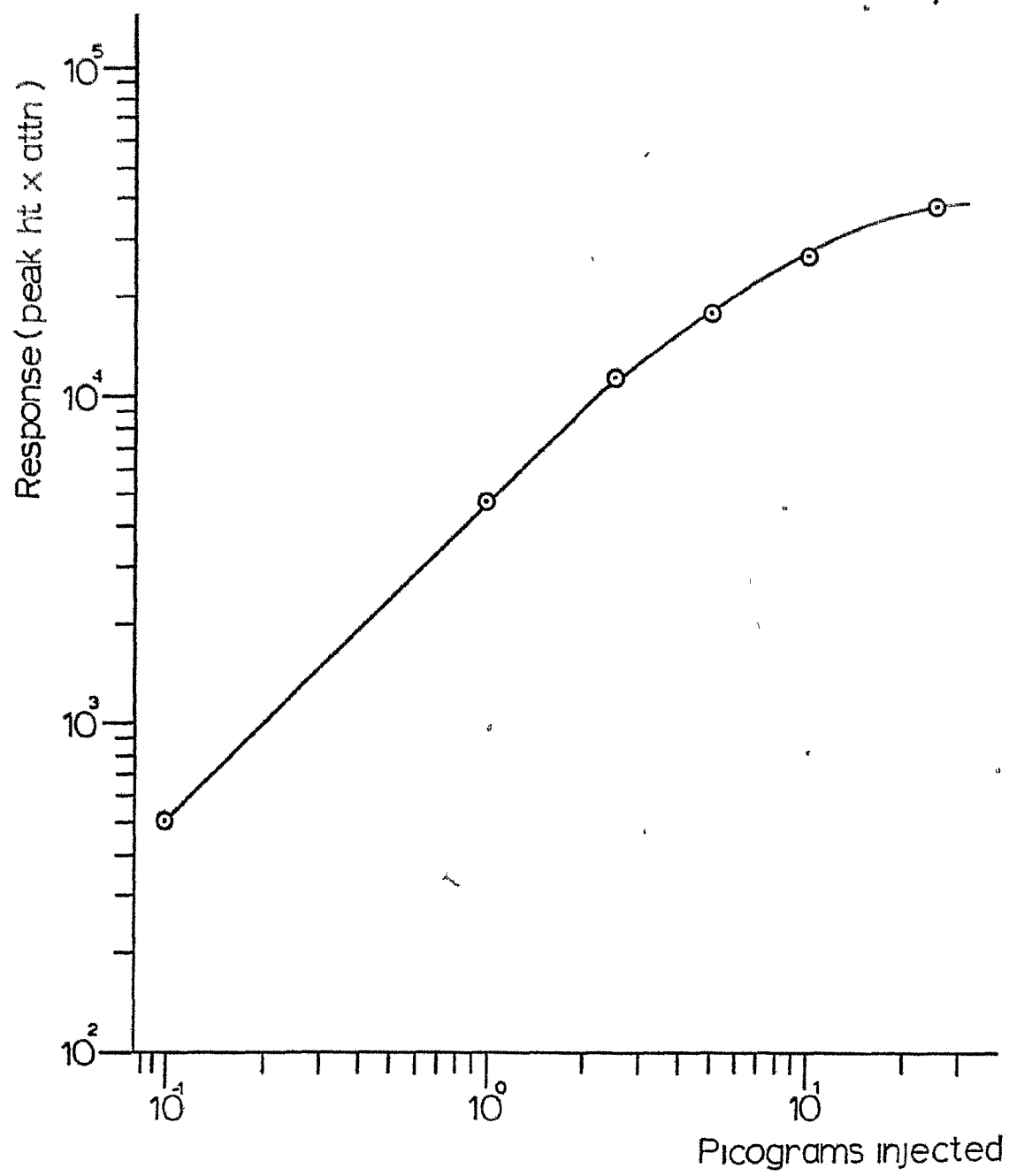
Figure 35

Calibration curve for 2,3,5,6-tetrachloronitro-
benzene obtained from the ECD operating at 25
psi overpressure. Column temperature 160°.
Carrier gas N_2.
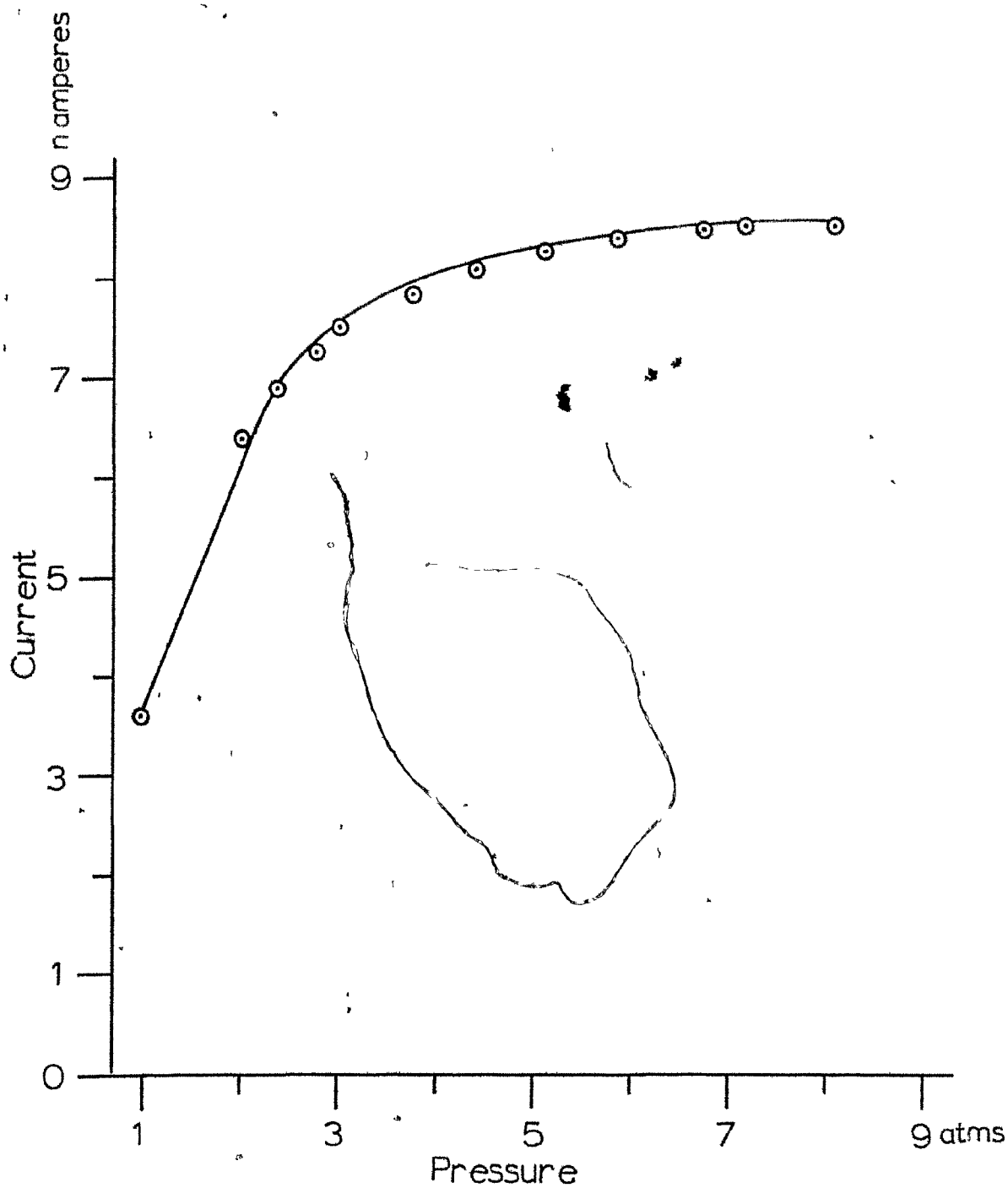
In accordance with Scolnick's results an increase in the number of charge carriers (background current) was observed with an increase in pressure until a plateau was reached; Figure 36 illustrates these results. These data were obtained after removing the chromatographic column.

