

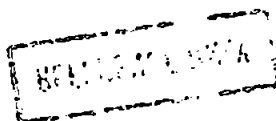
STUDIES OF TIN OXIDE GAS SENSORS FOR GAS
CHROMATOGRAPHIC DETECTION

by

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A thesis submitted in part
fulfilment of the requirements of the
Council for National Academic Awards
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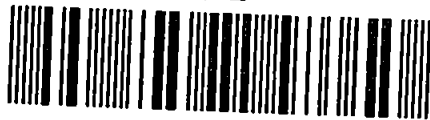
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ABSTRACT

Gas sensitive semiconductors have been known for many years and applied in static gas alarm systems for the monitoring of hazardous gases, however, their application has been limited by a lack of selectivity. In this work a semiconducting gas sensor has been configured for use as a gas chromatographic detector thus combining the sensitivity of semiconductor sensors with the selectivity of gas chromatography.

The study has been confined to tin oxide devices, more specifically the Taguchi gas sensor (TGS). The majority of this work has concentrated on the TGS 813 although the use of other TGS is described.

The development of suitable instrumentation is described and rigorous optimisation of the operating parameters e.g. heater voltage and column temperature has been performed using the variable step size simplex technique. Attention was concentrated on the response of the TGS 813 to hydrogen which was used as a test gas. A novel figure of merit, response multiplied by retention time and divided by skew factor was designed so that optimum response was obtained whilst maintaining adequate chromatographic separation. Optimum conditions were verified by univariate searches and the response was observed to be most dependant upon heater voltage. A limit of detection of 20 ppb v/v of hydrogen in a 1 ml sample was obtained at optimal conditions. Illustrative analyses of hydrogen were performed in human breath and laboratory air with results found to be in close agreement with literature values. Calibration was found to be linear over at least three orders of magnitude.

The response of the TGS 813 to low molecular weight alkanes has also been investigated. It was observed that different heater voltage optima existed for each of the C₁-C₅ alkanes and that the sensor was relatively more sensitive to the higher molecular weight compounds. As with hydrogen linear response was obtained over at least three orders of magnitude and an illustrative analysis of natural gas showed excellent agreement with known levels.

A compromise optimum heater voltage was used to study the response of the TGS 813 to alcohols, aldehydes, ketones and some C₆ hydrocarbons. Capillary columns were used in this investigation and it was noted that they had potentially wider application than packed columns due to the use of an inert carrier with an air make-up flow to the detector. This replaced the air carrier gas used previously which might degrade certain stationary phases.

Three different types of TGS: the 813; 822 and 831 were used in a study of the response and skew factor for the detection of halogen-containing compounds. Very high skew factors were often observed, although, for some compounds it appeared that symmetrical peaks could be obtained within narrow heater voltage ranges. Skewed response was observed to be dependant upon sensor type, heater voltage and halogen proportion and type.

Analysis of the three sensor types was performed and differences in potential surface area and tin oxide additives observed. The presence of additives was observed to adversely affect sensor recovery.

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CHAPTER 1 : INTRODUCTION

1.1 : GAS SENSITIVE SEMICONDUCTORS

The term gas sensitive semiconductor generally refers to a bulk semiconductor material whose conductivity can vary according to the composition of its gaseous environment . This phenomenon was noted as early as 1953 by Brattain and Bardeen who observed conductivity changes in germanium [1] . Since that time other workers including Morrison [2] and , Heiland , Molwo and Stockman [3] have confirmed these observations on germanium and in the case of Heiland and co-workers on metal oxides , notably zinc oxide (ZnO) .

It was not , however , until the early 1960s that the phenomenon of gas sensitivity began to be applied to the sensing of gases e.g. Seiyama and co-workers [4,5] . Since that time a great deal of development has taken place and currently a range of possible materials and devices are being studied for their applicability to gas sensing . The sensors being developed may be broadly classified into three main groups :

1. metal oxide semiconductors e.g. SnO_x [6] ;
2. organic semiconductors e.g. Phthalocyanines [7] ;
3. sensitised semiconductor devices e.g. field effect transistors [8] .

This project has been concerned with the first group of these . The reason for this is that the oxide semiconductors have been studied longest and are now commercially available sensors exhibiting many desirable properties such as :

- low cost ;
- chemical stability ;

rapid reaction ;
reproducible response ;
high sensitivity .

Many metal oxides have been studied including those of
zinc [3] ;
titanium [9] ;
zirconium [10] ;
tin [11] .

Of the materials studied zinc and tin are the best
characterised with tin oxide sensors by far the most widely
available commercially , commonly known as Taguchi Gas Sensors
(TGS) . For this reason and the fact that two prior studies ,
those of Wynne [12] and Rowley [13] , had both shown that the tin
oxide TGS were very promising chromatographic detectors , it was
decided that this work should continue using the TGS .

1.2 : THE SEMICONDUCTING PROPERTIES OF TIN OXIDE

Tin IV oxide (SnO_2) is a semiconductor with a band gap of about 3.5 eV , the valence band arising from the overlap of the filled oxygen 2p levels , the lower levels of the conduction band are formed in a similar manner from overlap of tin 5s levels [14] . However because tin oxide is a non-stoichiometric oxide i.e. where the tin : oxygen ratio is less than 2 (normally approximately 1.95) its electrical conductivity is higher than would be expected , with the oxygen deficiency causing donor levels to be formed just below the conduction band energy . The oxygen deficiency causes the tin oxide to be slightly electron rich and therefore a n-type semiconductor .

The conductivity of a semiconductor is governed by the simple equation :

$$\sigma = n.e.\mu$$

where :

σ = conductivity (mho m^{-1})

n = number of carriers

e = carrier charge (coulombs C)

μ = carrier mobility ($\text{m}^2\text{V}^{-1}\text{s}^{-1}$)

Since e is a constant there are two factors which can affect the conductivity of a semiconductor , namely the number and mobility of the charge carriers . In comparison with the number of charge carriers the carrier mobility is relatively insensitive to external effects such as temperature pressure and chemical composition of the semiconductor environment . It can therefore

be assumed that variations in the conductivity of semiconductors corresponding to changes in the chemical composition of their gaseous environment are caused by changes in the number of available charge carriers . The significance of this is that interpretation of the mechanisms governing the conductivity changes is made simpler by the requirement for changing the number of charge carriers .

1.3 : TIN OXIDE GAS SENSORS

The application of tin oxide as a gas sensor was noted as early as 1966 [5] by Seiyama and Kagawa . Following this work Taguchi among others [11,15-23] filed a series of patents covering the development of metal oxide (including tin) sensors from the early thin film devices to what is the essentially the current sensor design . The TGS (figure 1.3.1) consist of a cylindrical ceramic former covering a heating coil . On the surface of the former there are two gold electrodes covered by a layer of tin oxide . The tin oxide is deposited on the surface of the former by a method involving the cold pressing of a fine paste of the oxide onto the former and then drying and then sintering . The tin oxide paste also contains other compounds such as the oxides or chlorides of palladium , platinum , silver and bismuth , among others , which are reputed to sensitise the sensor to one type of compound or other . For example , it has been reported that the addition of silver [24] increased the sensitivity of tin oxide to hydrogen . Two other types of additive are also included in the paste , these are binding agents such as silica gel and alumina which increase the mechanical strength of the resultant sensor and compounds designed to increase the porosity of the oxide layer during drying and sintering (by thermal decomposition) such as stearic acid and waxes .

The TGS are available commercially , manufactured by Figaro Inc. of Japan and marketed in the U.K. by Envin (Environmental) Ltd. (5 , Grove Street , Wantage . Oxon .) . A range of the TGS are available , presumably containing differing amounts and types

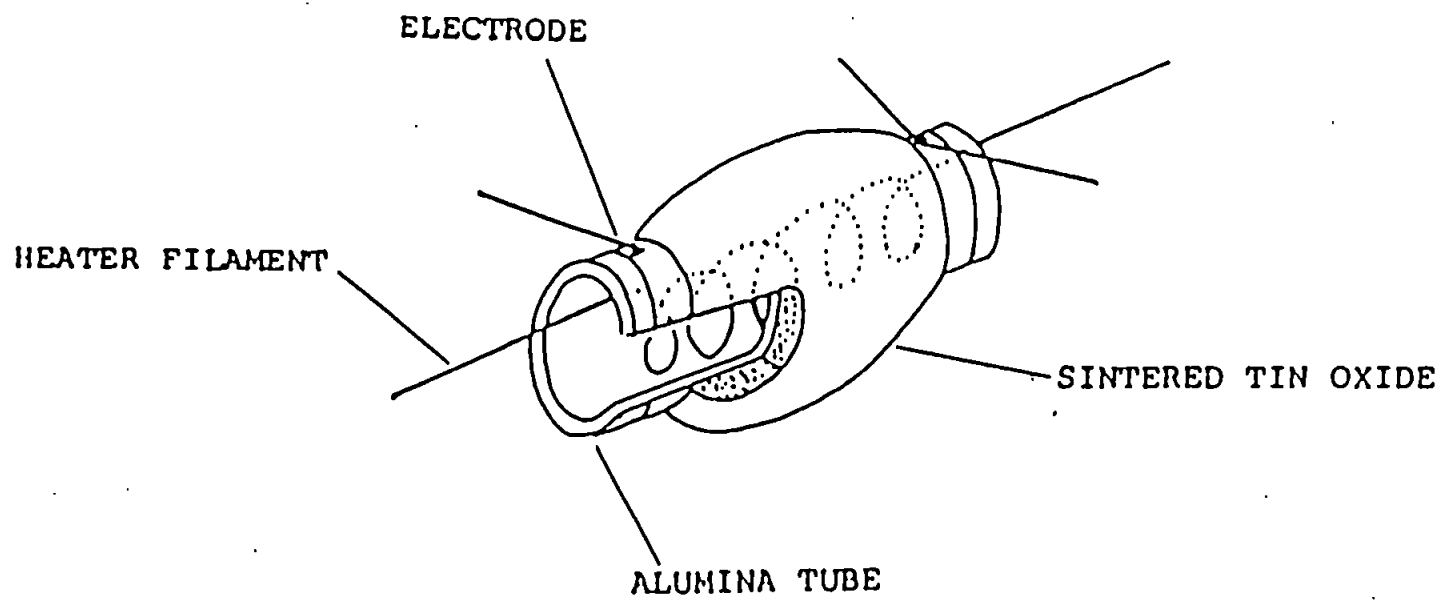


FIGURE 1.3.1 :
A TAGUCHI GAS SENSOR

of sensitiser (Table 1.3.1) . However , despite these sensitisers the TGS remain largely unselective .

TABLE 1.3.1 : THE RANGE OF TAGUCHI GAS SENSORS
COMMERCIALY AVAILABLE

SENSOR	REPORTED APPLICATION
TGS 100	carbon monoxide , hydrogen , petroleum vapour , cigarette smoke .
TGS 109	combustible gases <u>e.g.</u> propane natural gas , factory gas , petroleum vapour .
TGS 203	high selectivity to carbon monoxide .
TGS 800	as TGS 100 but more rugged sensor design .
TGS 813	combustible gases .
TGS 815	combustible gases , low dependence on humidity .
TGS 816	combustible gases , ceramic sensor housing .
TGS 822	ethanol vapour .
TGS 823	organic vapours <u>e.g.</u> toluene and xylene .
TGS 824	ammonia .
TGS 825	hydrogen sulphide .
TGS 830	freon (arcton) 113 .
TGS 831	freons (arcton) 21 , 22 .
TGS 880	volatile matter from foods .
TGS 881	as TGS 880 , with ceramic sensor housing
CMS 302	oxygen .

1.4 : THE INTERACTION OF GASES WITH TIN OXIDE SURFACES

According to Morrison [25] , there are a number of ways in which the gaseous environment may react with the surface of a semiconductor causing a reversible change in its conductivity , including :

1. reduction / oxidation of the semiconductor ;
2. ion exchange ;
3. adsorption / chemisorption ;
4. interaction with surface species .

It is generally accepted , however , that the most likely form of reaction at the surface of an oxide is the latter case [26-29] . Furthermore it is believed that the surface species involved are chemisorbed oxygen ions such as O_2^- , O_2^{2-} , O^- and O^{2-} [28] . The presence of the paramagnetic O_2^- has been observed using electron paramagnetic resonance (EPR) spectroscopy [30] also Chang [31] was able to observe the presence of O^- and O_2^- by the same technique , and it appears that the dominant species at temperatures above 150°C is O^- . Much work has been done by Harrison and co-workers [32-49] using transmission infra-red absorption spectroscopy to look at the interactions of the oxygen species with a wide range of gases and vapours , although only one paper [49] looks at the relationship between the conductivity of tin oxide and the spectra observed . However recent work by McAleer et.al. [50-52] has done much to clarify the relationship between surface chemistry and electrical conductivity of tin oxide . The main feature of this work was the postulation that the modulation of conductivity by a gas occurs via the

modulation of inter-granular Schottky barrier heights by interaction of the gas with nearby chemisorbed oxygen species . The work also presented strong evidence to suggest that conductivity is :

1. heavily dependant upon humidity / chemisorbed hydroxyl ions ;
2. dependant on the work function and surface chemistry of surface additives ;
3. more likely to be modulated by the products of surface catalysed combustion reactions than the reactant gases .

It has been widely recognised that further advances in the application and development of semiconductor gas sensors can only be achieved through a more thorough understanding of this area of research and it is hoped that this project can help to clarify some of the outstanding questions in this respect .

1.5 : THE APPLICABILITY OF TAGUCHI GAS SENSORS AS GAS CHROMATOGRAPHIC DETECTORS

Since Tswett [53,54] first described the separation of plant pigments on a column of chalk in 1906 , chromatography has developed rapidly . Gas Chromatography (G.C.) was first described by Martin and James [55] and has since developed into one of the most widely used techniques for chemical separation and analysis currently available . Obviously since Martin and James pioneered the work in 1952 the development of suitable detectors for G.C. has also progressed rapidly and currently there are a number of useful detectors available [56] . However , there is still room for further development in this field , especially in the areas of reduced cost , improved sensitivity , increased portability and enhanced selectivity . Tin oxide semiconductor sensors as typified by the TGS have many properties that would make them suitable GC detectors :

1. they are very low cost devices - currently £10 - £40 for the TGS from Figaro ;
2. they are highly sensitive to reducing gases ;
3. they have the potential to be used in portable gas chromatographs being lightweight , requiring only low power for operation , the electronic circuitry is simple ,and no fuel gases are required ;
4. they respond to a wide range of compounds ;
5. they use no flames or very high voltages and can therefore be used in potentially explosive locations .

To date few workers have recognised and attempted to use tin

oxide sensors as GC detectors , although a number , including Seiyama et.al. in 1962 [4] , have used gas chromatography as a means of investigating the response of the sensors . One of the first groups to describe the application of a TGS as a GC detector was that of Mallard [57] who , in conjunction with his co-workers , used a TGS 812 as the detector in a portable GC system to determine ethene concentrations in situ as a measure of nitrogenase activity . Other workers include Wynne who used TGS detectors to monitor 'Firedamp' in mine air [12] and Rowley who studied the use of TGS as GC detectors in the potentially explosive location of oil drilling sites [13] and for the analysis of a variety of other gases [58] .

1.6 : OUTLINE OF THE AIMS OF THIS RESEARCH

The primary aim of this work was to assess the applicability of currently available tin oxide gas sensors to gas chromatographic detection . To accomplish this , three representative sensors would be selected . The response of these sensors to a wide range of simple compounds including homologous series would be studied in terms of normal chromatographic figures of merit . These measurements would be combined with data from analysis of the response mechanisms and studies of the sensor composition and configuration . Critical analysis of all the data collected would then be used to assess the improvements in sensor design required for application as GC detectors .