Voltage profiles obtained at different pressures are shown in Figure 37. These reveal that as the pressure increases, the number of charge carriers and voltage necessary to collect them increases as well. This would be expected because an increase in pressure results in an increase in the probability of recombination of the thermal electrons and cations.

The increase in background current can be attributed to the increase in the efficiency of ionization resulting from the decrease in the range of β particles. β particles (^{63}Ni) travel up to 6-8 mm in nitrogen (at atmospheric pressure). Thus in a Tracor ^{63}Ni electron capture detector with a cell cavity of ~7 mm diameter, an appreciable portion of the β particles are lost before they lose their energy via ionization. With an increase in pressure the number of collisions between β particles and the carrier gas molecules increases resulting in an increase in the number of ion pairs. This conclusion was confirmed with the observations made on two detectors of similar design containing ^{63}Ni and ^{3}H foils. As expected,

Figure 36

Graph showing the effect of pressure on the background current obtained in a Tracor ^{63}NI ECD. Data were obtained without a chromatographic column.
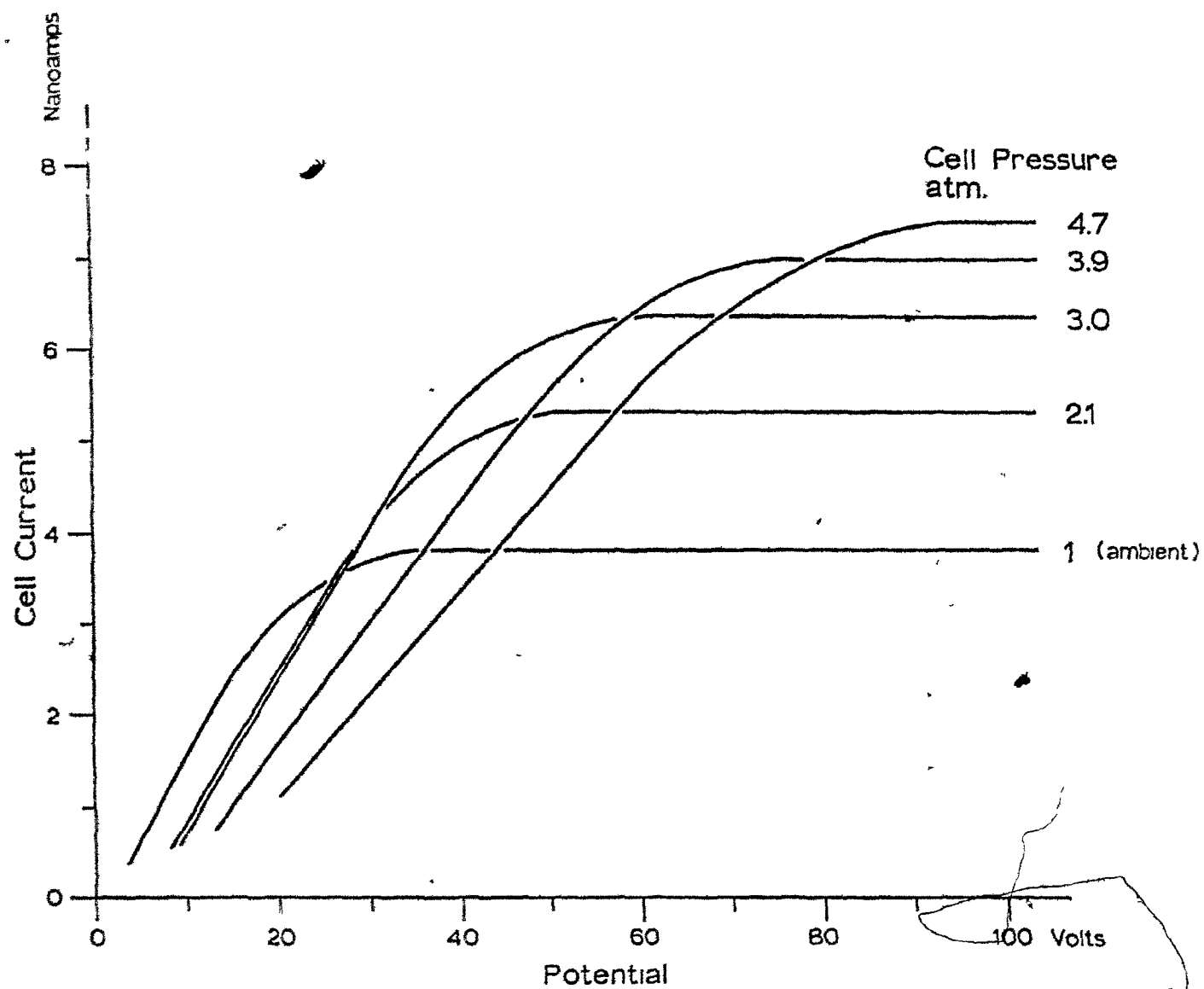
Figure 37