CHAPTER 2 : INSTRUMENTATION AND EXPERIMENTAL PROCEDURES

2.1 : GAS CHROMATOGRAPHY

The basic elements of a gas chromatographic system include :

1. a supply of carrier gas and a means of controlling its flow ;
2. a column packed with a material which separates the species of interest by their different affinities between carrier gas and column material ;
3. a means of introducing samples into the carrier gas for separation on the column ;
4. a detector to monitor the changes in the composition of the effluent gas from the column ;
5. a series of ovens capable of controlling the temperatures of column , sample introduction , and detector elements .

The gas chromatographic system used in this work contained all of the elements mentioned above , the choice of the particular units employed depended on the nature of the work done here and as such need to be described :

Carrier gas

It has been generally believed that the sensing mechanism of the tin oxide semiconductor is dependant on the presence of surface adsorbed / chemisorbed oxygen species [28] . For this reason air was used as carrier gas throughout the early part of this work . However because the presence of oxygen in the carrier gas precluded the use of most of the better stationary phases , many of the experiments carried out later in this work have used nitrogen (white spot grade) as carrier gas . The oxygen has

been added (as air) to the column effluent in the detector housing . Both the nitrogen and air were obtained in 25 litre cylinders , pressurised at 2500 psi , from Air products Ltd. (New Maldren , Surrey . U.K.) . The carrier gas was passed through a silica gel drying tube ('Puritube' Phase Sep Ltd. Clwyd. U.K.) before entering the column .

Two common types of carrier gas flow regulation have been employed during this work . In the first instance pressure regulation proved most suitable since it was better able to suppress fluctuations in flow rate (caused by the operation of a gas sampling valve) which caused pulses to be observed at the detector . Pressure regulation proved suitable in all cases involving isothermal chromatography . During temperature programmed separations however , the pressure regulation was found to be unsatisfactory since the changing viscosity of the carrier caused by the temperature changes resulted in appreciable drift in the chromatographic baseline . Therefore in the temperature programmed separations a volume flow controller was employed , this substantially reduced the drift affect noted with the pressure controller . Fortunately the separations involving temperature programming did ^{not} require measurement close to the pressure pulse and therefore no detrimental affect was observed in using the volume flow controller .

Sample introduction

A useful and versatile introduction system for gaseous samples into a gas chromatograph is via a gas sampling valve (figure 2.1.1) . Such a system has been employed in this work wherever possible . The specific system used was a 1ml , 6-port gas sampling valve (type : PU 4090 Philips Scientific , York Street , Cambridge . U.K.) . In cases where the use of a gas sampling valve was not possible , a 1ml gas tight syringe ('Pressurelok' , Dynatech Precision Sampling Corp. , Baton Rouge. Louisiana . U.S.A.) has been employed with samples introduced through a conventional packed column injector . In the later parts of this work where liquid samples were used , sample introduction has been carried out using normal glass syringes . Also in chapter 4 where capillary columns were used , an autoinjection system (type PU 4700 , Philips Scientific , York Street , Cambridge . U.K.) and a split / splitless injection port were required .

Temperature Control

The chromatographic oven system employed throughout this work was a Philips Scientific PU 4550 .

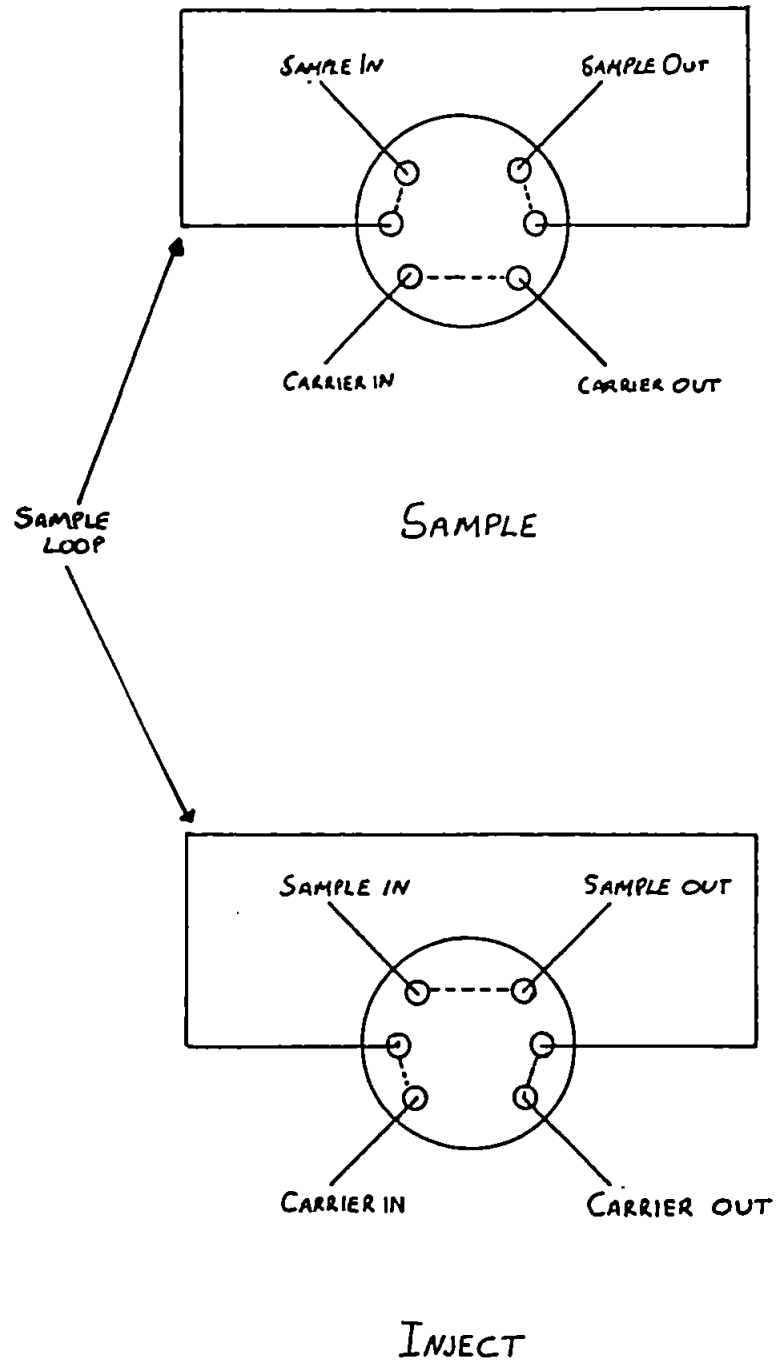
Detection System

As indicated above the detection system for this work was based on a Taguchi gas sensor .

Two different designs of housing for the sensor have been used in this work . Initial studies were carried out using the

FIGURE 2.1.1 :

A SIX-PORT GAS SAMPLING VALVE



design of Rowley [13] (figure 2.1.2) . This design was considered inconvenient since it could not readily be interfaced with the chromatograph used . The interface used for this design basically consisted of a length of stainless steel tubing between the end of the column and the detector housing . This lead to two potential problems :

1. it was possible that post column peak broadening could occur leading to a reduction in resolution ;
2. the temperature of the housing could not conveniently be controlled which and problems with drifting baseline reflecting changes in the ambient temperature could be encountered .

The second design of housing was based on the existing flame ionisation detector for the PU 4550 gas chromatograph (figure 2.1.3) . Since this therefore readily fitted into the PU 4550 detector oven , it allowed much greater control over the temperature of the housing and meant that the detector was very close to the end of the column . Also this design of detector housing offered flexibility and control of the addition of auxiliary gases to the detector through the existing fuel and oxidant inlets .

FIGURE 2.1.2 :

THE SENSOR HOUSING DESIGNED BY ROWLEY

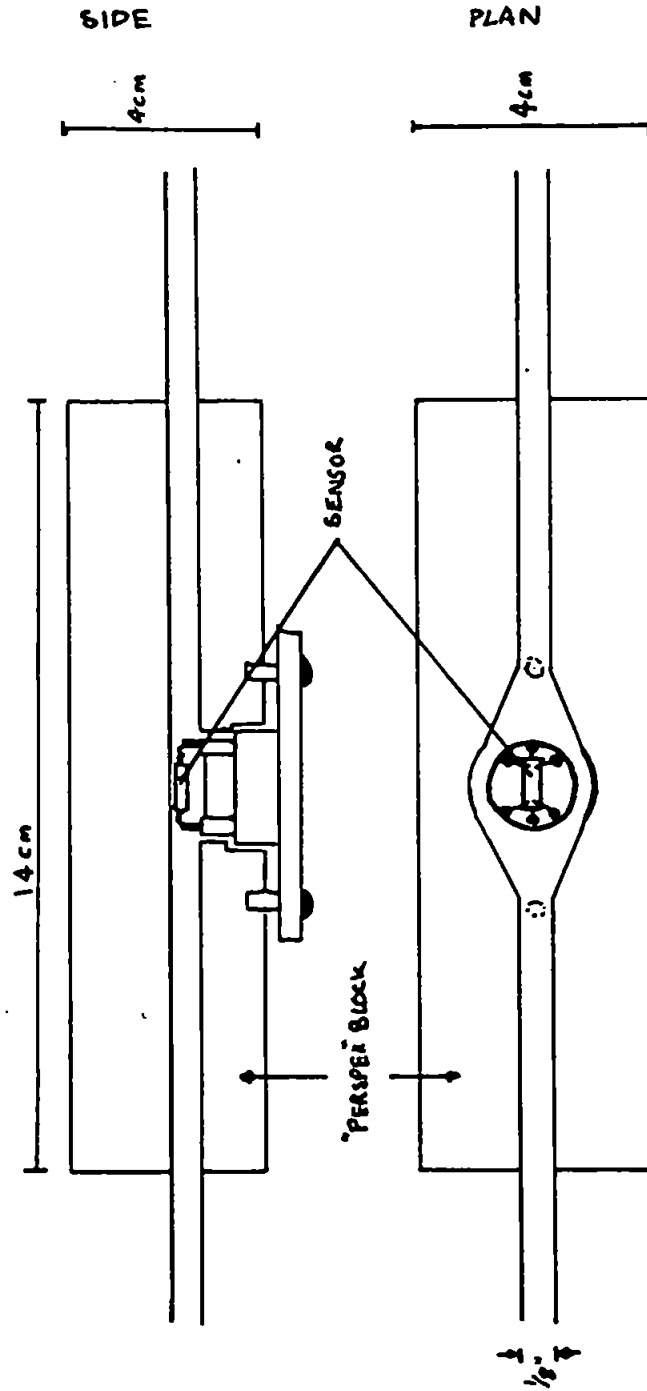
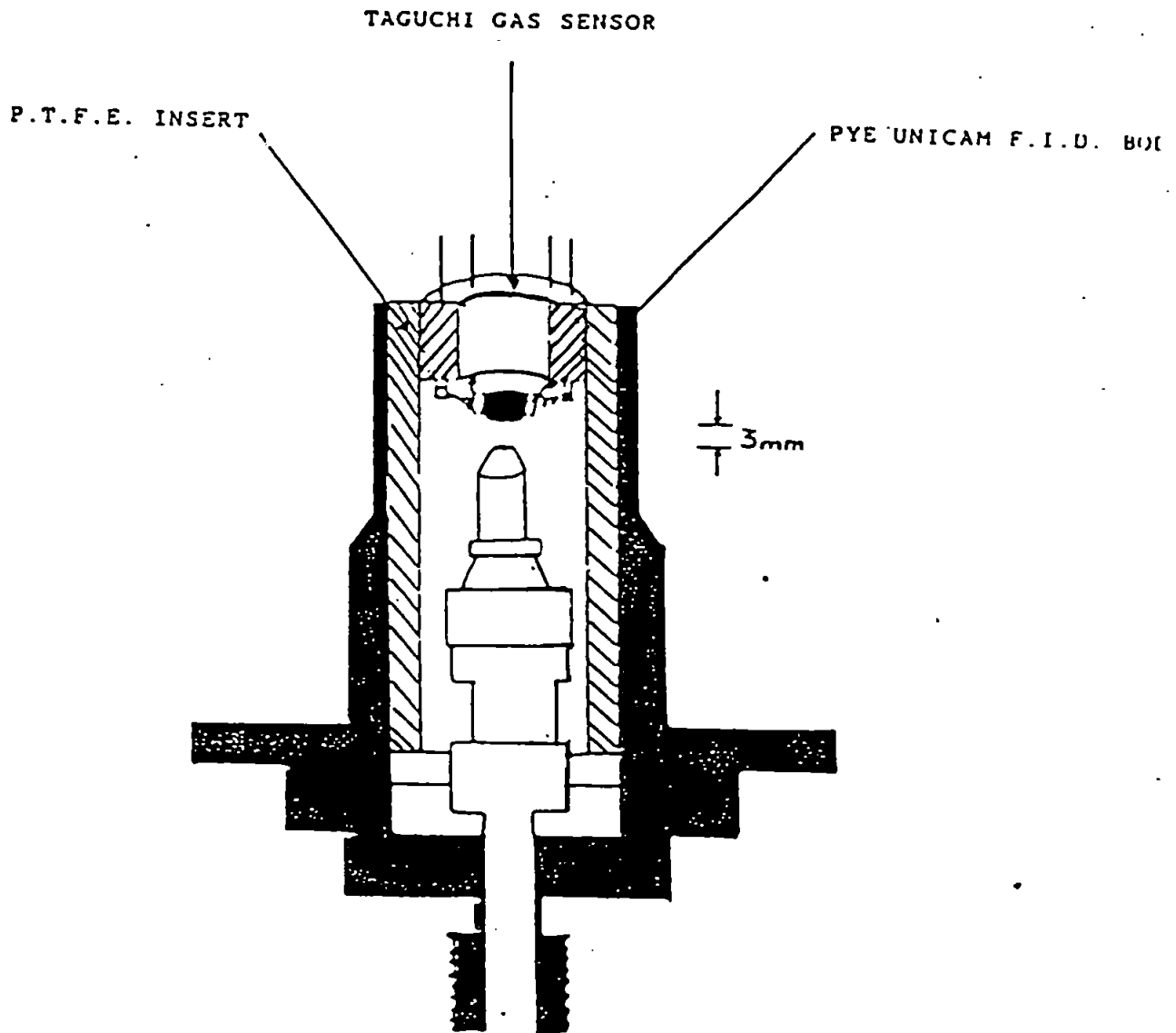


FIGURE 2.1.3 :
THE FID HOUSING MODIFIED FOR USE WITH A
TAGUCHI GAS SENSOR



2.2 : SENSOR ELECTRICAL CIRCUITS

There were two separate electrical requirements for the sensor :

1. a stable power supply to the integral sensor heating element :
2. a circuit to monitor the changes in sensor conductance and provide a suitable signal for output to a chart recorder or computing integrator .

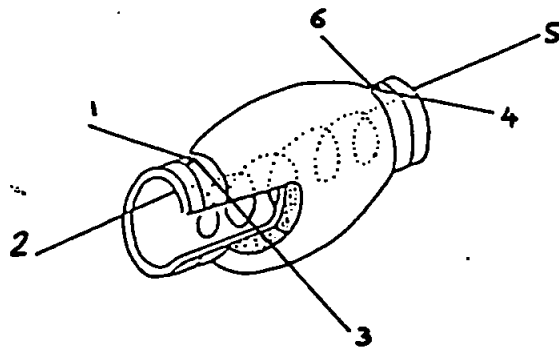
Figure 2.2.1 shows the electrical contacts for the sensor . The heater supply is connected across the two centre pins (2 and 5) and the conductance is measured between the two outside pairs of pins (1 and 3 and/or 4 and 6) .

The supply for the sensor heater was provided by a Farnell L-30-2 laboratory bench power supply (RS Components , Corby . Northants. U.K.) . The unit was capable of supplying 0-15V D.C. at currents between 0 and 3A , the voltage was controllable to 0.25V and stable to within $\pm 1\text{mV}$ at 5.0V .