'Voltage profiles' at different pressures.
Negative potential applied to the upper
electrode of a Tracor ^{63}Ni ECD.

10 n amps

Cell Current

8

6

4

2

0

${}^{3}H$
95mC

${}^{63}Ni$
15mC

1 2 3 4 atms.

Cell Pressure
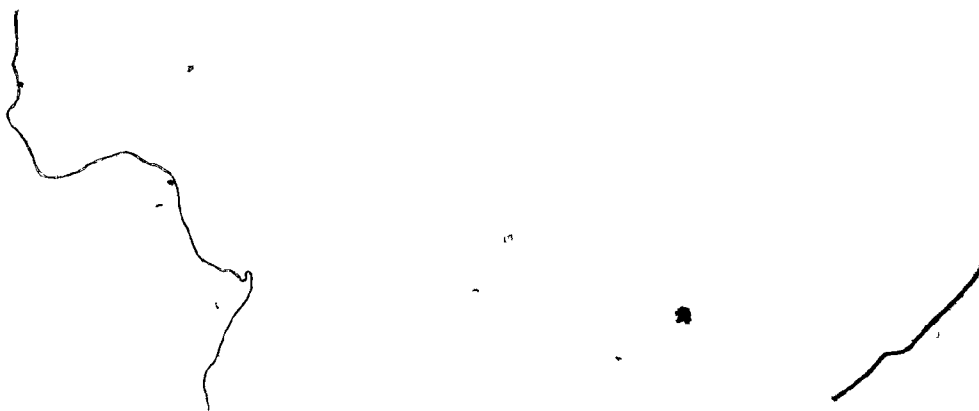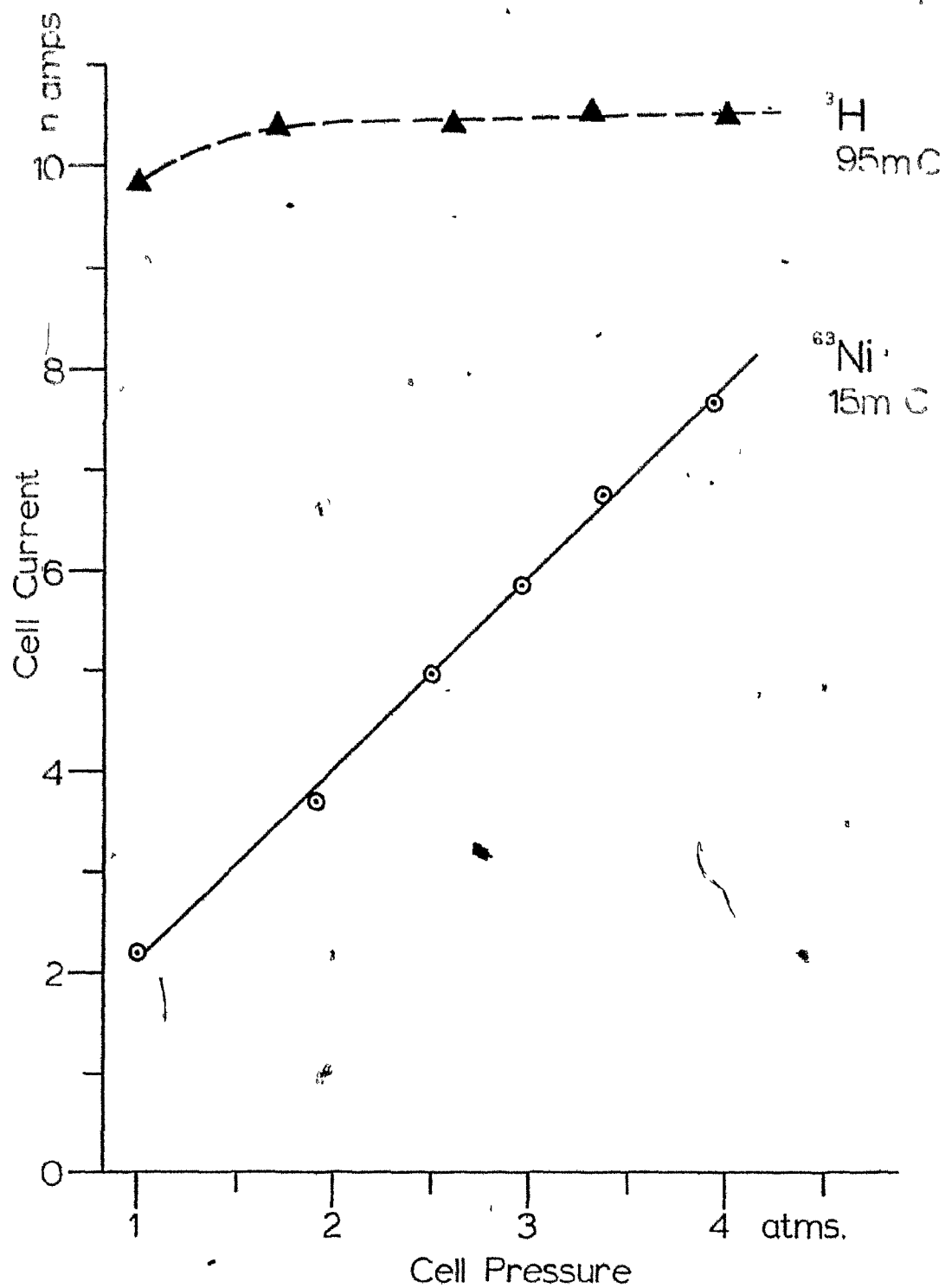
the increase in the background current of ^{63}Ni detector
was much greater when compared to the increase observed
for the ^{3}H detector (βrange ~ 2 mm) (Fig. 38).