Both Rowley [13] and Wynne [12] used a variety of circuits for measuring the sensor conductance . The present work has used a circuit developed by Rowley [59] , two minor modifications to the design (figure 2.2.2) were made , these were :

1. the use of better quality operational amplifiers (A and B) than the originals;
2. the inclusion of capacitors (C) , for decoupling the power supply rails and smoothing the feedback loops on the operational amplifiers .

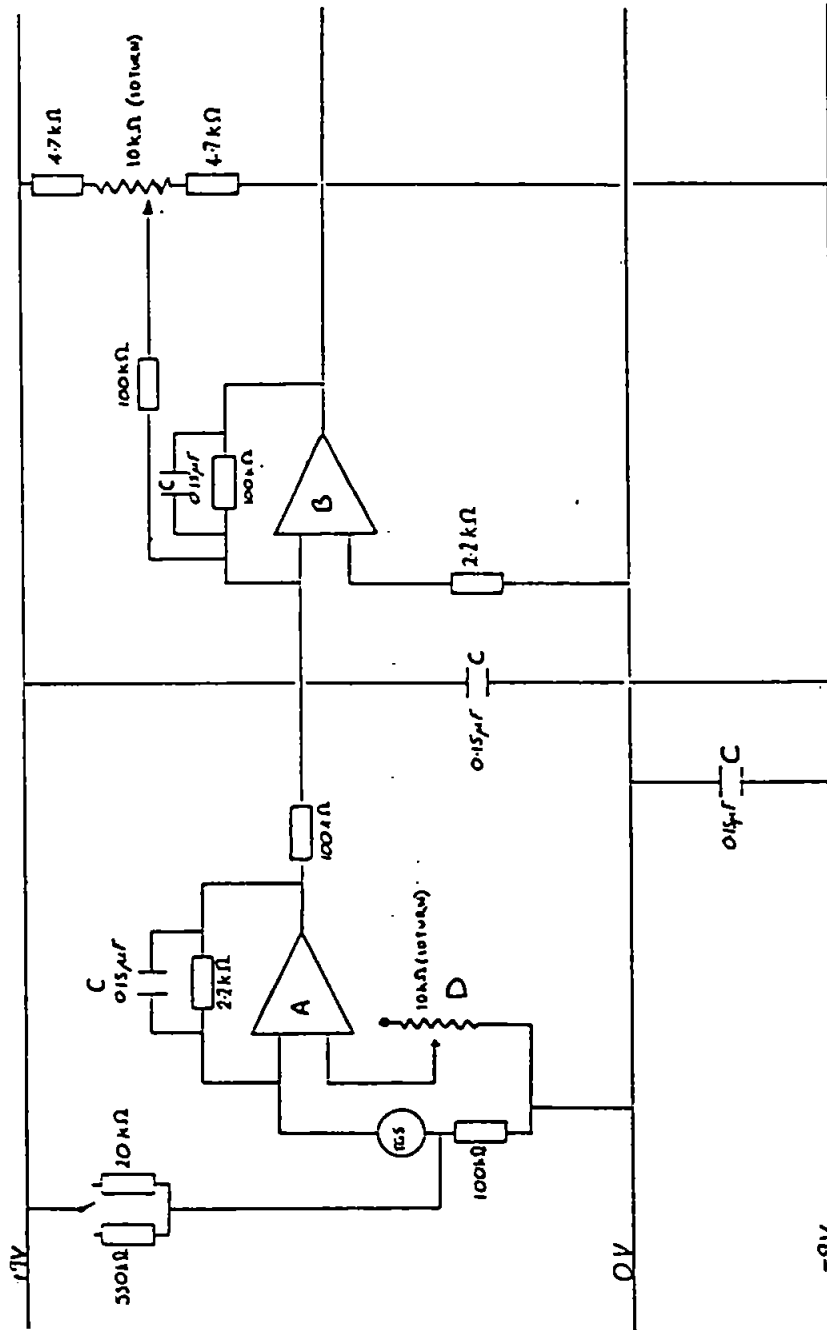
FIGURE 2.2.1 :
THE ELECTRICAL CONTACTS TO A TAGUCHI GAS SENSOR



PIN NUMBERS

FIGURE 2.2.2 :

THE RESPONSE MEASUREMENT CIRCUIT USED IN THIS WORK



The modifications made reduced the electrical 'noise' on the output by a factor of 2 .

In later work it was found that more adjustment of the level of the output was required , this lead to the inclusion of the variable resistance on the earth connection of the first operational amplifier (A) *D* .

2.3 : GAS STANDARDS AND CALIBRATION

2.3.1 Gas Standards

The preparation of accurate gas standards is a difficult problem in gas analysis . The reason for this lies in the affects on gas density of pressure and temperature . The preferred method of preparing gas standards is gravimetric dilution . There are however a number of problems associated with this due to the low density of gases at normal temperatures and pressures . The problem is one of attempting to measure a small weight change in what is normally a much larger total weight . This process involves the use of specialised equipment and means that gravimetric gas standards tend to be expensive .

The preparation of volumetric gas standards is somewhat simpler and can be achieved by pressurising a fixed volume with the gases of interest making allowances for deviations from ideal gas behaviour at high pressures . Comprehensive coverage of this subject can be found elsewhere (60) . For the reasons outlined above it was decided that gas standards should be purchased from specialist suppliers . The following standard mixtures were obtained :

1. 0.083% hydrogen in air ;
2. 0.1% v/v each in air of :
 - methane ;
 - ethane ;
 - propane ;
 - butane ;
 - pentane .

The mixtures (purchased from P.K. Morgan Ltd. Chatham . Kent . U.K.) were volumetrically prepared , also in the case of the hydrogen mixture a certificate of analysis was obtained .

2.3.2 : Calibration mixtures

To enable calibration of the detector it was necessary to be able to dilute the purchased standards with a reasonable degree of accuracy and precision . To comply with this requirement a Gas blender (type 852 V5S , Signal Instrument Co. , Camberley . Surrey . U.K.) was obtained . This instrument was capable of mixing two gas streams in a continuously variable ratio (sample : diluent) between 0.01% and 100% . Mixing occurred in a temperature controlled microporous block , incorporating pressure feedback loops to ensure precise volumetric mixing . The ratio was controlled by a needle valve calibrated by the manufacturer . The blender required both input gas streams to be at a pressure of approximately 30psi and gave an output flow of up to 5 litres per minute at 5psi . This output could be fed directly to the gas sampling valve of the gas chromatograph .

The only disadvantages experienced with this system were that the mixing ratio depended upon the specific gravities of the gases , as well as the position of the needle valve , and the pressure requirement of the input gas streams which limited the available samples to those obtainable in pressurised gas cylinders thereby raising the cost of the analyses .

CHAPTER 3 : CONFIGURATION AND OPTIMISATION OF THE
TAGUCHI GAS SENSOR FOR GAS CHROMATOGRAPHIC DETECTION

3.1 : INTRODUCTION

In order that the TGS could be properly assessed for its applicability as a GC detector it was necessary that the studies were carried out under the optimum conditions available . The reason for this was that only then could its true potential be discovered and therefore allow assumption that any areas requiring improvement were the result of deficiencies in the sensor design for this application .

The choice of test gas for the determination of the optimal configuration of the sensor and chromatographic conditions was very important . Firstly it had to be a reducing gas , secondly it had to be chemically very simple to minimise the possibility of non-typical interaction with the sensor and thirdly it should have a short retention on the chromatographic column . These factors considered it was decided that initial experiments be carried out using hydrogen as the test gas .

The chromatographic column used in all of these initial studies was a 1 m x 4 mm (i.d.) glass column packed with 60/80 mesh activated alumina (Philips Scientific) . This provided adequate retention of low molecular weight gases such as hydrogen without resort to the use of sub-ambient column temperatures . The column was also compatible with the use of air as the carrier gas which has been employed throughout these initial studies . Sample introduction was achieved using the 1ml gas sampling valve in conjunction with the gas blender described in section 2.3.2 .

The sensor used for the initial studies was a TGS 813 which was reputed to have a low selectivity for reducing gases .

3.2 : REPRODUCIBILITY

Reproducibility of response is a fundamental requirement in any analytical detection system and therefore had to be determined . The measurement was carried out using the FID type housing (figure 2.1.3) . The chromatographic conditions employed were :

COLUMN	1 m x 4 mm activated alumina
COLUMN TEMPERATURE	70°C
CARRIER GAS	air
CARRIER FLOW	40 ml min ⁻¹
INJECTOR	1 ml gas sampling valve
INJECTOR TEMPERATURE	20°C
DETECTOR	TGS 813
DETECTOR TEMPERATURE	100°C

The heater voltage used was 5.0V as recommended by the manufacturer for the conventional use of TGS .

The reproducibility was measured by calculating the percentage relative standard deviation (RSD) of the response of the TGS to ten injections of a 50 vpm (parts per million , volume : volume ratio) mixture of hydrogen in air . The response was defined as the peak area determined using a computing integrator (type HP 3390A , Hewlett Packard , Winnersh Triangle , Reading . Berks . U.K.) .

The reproducibility of the system was found to be 3.5% which is significantly less than the generally accepted limit of 5% for useable instrument reproducibility .

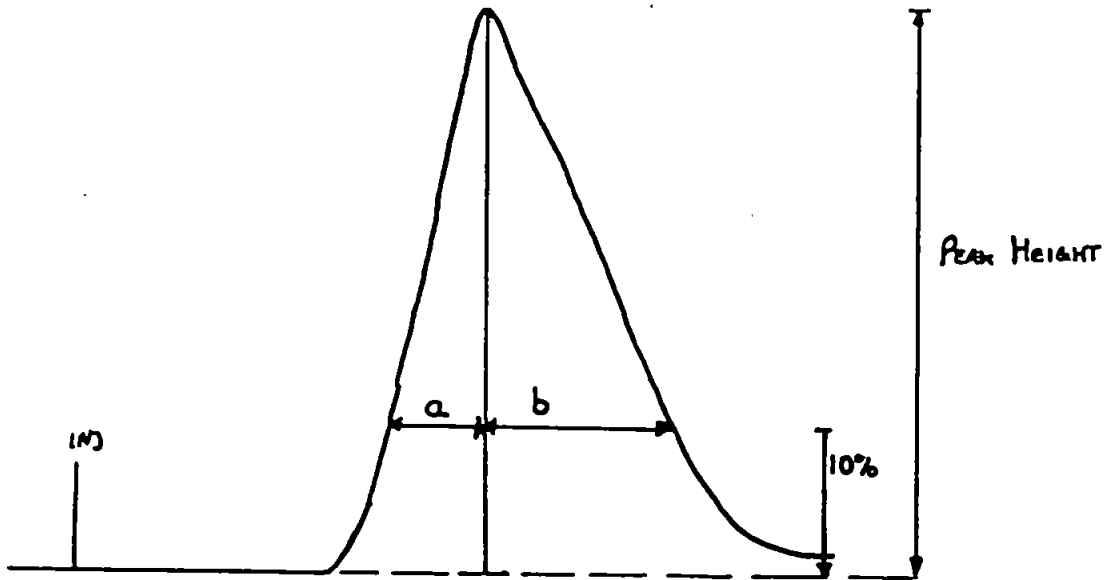
3.3 THE IMPORTANCE OF HEATER VOLTAGE

It has already been well established by Wynne [12] and Rowley [13] that the heater voltage or more specifically the surface temperature of the sensor has an important affect on its response . The surface temperature affects both important sensor response parameters (peak height and peak shape) . It was therefore necessary to study closely the relationship between heater voltage and the two parameters .

In this investigation the chromatographic conditions were as described above . The heater voltage was raised from 4.0V to 7.0V and then reduced to 4.0V in a steps of 0.5V . After each change in voltage the system was left to equilibrate for 30 minutes . The responses to ten injections of 50vpm hydrogen in air were measured at each voltage studied . The peaks obtained were recorded using a single line chart recorder (J.J. Instruments) . Peak height was determined by constructing the baseline under the peak and measuring the perpendicular distance from baseline to peak maximum . The parameter used to define peak shape was the 90% skew factor i.e. the distance from the peak maximum - baseline perpendicular to the 90% recovery point on the curve (parallel to the baseline) divided by the distance from the 10% peak rise point to the peak maximum - baseline perpendicular as shown in figure 3.3.1 .

Figures 3.3.2 and 3.3.4 show the results of this study . In contrast to that observed by Rowley [13] no hysteresis in response or skew factor was observed . The reason for this was probably due to the longer (and fixed) equilibration time allowed in this study than that allowed previously by Rowley [13] .