A more astonishing effect of the pressure was
observed in terms of the response of the detector in the
DC mode. An increase in the pressure resulted in a steep
increase in response, as shown in Figure 39 for the
fungicide tecnazene (2,3,5,6-tetrachloronitrobenzene).
The increase in response appears to be a linear function
of pressure in the measured range (up to 5 atmospheres).
It is interesting to note that the response at 1 atmosphere,
i.e. under normal operating conditions, is less dependent on
pressure and falls close to the coulometric range (considering
the fact that tecnazene forms strongly electron capturing
products). Little change in the linear range (approximately
10^2) was observed although it shifts to lower concentrations.

The increase in response can result from (a) increased
attachment and recombination, or (b) development of a space
charge. As stated earlier, an increase in pressure results
in an increase in the number of available electrons and also
leads to an increased probability of recombination which, in
turn, should result in a higher response; however, such an
increase for small amounts of strong electron absorbers
should be fairly small.

Figure 38

Graph showing the effect of pressure on the standing current of two detectors of same geometry (coaxial) but with ^{63}Ni and ^{3}H as the β source.
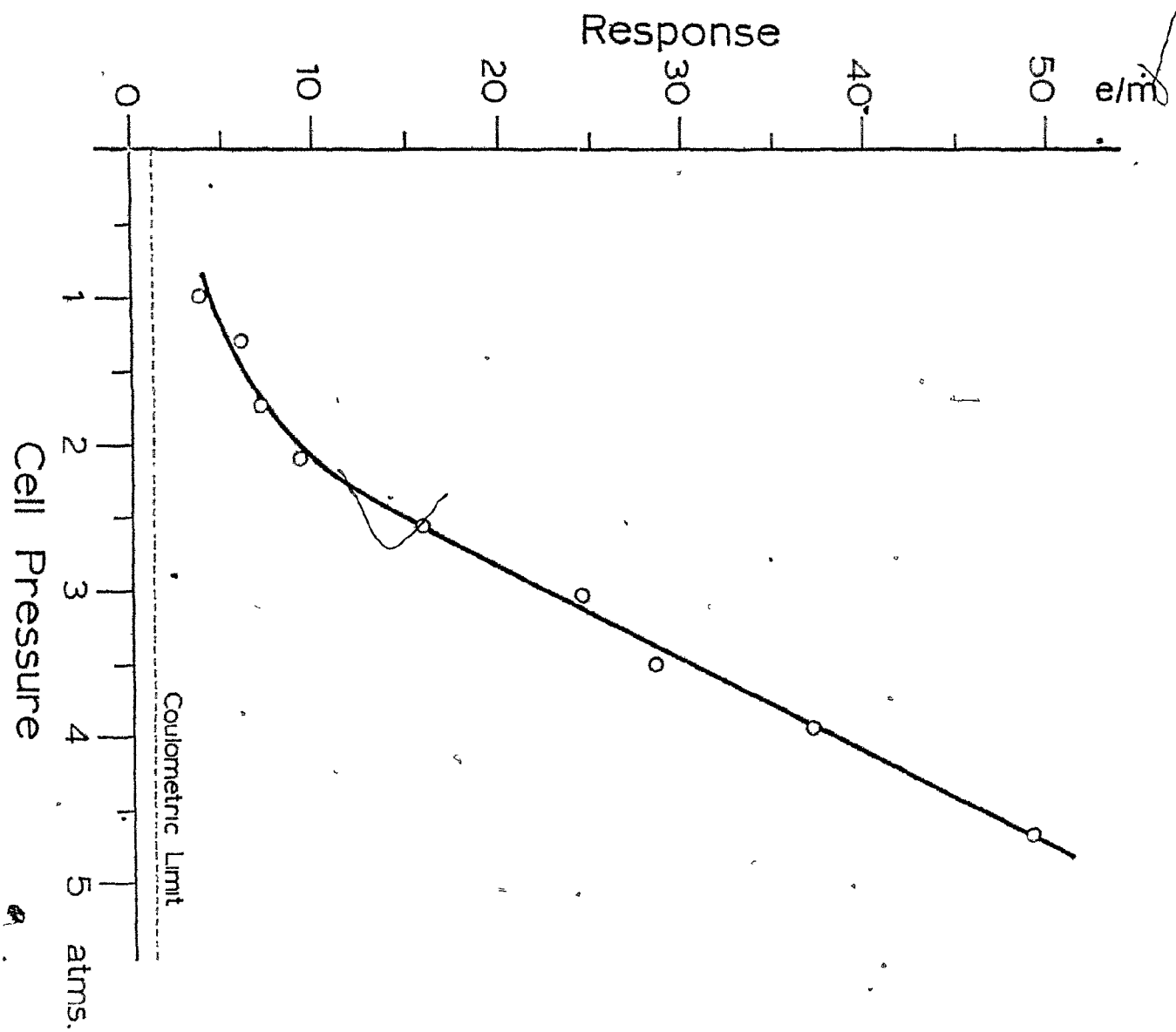
Figure 39

Detector response at different pressures
to 1 pg of tecnazene (tetrachloronitrobenzene)
measured in faradays peak area per mole of
analyte, at optimum voltage conditions. Gas
flow enters from the bottom of a Tracor ^{63}Ni ECD.

Response

8 e/m

6

4

2

0

Cell Pressure

1

2

3

4 atms.

Pulse

DC
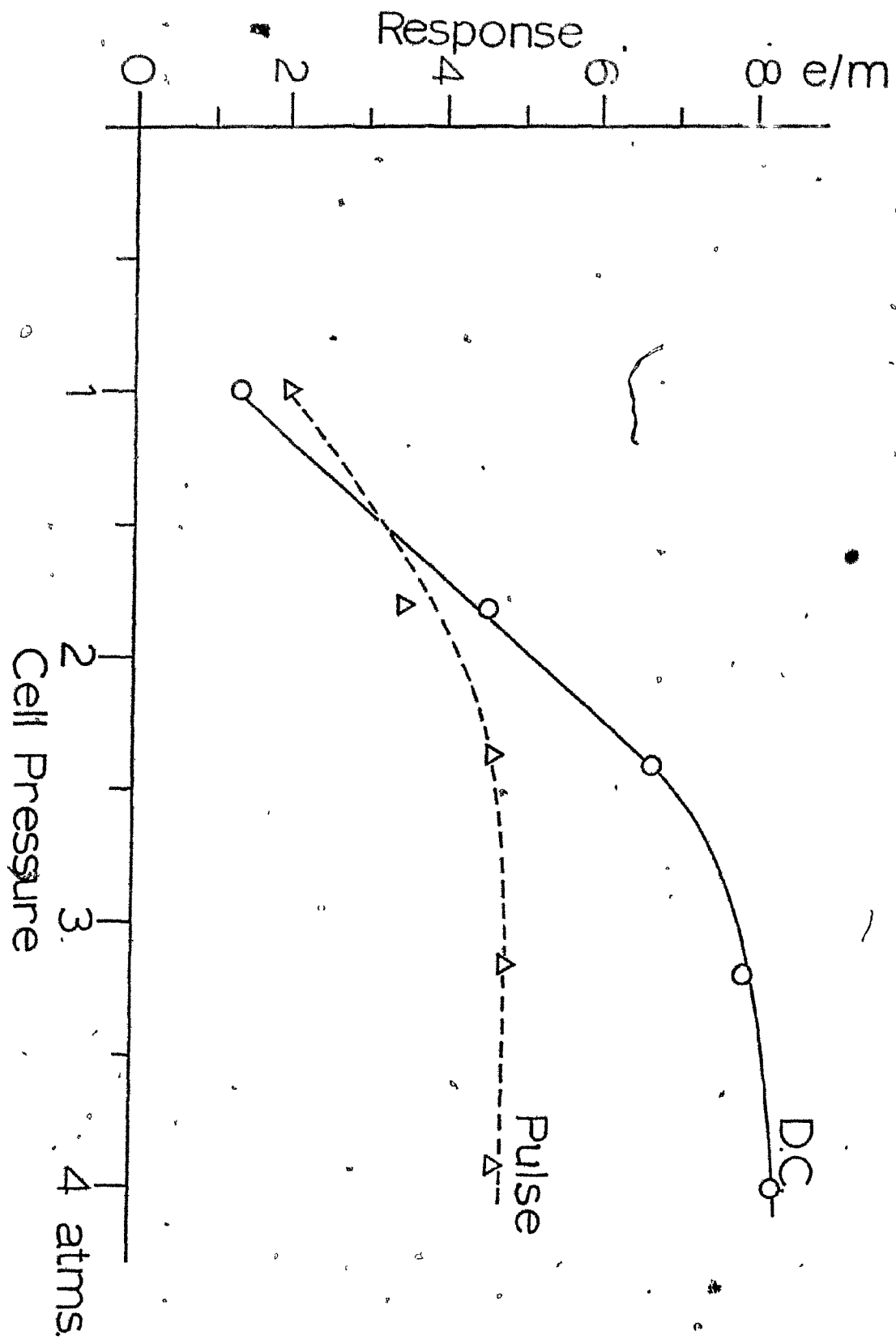
The capture of electrons by solute molecules results in the formation of anions. Such anions are less mobile and under suitable conditions could lead to development of an additional space charge, creating a field opposite to the applied field resulting in a decrease in the number of electrons collected i.e. an increased response.