FIGURE 3.3.1 :
THE MEASUREMENT OF SKEW FACTOR



$$\text{SKEW FACTOR} = \frac{a}{b}$$

FIGURE 3.3.2

THE AFFECT OF HEATER VOLTAGE ON THE PEAK
HEIGHT RESPONSE OF A TGS 813 TO HYDROGEN

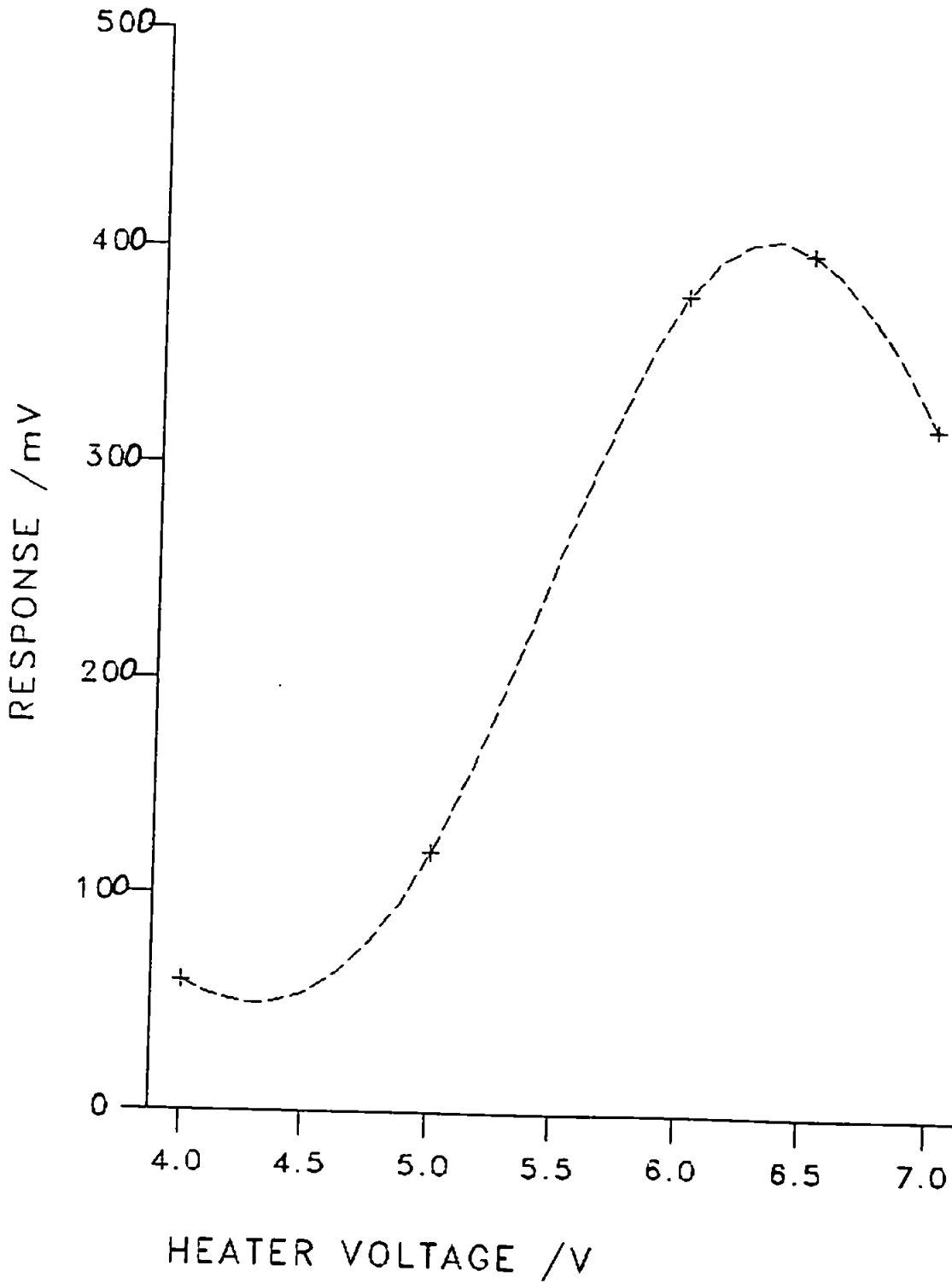


FIGURE 3.3.4

THE AFFECT OF HEATER VOLTAGE ON THE SKEW
FACTOR FOR HYDROGEN ON A TGS 813

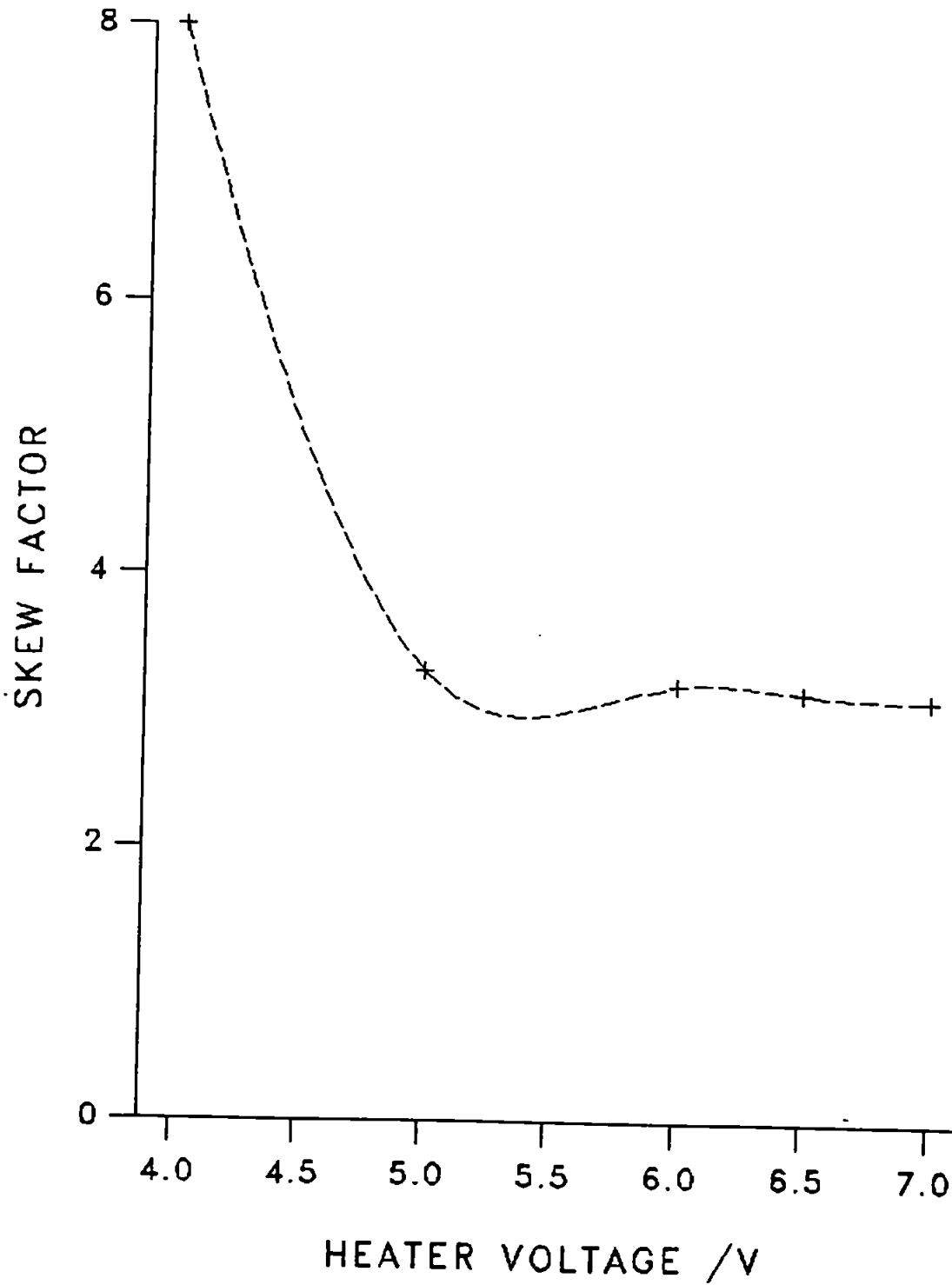
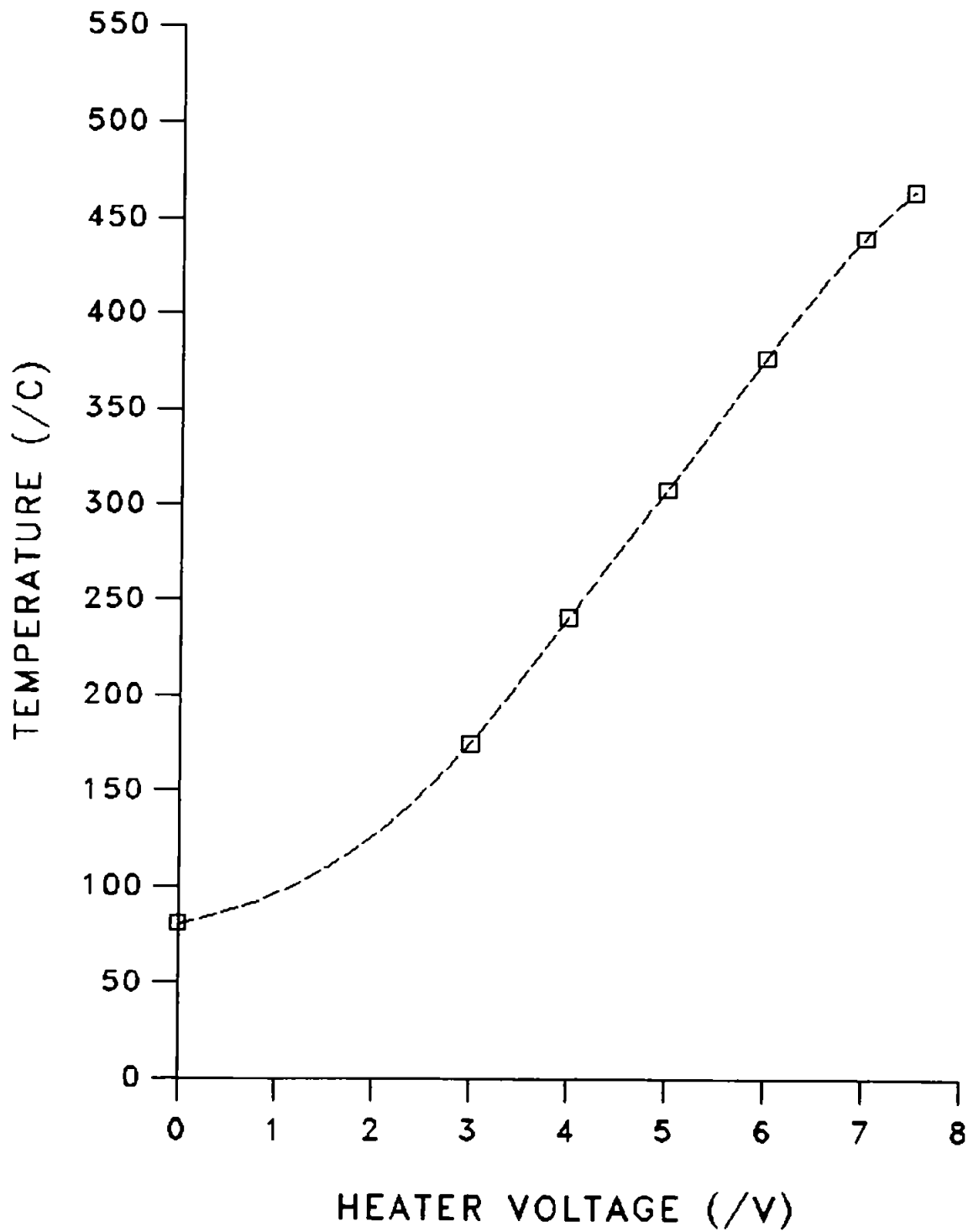


Figure 3.3.2 clearly shows the existence of an optimum surface temperature for the peak height response to hydrogen . The presence of a temperature optimum can be explained in terms of the physical processes and kinetics of the reactions occurring at or near to the tin oxide surface . McAleer et.al. suggest that combustion occurs in a zone near to the tin oxide surface and that it is the water produced which reacts with chemisorbed oxygen species close to the Schottky barriers causing a change in conductivity . Assuming that this is true , then as the temperature increases so does the rate of the hydrogen combustion and hence the amount of water produced . The increase in the water production leads to a larger response at higher temperatures . However at high temperatures other processes occur which tend to limit the response . Firstly the combustion zone will be extended further from the surface of the tin oxide thereby reducing the probability of the product surface interaction . Secondly and perhaps of greater significance is that the product of the water/surface reaction , hydroxyl ions , are much less stable at high temperatures and tend to be easily lost from the surface by condensation of adjacent hydroxyls to reproduce water . This means that the probability of the initial reaction of the water from the combustion is reduced at higher temperatures . Figure 3.3.3 shows the relationship between heater voltage and surface temperature under the conditions used in this experiment . The graph shows that the surface temperature response maximum occurs at $\sim 400^{\circ}\text{C}$. This value is in agreement with that found by McAleer et.al. [50] and corresponds to the

FIGURE 3.3.3
THE SURFACE TEMPERATURE DEPENDENCE OF
A TGS 813 ON APPLIED HEATER VOLTAGE



temperature quoted by Yamazoe et.al. [61] at which the loss of OH- (as H₂O) occurs .

To date , very little attention has been paid to the recovery of the sensor after interaction with a reducing gas . However , in many ways it is equally as important to a sensor as the initial response , this is especially true for the chromatographic application described here . Figure 3.3.4 shows the affect of heater voltage on skew factor . The graph showed two distinct regions :

1. at low heater voltages skew factor improved rapidly ;
2. above 5.0V little further improvement was observed .

The explanation of this phenomenon is unclear . Perhaps , since it is known that the analyte gas is oxidised by interaction with the tin oxide , it might be reasonable to propose that the recovery mechanism involves re-oxidation of the tin oxide surface . Furthermore the rapid improvement phase of figure 3.3.4 could be attributed to the increasing rate of oxygen chemisorption reaction(s) . The limiting of the chemisorption reaction rate(s) is the major problem . According to Yamazoe et.al. desorption of the oxygen surface species does not occur below temperatures of ca. 520°C . Since the limiting of the improvement (reduction) in skew factor starts at ca. 300°C it is unlikely that the desorption rate of the oxygen species is the limiting factor . One possible explanation is that there are two types of chemisorption sites as suggested by Bobyshev and Radtsig [30] , possibly corresponding to different crystal planes , on one of which chemisorption is hindered thereby limiting the rate

of recovery to that of the least receptive sites .

3.4 : SELECTION OF HOUSING DESIGN

In section 2.1 the two housing designs used in this study were described , and a preference for the design based upon the flame ionisation detector (FID) was expressed . The preference for the FID-based housing was formed on the basis of convenience for interfacing with the GC and upon observations that the Rowley housing was more susceptible to drifting chromatographic baselines . In order that the FID-based housing could be adopted for further study it was necessary to compare the response parameters of the two designs . The comparison was made by measuring four common response parameters :

peak height ;

skew factor ;

peak width at 50% of peak height (half width) ;

rise time (taken from initial baseline disturbance to peak maximum) .

The chromatographic baselines i.e. the steady state conductivities were observed to be different in each housing at similar heater voltages and chromatographic conditions . The most probable explanation for this being that the temperature of the tin oxide differed due to different thermal insulation in the two housings . The importance of the oxide surface temperature upon response has already been demonstrated in the preceding section , it was therefore necessary for this experiment to be carried out at slightly different heater voltages such that the two baseline levels were similar thus ensuring similar sensor temperatures . The conditions used in this experiment were :

COLUMN	1 m x 4 mm activated alumina
COLUMN TEMPERATURE	70°C
CARRIER GAS	air
CARRIER FLOW	50 ml min ⁻¹
INJECTOR	1 ml gas sampling valve
INJECTOR TEMPERATURE	20°C
DETECTOR	TGS 813
DETECTOR TEMPERATURE	Rowley type 20°C : FID type 70°C
HEATER VOLTAGE	Rowley type 6.4 V : FID type 6.95 V

The four parameters chosen were measured for ten injections of 50vpm hydrogen . The peaks were recorded on the chart recorder used previously .

The results of the comparison are summarised in table 3.4.1 in terms of the average value of each measurement together with an estimate of the precision of the measurements (plus or minus three times the standard deviation found) . Table 3.4.1 shows that there was very little difference between the two sensor housings studied and it was therefore possible to adopt the FID-type housing on the grounds of its greater compatibility with the GC and superior thermal stability .

TABLE 3.4.1 : COMPARISON OF THE TWO SENSOR HOUSINGS AVAILABLE

PARAMETER	FID-TYPE	ROWLEY-TYPE
RESPONSE (/mV)	402 ± 10	416 ± 16
RISE TIME (/s)	2.1 ± 0.2	2.3 ± 0.3
HALF WIDTH (/s)	2.8 ± 0.2	2.6 ± 0.3
SKEW FACTOR	2.0 ± 0.4	1.6 ± 0.3

3.5 : SIMPLEX OPTIMISATION OF THE SENSOR OPERATING CONDITIONS

The importance of studying the sensor at its optimum conditions was discussed in section 3.1 . For those reasons it was decided that all of the operating conditions should be rigorously optimised . The variables which were observed to affect the detector response were :

heater voltage ;
column flow rate ;
column temperature .

Because the individual affects of these variables are dependant upon the others i.e. the variables are not independent , the normal procedure of performing univariate searches of each variable was unlikely to identify the true optimum . The Variable Step-size Simplex Algorithm [62] has proven to be very successful in the optimisation of systems with non independent variables (e.g. Inductively Coupled Plasma Atomic Emission Spectrometry [63]) and was therefore selected for use in this work .

There are three important considerations in simplex optimisation :

1. the boundary conditions within which the optimisation will be confined . These conditions should be set as wide as possible without allowing sets of conditions unsuitable for the instrumentation such as very high or very low column temperatures , zero carrier gas flow or very high heater voltages . The barrier conditions selected for the

optimisation of the operating conditions are given in table 3.5.1 .

2. the figure of merit (FOM) which is the parameter to be optimised . In this study on hydrogen the criteria for optimum operating conditions were :

- a. the response to hydrogen should be as high as possible ;
- b. the skew factor should be as low as possible ;
- c. adequate retention of hydrogen on the column should be maintained .

The figure of merit was therefore selected to incorporate all three criteria and was defined by the equation :

$$\text{FOM} = \frac{\text{PEAK HEIGHT} \times \text{RETENTION TIME}}{\text{SKEW FACTOR}}$$

The maximisation of the FOM thus tends towards large peaks , long retention time and symmetrical peaks . In this study it was felt that the three criteria were of approximately equal importance and therefore none of the criteria received an exponential weighting that can be used to stress one criterion or another (e.g. squaring the peak height term in the FOM equation) ;

3. termination of the optimisation iteration . One common method of termination is to test that the figures of merit from $n+1$ (n = number of variables optimised) sets of conditions do not differ significantly . This is achieved by

TABLE 3.5.1 : BOUNDARY AND OPTIMUM CONDITIONS FOR THE
SIMPLEX OPTIMISATION OF THE RESPONSE OF A
TAGUCHI GAS SENSOR TO HYDROGEN

PARAMETER	BOUNDARY CONDITIONS	OPTIMUM CONDITIONS
CARRIER GAS FLOW RATE (ml min ⁻¹)	15 - 45	30
COLUMN TEMPERATURE (C)	30 - 150	118
HEATER VOLTAGE (V)	3.5 - 7.0	4.85

setting a percentage difference factor for the FOM . The factor depends upon the uncertainty of the determination of the FOM and is perhaps one of the drawbacks in using a complex figure of merit such as that above . The reason for this is that the uncertainty of the FOM increases with the number of measurements included due to the errors on each measurement . In the optimisation performed here the iteration was terminated when the four best figures of merit obtained differed by less than 8% .