In another study on the effect of pressure in DC and pulsed mode, it was observed that the enhancement in response was larger in the DC mode than the pulse mode (Fig. 40). This would be expected if the enhancement is related to the development of space charges. Whereas the potential free period in pulse mode reduces the separation of charges and thus the development of space charge, the opposite is true when continuous potential (DC) is applied.

Figure 40

Response at different pressures to 10 pg of
tecnazene measured in faradays peak area per
mole of analyte, obtained with a modified
coaxial detector operating at optimum conditions
in pulse and DC modes. Column temperature 150°.
Carrier gas N_2.

Operating Conditions

Cell Pressure	DC	Pulse		
atms	volts	interval	width	amplitude
1	-6	270	10	-30
1.8	-7	210	10	-30
2.4	-11	180	10	-30
3.2	-14	140	10	-30

SUMMARY

A chromatographic system for observing the neutral, electron absorbing products formed in an electron capture detector was constructed. The system consisted of two electron capture detectors and two chromatographic columns arranged in a series configuration. Both stable neutral products formed in the first detector and the parent compound were separated in the second column and detected by the second detector.

The effect of various parameters (voltage, detector temperature, the presence of other reactive species and different carrier gases) on the formation of these products was studied in detail.

It was observed that while all strongly electron capturing compounds shared a common voltage profile, product formation depended on the individual structure.

Detector temperature had little or no effect on such products. Addition of various substances to the carrier gas also had little effect on the formation of these products, excepting higher hydrocarbons (pentane, hexane, heptane and iso-octane) which enhanced the formation of smaller molecular weight products.

A limited attempt was made to identify some of the product peaks obtained from a few selected compounds. It was observed that some of the products obtained from nitro-halo aromatics may result from the loss of the nitro group, while others may be formed by removal of halogens.

In the series configuration, an enhanced response was observed for the first detector, which was attributed to the elevated operating pressure. A detailed study of the effect of pressure on the response of an electron capture detector revealed that the response of an ECD operating in DC mode increases with an increase in pressure; however, such increase is less pronounced for a detector operating in the pulse mode. It was observed that under suitable conditions (high pressure and optimum DC voltage) the response of the detector for certain strongly electron capturing species was well above the supposedly limiting coulometric value of 1 faraday/mole. Under these conditions, 20 femtograms of hexachloroethane gave a signal four times higher than the noise.

The effect of various operational parameters on the response of an electron capture detector (operating in pulse mode) was also studied. The results obtained showed that the electron capture detector response for the strongly electron capturing substances in a 'clean' system is relatively immune to the changes in various operating parameters. Under such conditions an electron capture detector can be used with temperature programmed gas chromatography.

CONCLUSION

This study was primarily concerned with the observation of neutral electron capturing products formed in an electron capture detector. The results obtained indicate that such neutral electron capturing products are formed and the number and amount of products formed depends on the structure of the parent molecule. Thus the "absolute" determination[106,114] of electron capturing substances can only be made for compounds that do not give any neutral electron capturing product. Results obtained without this knowledge may be in error.

The 'product spectra' (product patterns obtained for selected compounds) show that such spectra can be used in 'finger printing' and identification of many electron capturing compounds at ultra trace levels. The tentative identification of some of the products seems to indicate that the major products peaks obtained for chlorinated nitrobenzenes may be formed by the loss of the nitro group.

The formation of these products can be stopped by applying a high DC potential. The magnitude of applied potential needed is governed by the direction of field and the geometry of the detector.

The detector operating at high pressure (above 1.5 atm) gives response higher than the coulometric limit, this 'hypercoulometric' response is dependent upon the mode of

operation (higher for DC) and the detector cell geometry. Furthermore, an increase in standing current with an increase in the flow rate of the carrier gas described in literature[91,92] may actually be due to the corresponding increase in pressure (gas density) in the detector cell.

Finally, the series configuration used in the present study, can easily be adapted for other reaction techniques for identification of various compounds by gas chromatography.

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Publications and presentations which have resulted
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