After the optimisation is terminated the centroid set of conditions can be calculated from the optima defined . In this case the centroid was calculated by weighting each optimum condition with its figure of merit and then taking the average value i.e. :

$$V_{\text{optimum}} = \frac{[(V1 \times F1) + (V2 \times F2) + (V3 \times F3) + (V4 \times F4)]}{[F1 + F2 + F3 + F4]}$$

Where :

F1-F4 = The four highest figures of merit .

V1-V4 = The respective values of variable V for each figure of merit .

The optimisation was performed by taking the average measurements from three injections of 50vpm hydrogen at each set of conditions generated by the algorithm . At least thirty minutes was allowed for equilibration between different sets of conditions before the FOM was determined .

The optimum conditions obtained are given in table 3.5.1 . The dependence of the FOM on each of the variables individually

was then determined by performing univariate searches about the optimum of each variable . Figures 3.5.1 , 3.5.2 and 3.5.3 show the results of the investigation . A number of observations could be made from these results :

Firstly the optimum conditions determined by the simplex algorithm coincide with either the maxima of the univariate search curves , or as in the case of column flow rate , the edge of a response plateau . This indicated that the optimisation had performed properly . The tendency to rest at the edges of plateaux is a feature of the simplex algorithm , the reason it occurs is due to the fact that there is insufficient increase in figure of merit to be gained from moving to the centre and yet as would be expected the value of the FOM falls away if the simplex moves away from the plateau . There are however practical advantages to be gained from using the middle of response plateaux in terms of operational stability since small variations in the variable cause little change in response .

The second observation was that the chromatographic parameters (column temperature and carrier gas flow rate) had only a small influence upon the FOM in comparison with the heater voltage . The reason for this was that the influence of the chromatographic parameters was primarily on the retention time of the hydrogen , which , because of its physical properties , was not altered by a great deal . There were however two secondary affects of the chromatographic parameters :

1. the flow rate and temperature of the carrier gas controlled the cooling of the sensor surface ;

FIGURE 3.5.1

THE AFFECT OF HEATER VOLTAGE ON
THE FIGURE OF MERIT

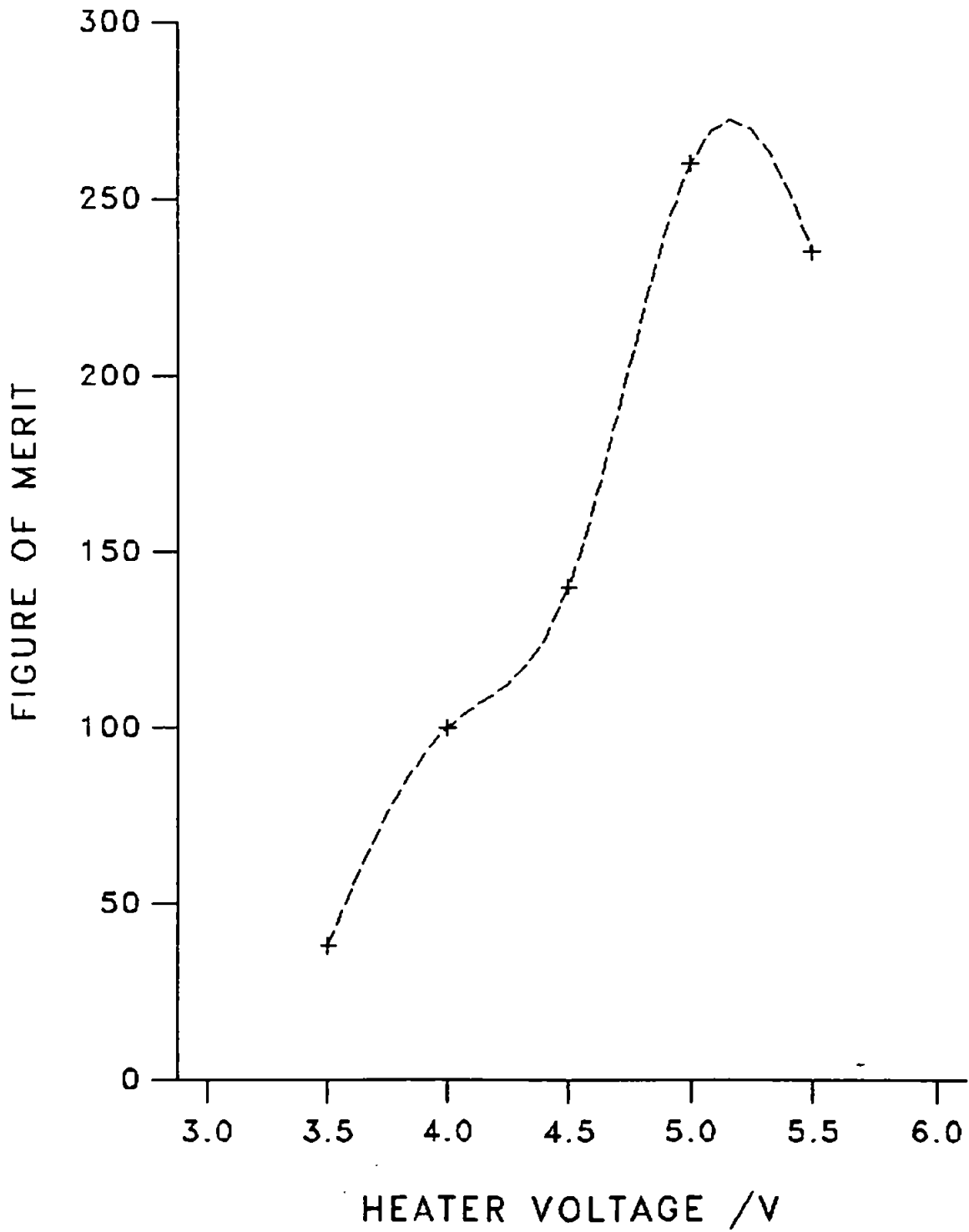


FIGURE 3.5.2

THE AFFECT OF COLUMN TEMPERATURE ON
THE FIGURE OF MERIT

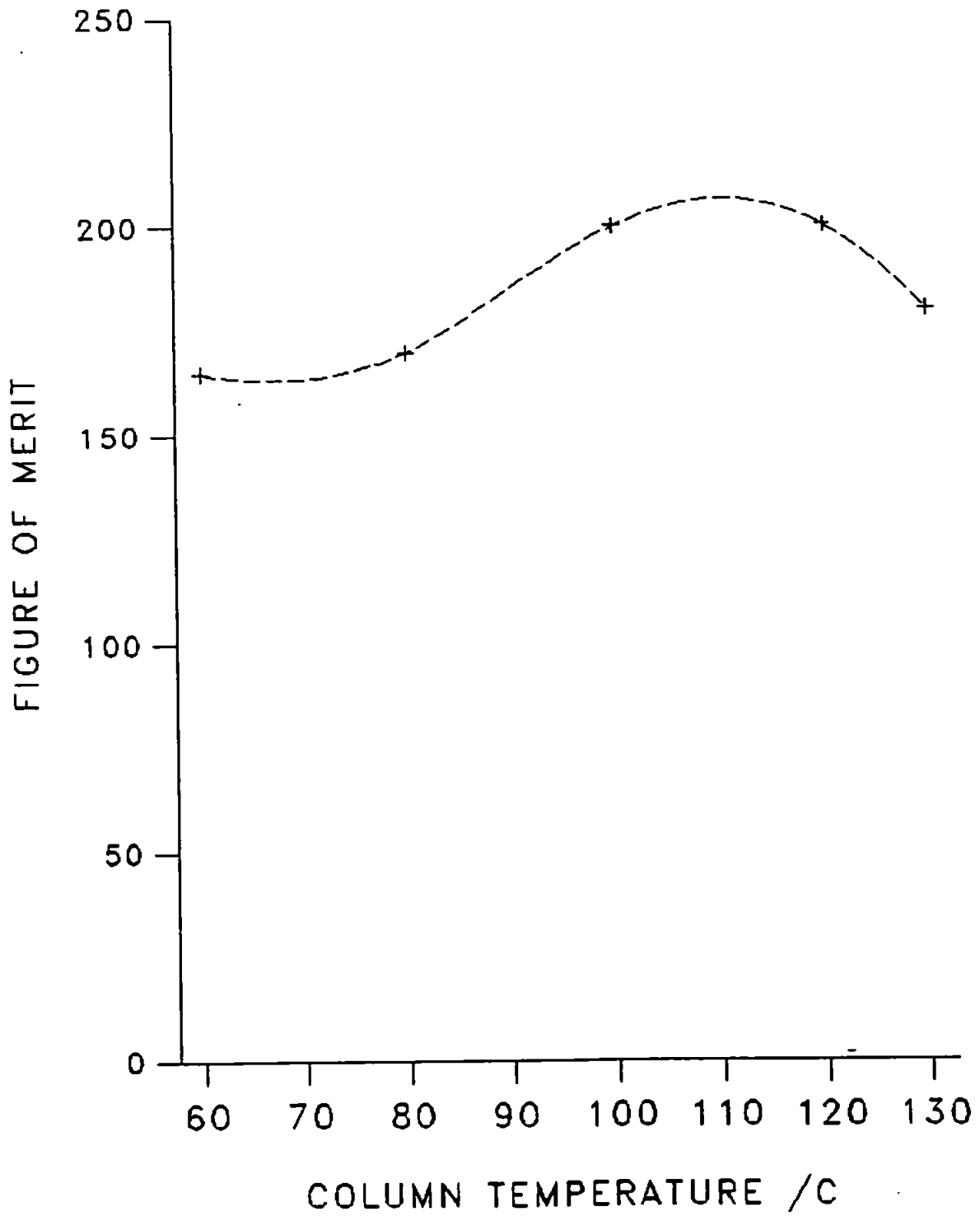
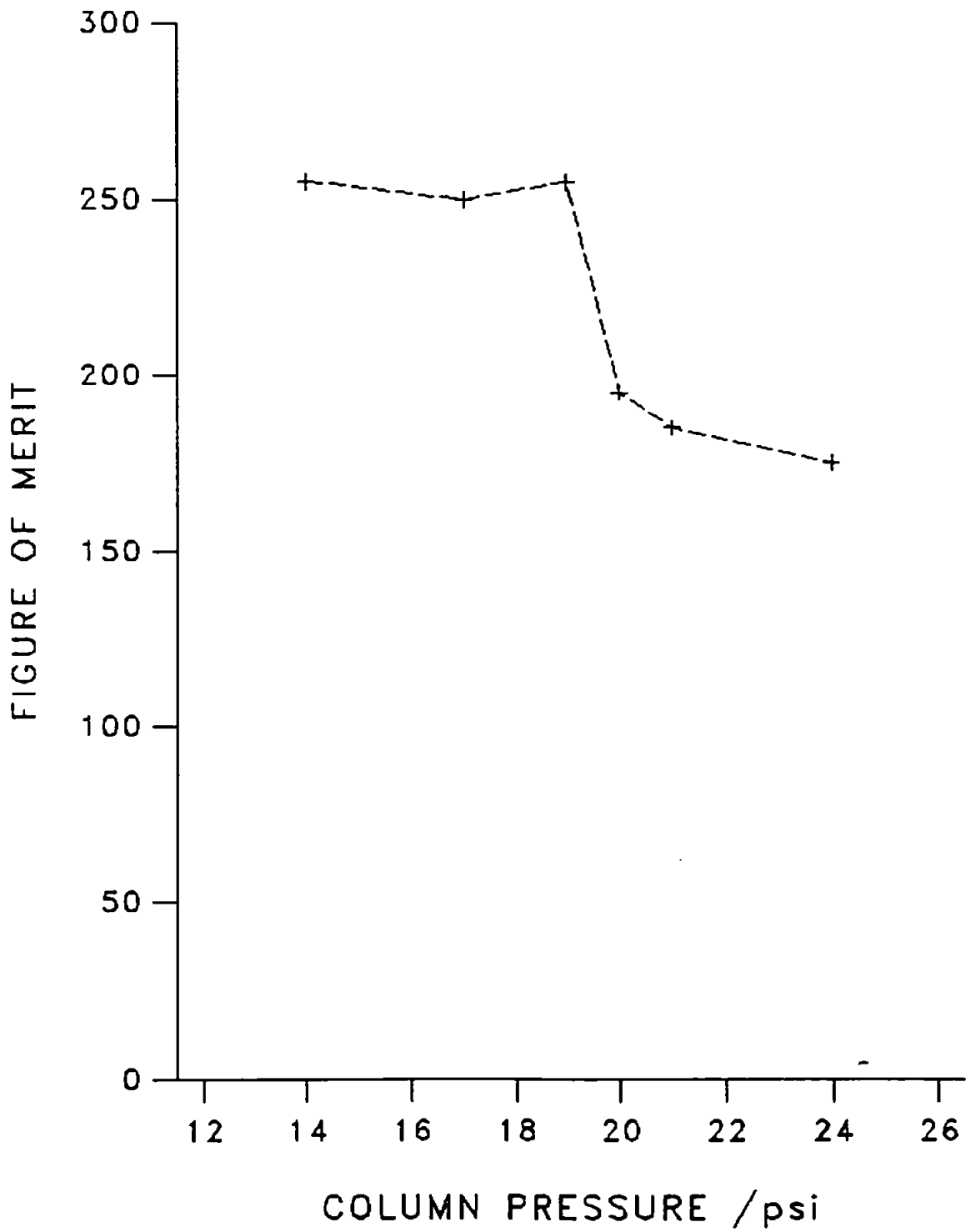


FIGURE 3.5.3

THE AFFECT OF COLUMN HEAD PRESSURE
ON THE FIGURE OF MERIT



2. the flow rate of the carrier gas determined the residence time of the hydrogen in the sensor housing .

The third observation , that the greatest influence over FOM was the heater voltage supported the indications given by previous experiments . The indication was that the surface temperature was the critical factor affecting the sensor response characteristics , and since the heater voltage is the dominant factor affecting surface temperature the dependence of response on heater voltage is clearly shown .

The major conclusion to be drawn from these observations is that the chromatographic variables may be considered independently of heater voltage without a large reduction in the figure of merit . This is advantageous since it indicates that the sensor may be used as a GC detector without limiting the range of chromatographic conditions available .

In the discussion of the influence of the chromatographic variable it was mentioned that the carrier gas flow rate determined the residence time of the hydrogen in the detector housing . It was felt that minimisation of the skew factor would be aided by efficient flushing of the detector housing . Rowley [13] performed a simplex optimisation incorporating the detector flow rate . However in the experimental design the carrier gas was split before entering the detector . This had two disadvantages :

1. the experiment was restricted to detector gas flows of less than or equal to the carrier gas flow ;
2. splitting off the column effluent restricted the amount of sample reaching the sensor , possibly

reducing the peak height response .

Also the optimisation performed by Rowley made no mention of peak shape and concentrated on sensitivity . The influence of carrier gas flow rate found earlier and the results produced by Rowley warranted further investigation . This conclusion was further encouraged when the response of the sensor to light hydrocarbons was studied with and without an auxiliary flow of gas through the detector housing . The auxiliary flow was directed through the oxidant flow inlet of the FID housing , the gas therefore entered the housing around the base of the flame jet (figure 2.1.2) . Figure 3.5.4 shows two of the chromatograms obtained during this experiment , clearly the tailing of the hydrocarbon peaks had been reduced by the inclusion of the auxiliary flow . It was also noted that the peak heights had been reduced , possibly by the increased cooling of the sensor by the extra gas flow . It was decided that the best method of studying the effects of an auxiliary flow would be to perform another simplex optimisation including the auxiliary flow rate .

For continuity and comparison the optimisation was performed using the same boundary conditions , FOM and precision factor as before . The auxiliary gas flow was varied using a pressure controller , the optimisation was therefore carried out by using the auxiliary gas pressure and the boundary conditions set between 1 and 10psi table 3.5.2 shows the boundary and optimum conditions for this simplex optimisation , the 1.5psi auxiliary gas pressure optimum corresponded to a flow of approximately 10 ml min⁻¹ .

FIGURE 3.5.4 :

TYPICAL CHROMATOGRAMS OBTAINED FROM THE SEPARATION OF THE
ALKANES SHOWING THE OBSERVED IMPROVEMENT IN SKEW FACTOR
WHEN AN AUXILIARY DETECTOR GAS FLOW WAS INCORPORATED



TABLE 3.5.2 : BOUNDARY AND OPTIMUM CONDITIONS FOR
THE SIMPLEX OPTIMISATION OF THE RESPONSE OF A
TAGUCHI GAS SENSOR TO HYDROGEN WITH THE
INCORPORATION OF AN AUXILIARY DETECTOR GAS FLOW

PARAMETER	BOUNDARY CONDITIONS	OPTIMUM CONDITIONS
CARRIER GAS FLOW RATE (ml min ⁻¹)	15 - 45	10.5
COLUMN TEMPERATURE (°C)	30 - 150	50
HEATER VOLTAGE (V)	3.5 - 7.0	4.12
AUXILIARY GAS PRESSURE (psi)	0.5 - 10	1.5

The first observation made was that the optimum conditions were noticeably different from those identified in the previous optimisation . The chromatographic conditions had moved towards greater retention of the hydrogen . The significance of this was that in contrast to the previous simplex , the chromatographic conditions had behaved as would have been expected , maximising the retention time of the hydrogen . The most probable explanation is that the inclusion of the auxiliary flow had increased the deconvolution of the chromatographic variables from the response characteristics .

The second observation was that the maximised figure of merit was much less (FOM=134) than that from the first simplex (FOM=244) . This is almost certainly due to the inclusion of the auxiliary gas . From this it appears that the reduction in FOM was not due to a temperature effect , as at first thought since this would have been removed by the simplex optimisation . It therefore appears that that the reduction in peak height is an independent effect of including the auxiliary gas . Observation of the values obtained for the criteria in the FOM suggest that the peak height was most reduced , it is therefore probable that the inclusion of auxiliary gases reduces the peak height by diluting the gas inside the detector housing . It therefore appears that the price for improved peak shape and deconvolution of chromatographic variables is a degree of sensitivity .

Univariate searches of both heater voltage and auxiliary gas pressure were performed with respect to FOM , peak height and skew factor (figures 3.5.5 to 3.5.10) . The chromatographic variables were not searched due to the much smaller influence

FIGURE 3.5.5

THE AFFECT OF HEATER VOLTAGE ON THE
FIGURE OF MERIT

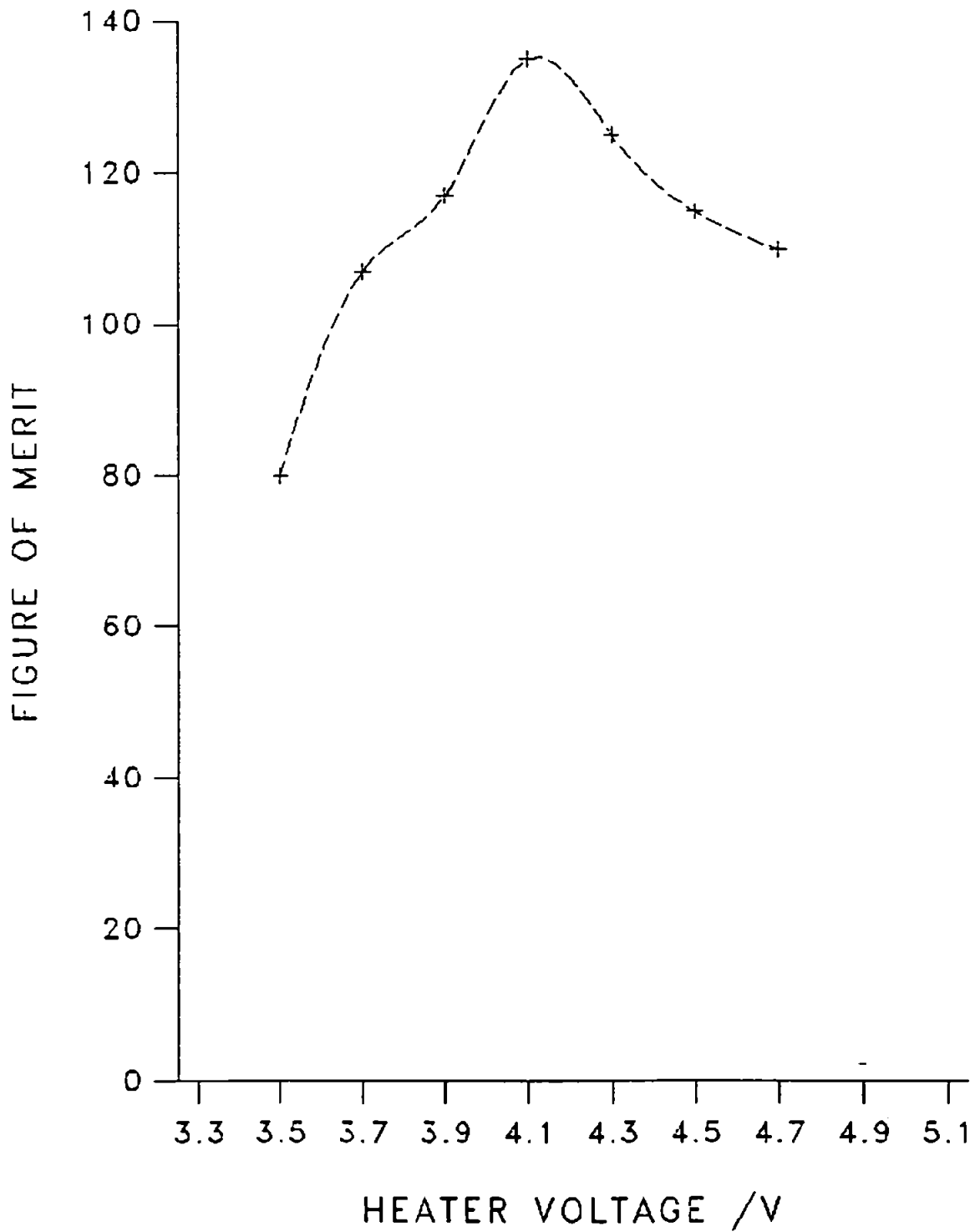


FIGURE 3.5.6
THE AFFECT OF HEATER VOLTAGE
ON SKEW FACTOR

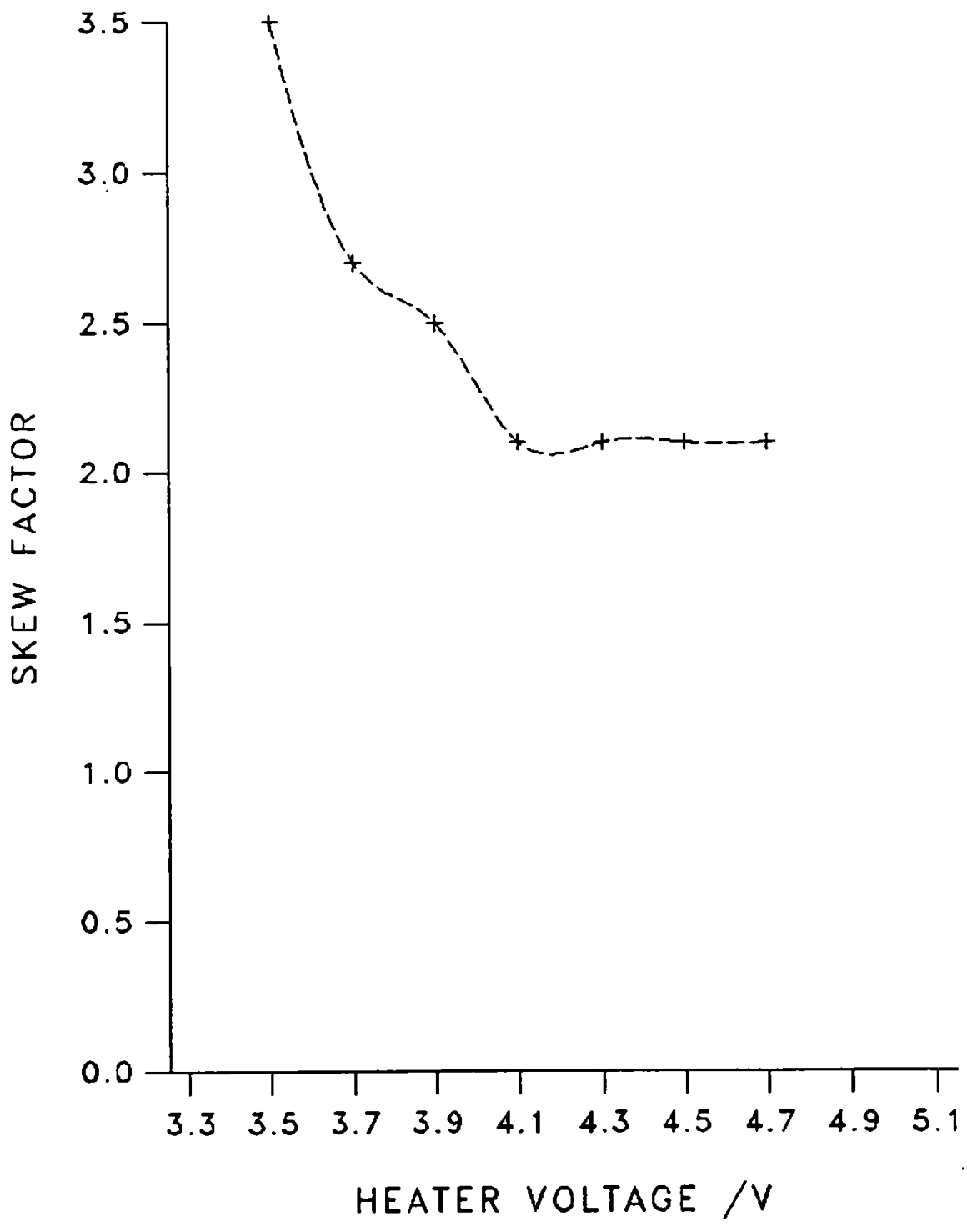


FIGURE 3.5.7
THE AFFECT OF HEATER VOLTAGE
ON PEAK HEIGHT

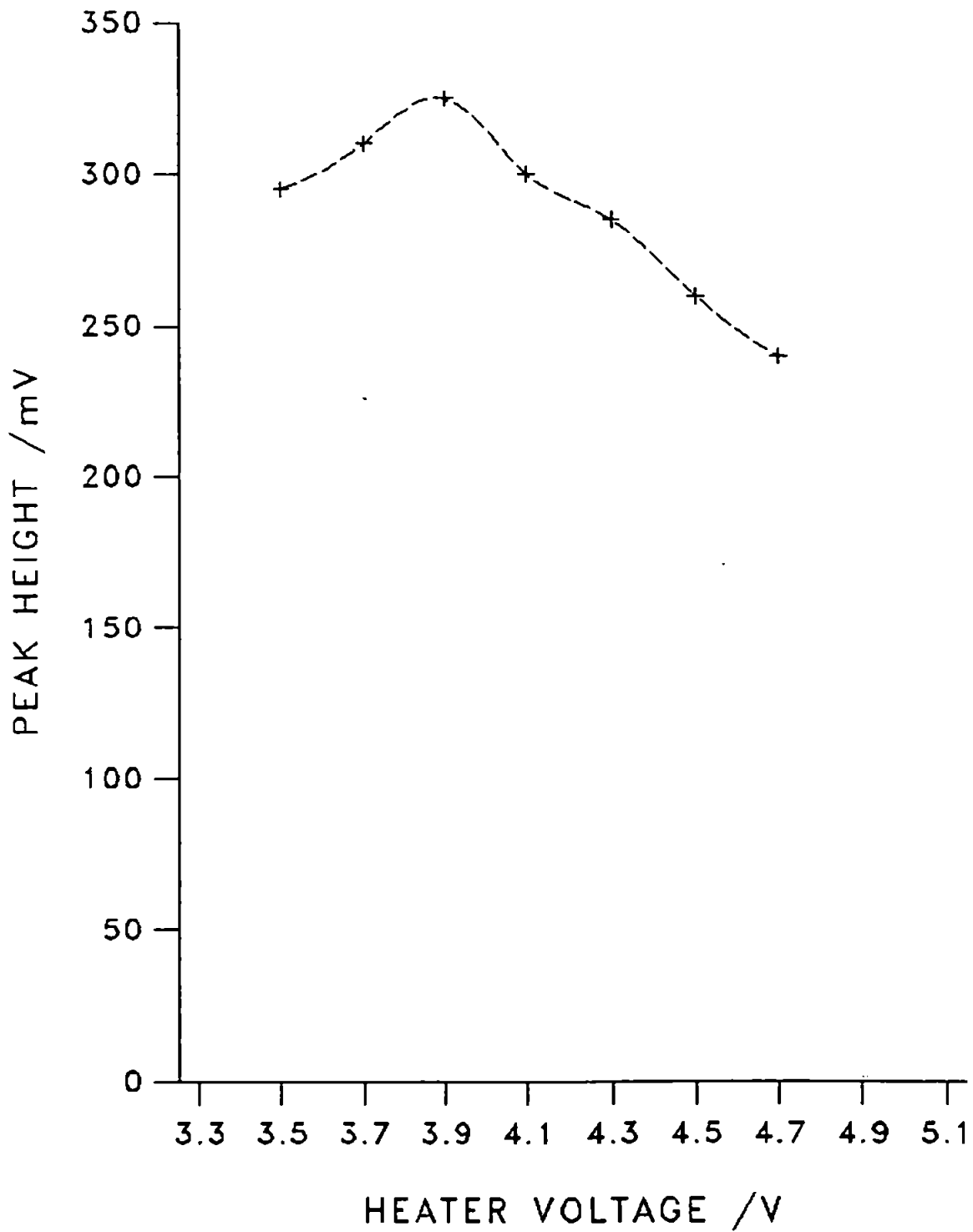


FIGURE 3.5.8

THE AFFECT OF AN AUXILIARY DETECTOR GAS
ON THE FIGURE OF MERIT

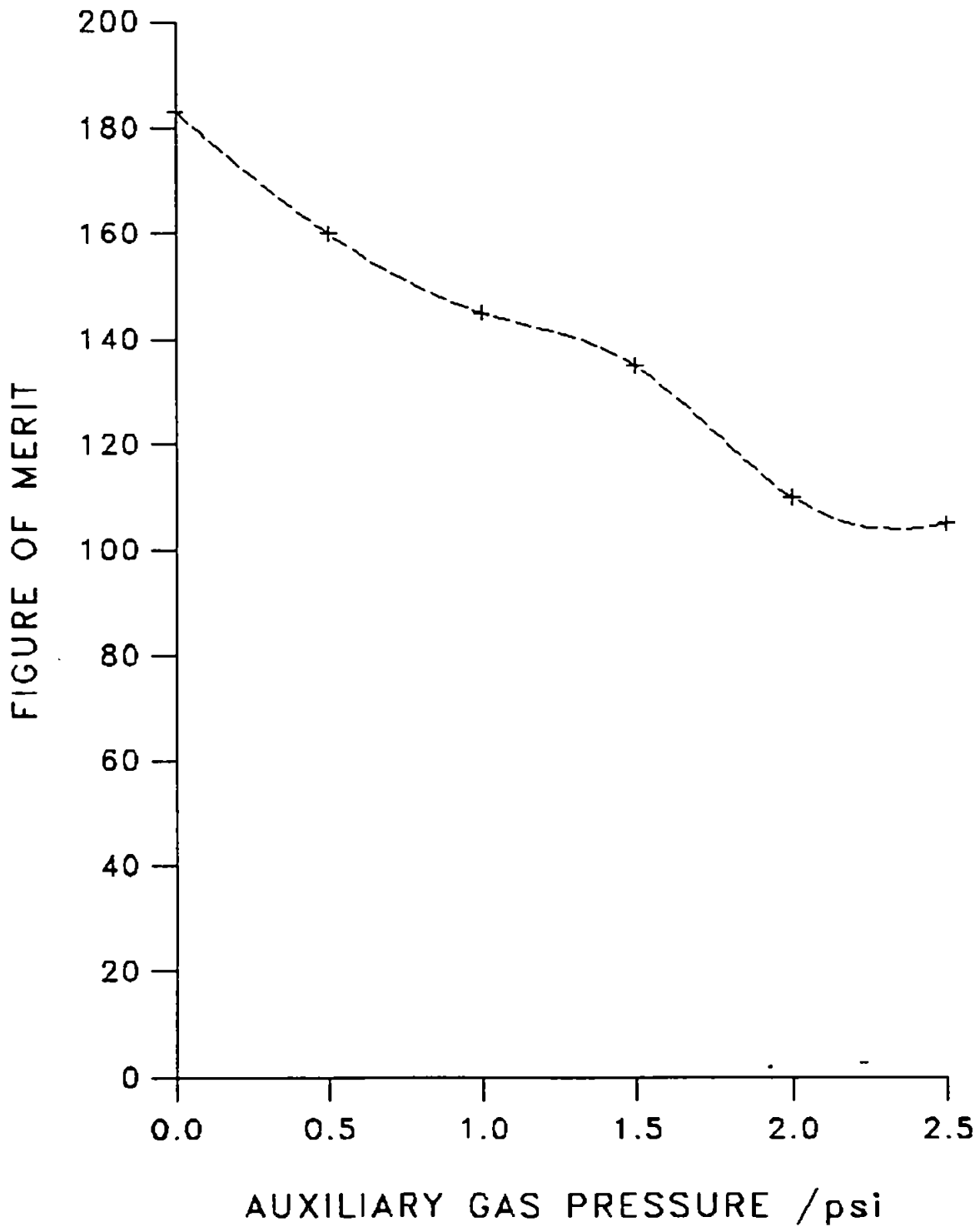


FIGURE 3.5.9

THE AFFECT OF AN AUXILIARY DETECTOR

GAS ON PEAK HEIGHT

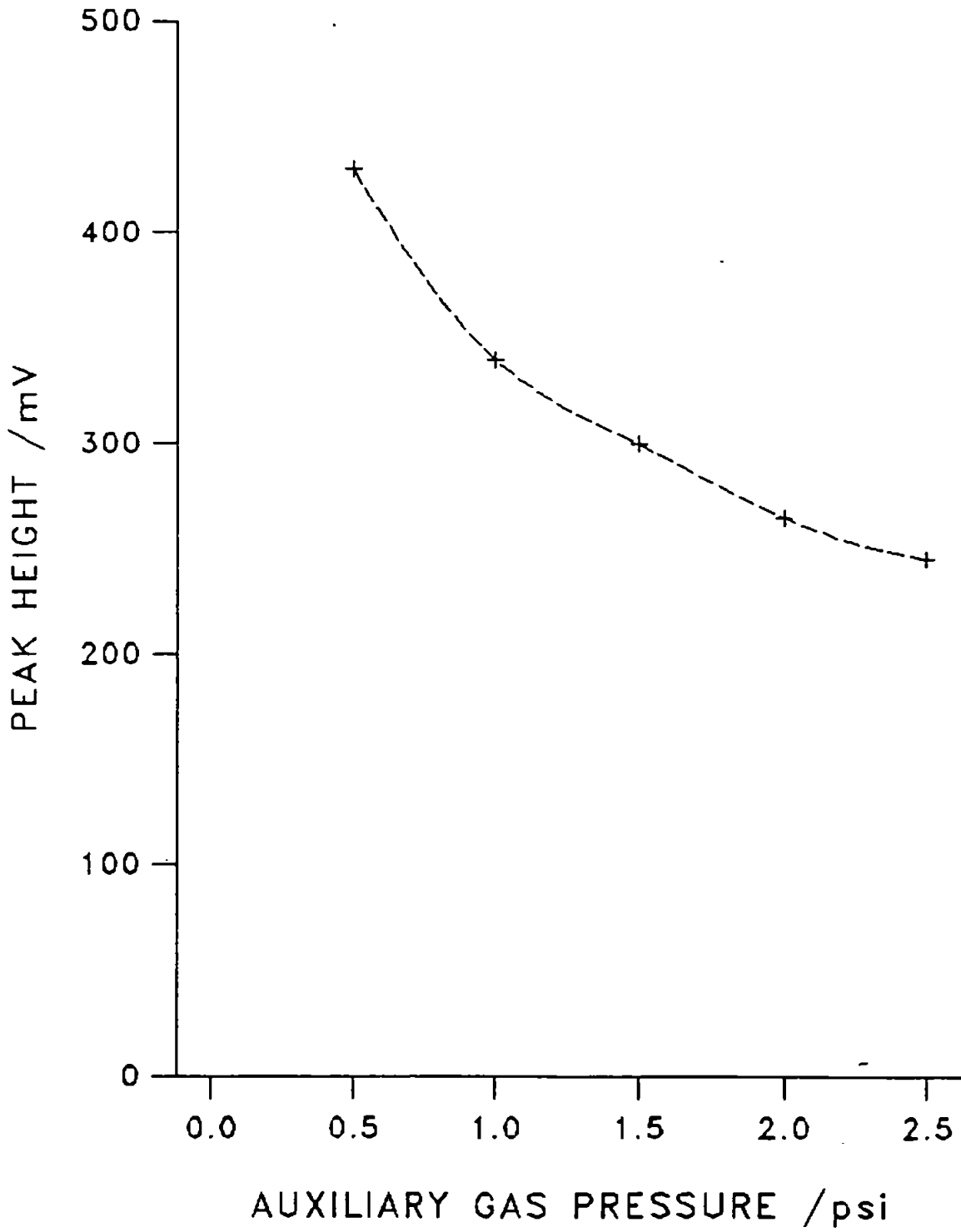
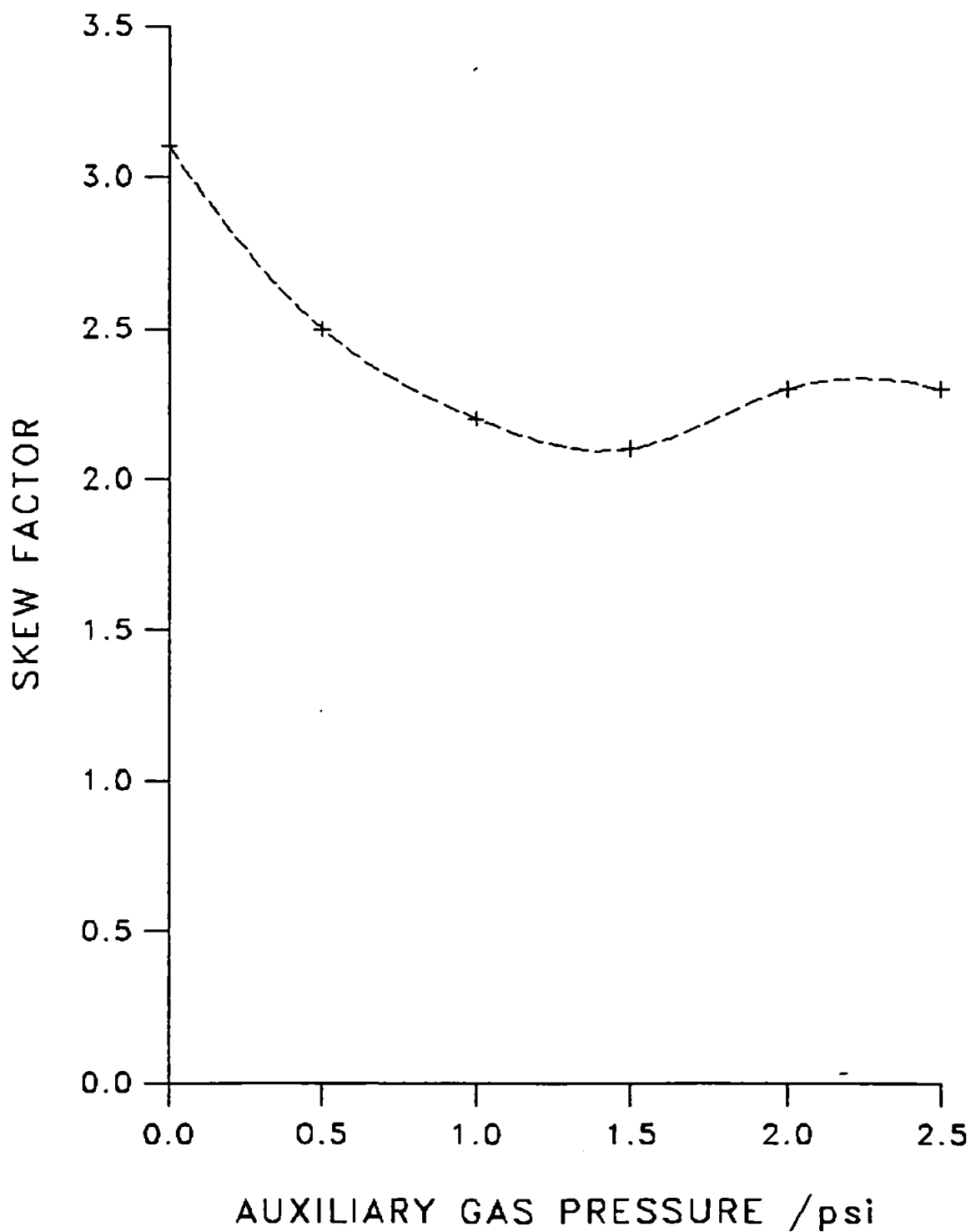


FIGURE 3.5.10

THE AFFECT OF AN AUXILIARY DETECTOR GAS
ON THE SKEW FACTOR



over FOM demonstrated earlier .

The heater voltage - FOM search (figure 3.5.5) shows the same optimum as that identified by the simplex , demonstrating that the optimisation had performed correctly . The affect of heater voltage on skew factor (figure 3.5.6) had the same shape as that found previously . The simplex identified the edge of the plateau for minimum skew factor again showing this characteristic of the algorithm . Figure 3.5.7 the heater voltage - peak height univariate search showed showed that the optimum peak height had not been selected this was probably due to the influence of the skew factor .

The auxiliary gas pressure - FOM univariate search (figure 3.5.8) demonstrated that the inclusion of an auxiliary gas flow only reduced the figure of merit . The point selected by the simplex did not appear to be the optimum although there was not a significant difference (<8%) between the FOM for 1psi (the boundary value) as opposed to 1.5psi (the defined optimum) . Figure 3.5.9 the univariate search of auxiliary gas pressure versus peak height demonstrated why the FOM had been reduced as it showed that the peak height was significantly reduced by the auxiliary gas flow . The heater voltage - peak height univariate and the actual lowering of the optimum peak height as compared with the first optimisation , had already demonstrated that the influence of the auxiliary gas was not a temperature affect . It was therefore concluded that the reduction in FOM was caused by dilution of the analyte in the detector housing . This inferred that the sensors were concentration sensitive rather than mass sensitive devices . The univariate search of the affect of

auxiliary gas pressure upon skew factor (figure 3.5.10) showed why the simplex algorithm had not selected the minimum auxiliary gas pressure , since the optimum found , coincided with the minimum skew factor .

From this investigation it was concluded that an auxiliary gas flow in the detector housing had two benefits :

1. the gas deconvoluted the carrier gas flow rate from the detector housing flow requirements ;
2. the inclusion of auxiliary gas flow enabled minimisation of skew factor .

The disadvantage was that in order to achieve these relatively minor benefits there was a reduction in sensitivity by a factor of 2 . It was therefore concluded that an auxiliary gas flow would not be used in further studies with air carrier gas .

3.6 THE INFLUENCE OF THE OXYGEN CONCENTRATION IN THE CARRIER GAS ON PEAK HEIGHT AND SKEW FACTOR

In section 1.4 it was shown that there is evidence to suggest that various oxygen species (either chemisorbed from atmosphere or surface oxide) are very important in the interaction of gases with tin oxide surfaces. It was decided to study the affect of the oxygen concentration in the carrier gas on the two detector response parameters.

The study was carried out at the chromatographic and heater voltage conditions identified by the first simplex optimisation. The response parameters were measured for ten injections of 50vpm hydrogen in air using the gas blender and gas sampling valve introduction system. The concentration of oxygen in the carrier gas was varied by mixing air with white spot nitrogen using a second gas blender capable of supplying output pressures at up to 60psi. Studies of the equilibration time showed that it was necessary to allow at least 16 hours between changes in carrier gas composition.

Figures 3.6.1 and 3.6.2 show the trends observed in peak height and skew factor respectively with the variation in carrier gas composition. Figure 3.6.1 showed an improvement in skew factor with increasing oxygen concentration. The indication of this was that surface oxygen species were depleted by exposure to the analyte and that sensor recovery depended on interaction of oxygen from the sensor environment with the tin oxide surface.

The rise times were not observed to change with oxygen composition. The recovery of the sensor at 0% oxygen was

FIGURE 3.6.1

THE AFFECT ON SKEW FACTOR OF THE
OXYGEN CONCENTRATION IN THE CARRIER GAS

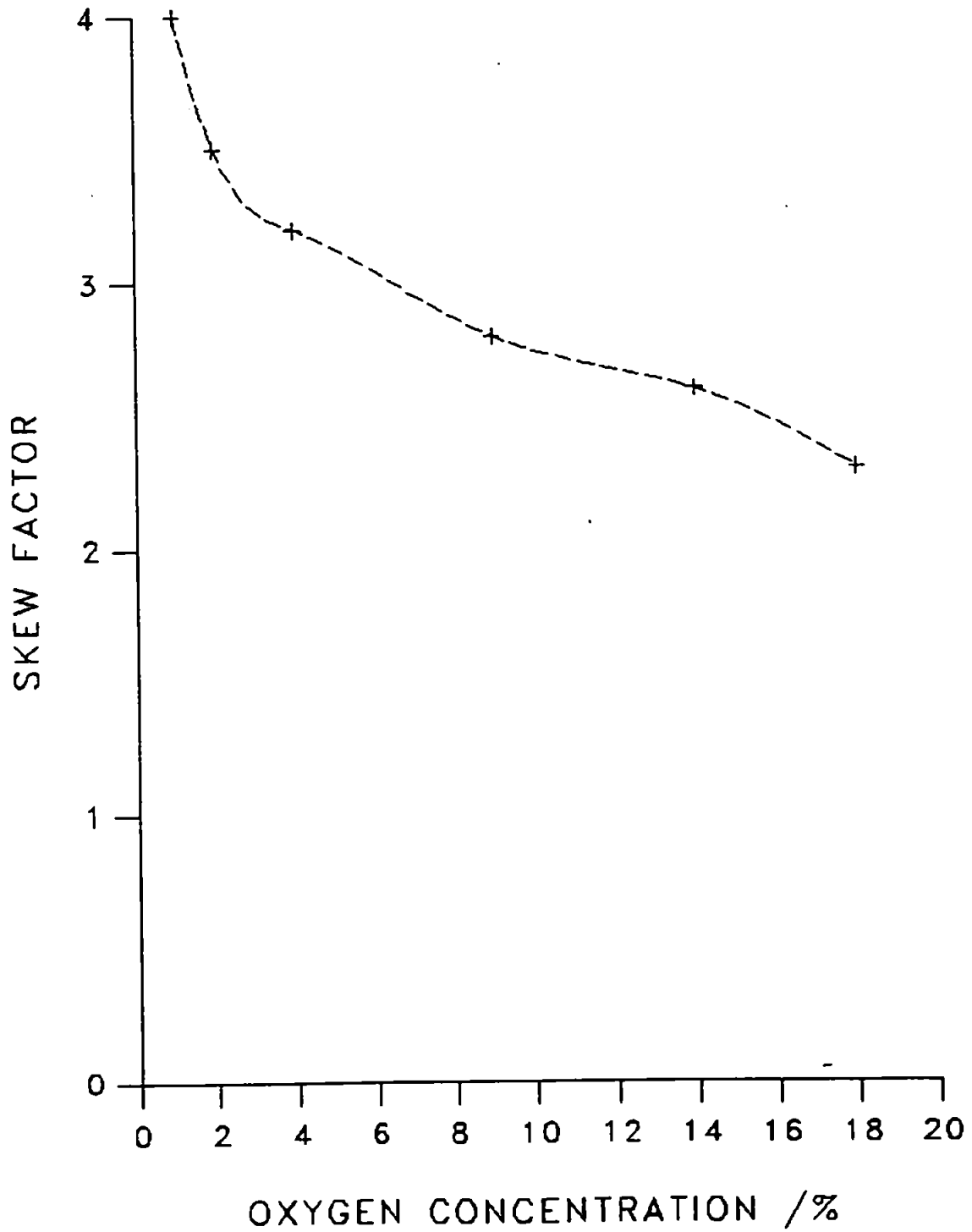
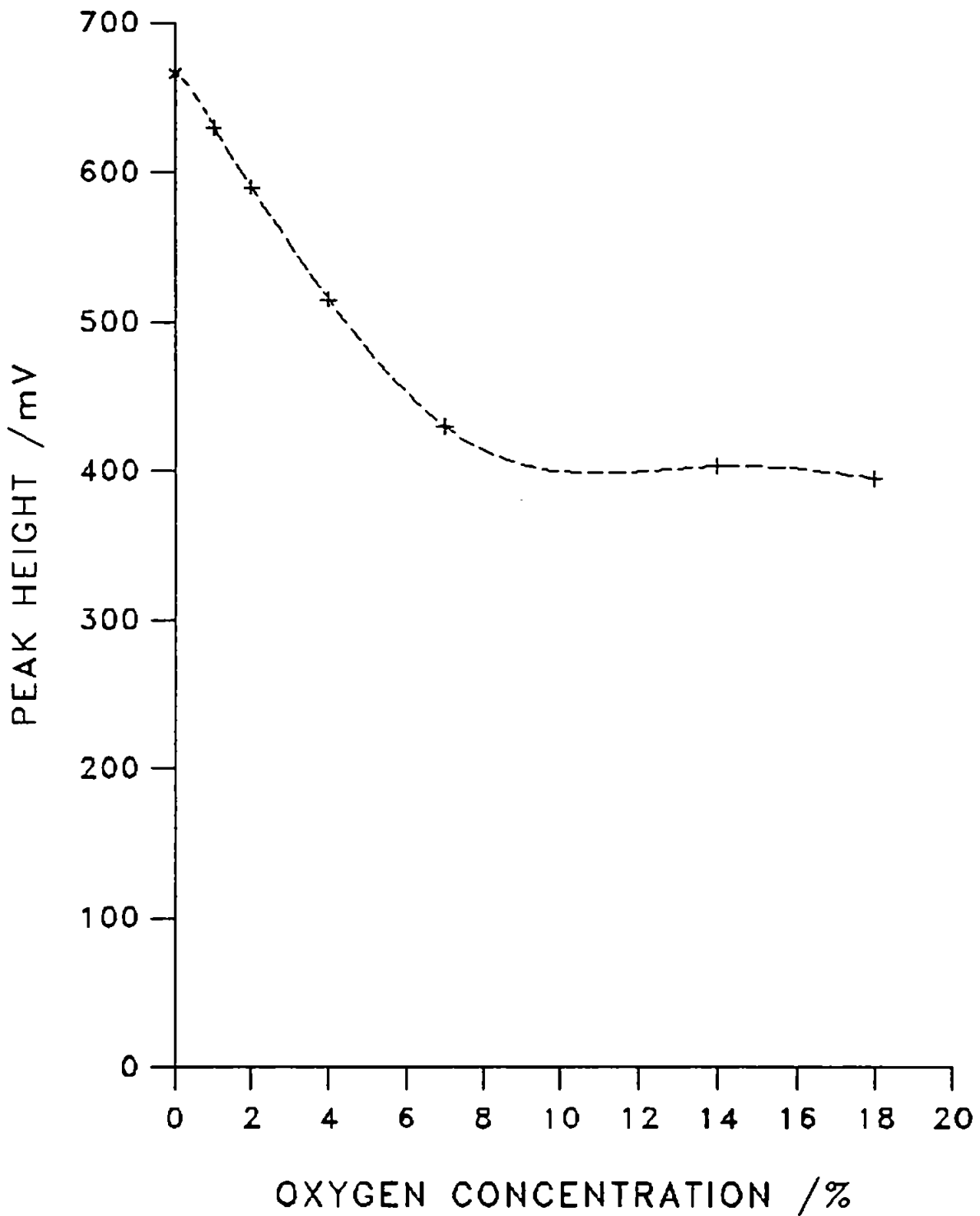


FIGURE 3.6.2

THE AFFECT ON PEAK HEIGHT OF THE
OXYGEN CONCENTRATION IN THE CARRIER GAS



probably facilitated by both the small amount of oxygen in the white spot nitrogen and by diffusion of atmospheric oxygen into the detector housing . Figure 3.6.2 showed a reduction in peak height at increasing oxygen concentration . This result seems inconsistent with the generally proposed view that the interaction of analyte with the oxide surface occurs via chemisorbed oxygen species and supported by the skew factor observations . One possible explanation for the above observation was given by Wynne [12] who carried out similar work with a TGS 711 . Wynne suggested that two types of mechanism existed . Firstly at low oxygen concentration , direct interaction of the analyte with the sensor surface occurred , whilst secondly , at higher oxygen concentrations , interaction proceeded via the chemisorbed oxygen species . However Wynne made no measurement of skew factor in his experiments . The dependence of skew factor on oxygen concentration observed in this experiment tends to disagree with Wynne's theory . The disagreement lies in the assumption of direct interaction with the surface by the analyte . Since the oxygen concentration affects the recovery it should be reasonable to assume that (provided Wynne allowed the sensors to recover) interaction always occurred with surface oxygen species since these must be present to attain the baseline level . Perhaps a better explanation lies in the assumption that surface interactions proceed via 'spillover catalysis' [73] from activator sites such as Pt , Pd , Ag etc. commonly included in tin oxide sensors [e.g. 212] . Spillover catalysis relies upon

the primary interaction of the analyte being with the activating agent . The activator adsorbs the analyte , polarising its electron cloud which then makes it more attractive to the oxygen species and transfer duly occurs . The explanation of the high sensitivity at low oxygen concentration relies upon the fact that the activators are relatively unselective and adsorb many gases besides hydrogen and including oxygen [64] . It is therefore feasible that at relatively high oxygen concentrations adsorption of the analyte at the activator sites , prior to spillover onto the tin oxide , is hindered by previously adsorbed oxygen leading to lower sensitivity of the sensor to the analyte at high oxygen concentration .

Despite the benefits in sensitivity to be gained in operating the sensor at low carrier gas oxygen concentrations , it must be remembered that peak shape is of major importance in chromatography and therefore some sensitivity must be sacrificed .

In order to assess the improvement in skew factor to be obtained by increasing the oxygen concentration , a carrier gas composition of 95% O₂ was studied . The parameters found were a peak height of 250mV and skew factor of 1.7 . It was clear from this that there would have been only minor improvement in skew factor from doing this . It was felt that the benefit was outweighed by a number of factors :

1. the reduction in sensitivity ;
2. decreased compatibility of carrier with stationary phases ;
3. cost effectiveness (air is cheaper than oxygen) ;

4. safety (pressurised oxygen cylinders present a potential hazard in any laboratory) .

These factors considered it was decided that air should continue to be used as the carrier gas .

3.7 : HYDROGEN DETERMINATIONS

The results obtained so far have shown that useable chromatographic response can be obtained from the tin oxide sensor . Following this success the applicability of the TGS was further assessed by performing some determinations of hydrogen in real samples .

There are a number of applications for hydrogen determination including :

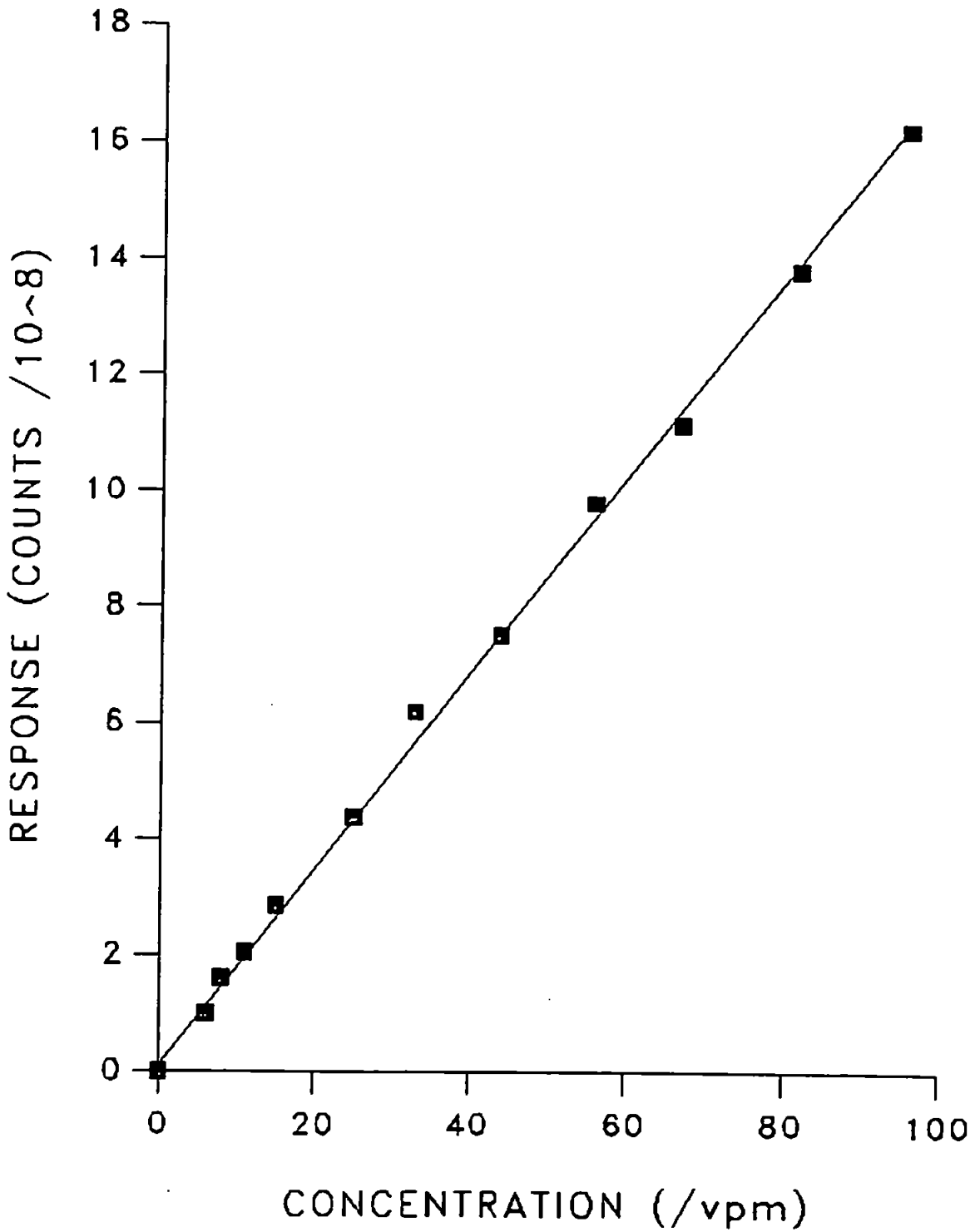
1. in human breath ;
2. in transformer oil headspace ;
3. in diesel and petrol engine exhausts ;
4. local atmosphere monitoring for leak detection , early fire warning etc. .

Two of the above were chosen as illustrative examples for reasons of concentration level and sample availability .

The chromatographic conditions employed for these studies were those obtained by the first simplex optimisation . Calibration of the detector was achieved using the standardised 0.083% (v/v) hydrogen in air mixture . Samples were diluted with white spot nitrogen using the gas blender and injected using the gas sampling valve . The average peak height (nitrogen blank corrected) from five 1ml samples of each calibration mixture in the range 0.2 to 15 vpm were used in the calibration . Figure 3.7.1 shows the calibration graph obtained , it exhibited good linearity with a correlation coefficient of 0.993 . A limit of detection was calculated by taking the gradient of the calibration line and comparing with twice the peak to peak

FIGURE 3.7.1

THE CALIBRATION CURVE OBTAINED FROM A
TGS 813 FOR HYDROGEN CONCENTRATION



baseline noise level . The figure obtained using this calculation method was 20 vpb (parts per 10^9) . It is appreciated that the calculation method used was not that recommended by the International Union for Pure and Applied Chemistry (IUPAC.) , although experience has shown that the method used does give a reasonable approximation to that calculated by the recommended method . The reasons why the IUPAC method was not used were that :

1. 0.2vpm was the limit of dilution obtainable with the blender and a lower calibration standard was not available ;
2. the method used was the same as that of other workers [13] and therefore allowed direct comparison .

The limit of detection (lod) calculated was the same as that obtained by Wynne [12] for a TGS 711 , but lower than the 40vpb quoted by Rowley [58] and is lower than that for most of the commonly used GC detectors with the exception of the Microwave Plasma Atomic Emission detector [65] .

The samples of human breath and laboratory air were collected using gas sampling bags (Varian Instrument Division , 220 Humboldt Court , Sunnyvale . California . USA.) . Seven samples of laboratory air were injected , and duplicate injections of the breath of eight human subjects were used in the analyses .

The samples were injected by drawing the sample gas from the bag through the gas sampling valve using a 100ml ground glass syringe (to provide suction) . The pressure in the gas sampling valve was allowed to equalize with atmospheric for five seconds after at least 50ml of sample had been drawn through the loop .

the sample was then injected .

The results of these analyses together with some literature values are shown in Table 3.7.1 . The good agreement observed further illustrated the applicability of the TGS to gas chromatographic detection .

TABLE 3.7.1 : RESULTS OBTAINED FROM TWO HYDROGEN ANALYSES
PERFORMED WITH A TAGUCHI GAS SENSOR AS THE GAS
CHROMATOGRAPHIC DETECTOR

SAMPLE	FOUND / vpm	LITERATURE VALUE /vpm
HUMAN BREATH	4.2 (range 1.4-7.6)	5.4 _{±7} ¹
LABORATORY AIR	1.0 ± 0.06	0.5 ²

1. Sannolo, N. , Vajro, P. , Dioguardi, G. , Mensitieri, R.
and Longo, D. J. Chromatogr. (Biomed) 276 (1983) 257
2. As H₂ in normal dry air "Handbook of Chemistry and
Physics", CRC Press Inc. 65ed. 1984 Boca Raton. Florida.
USA

CHAPTER 4 : STUDIES AND ANALYSIS OF THE RESPONSE OF
TAGUCHI GAS SENSORS TO ALKANES ALCOHOLS ALDEHYDES AND
KETONES

4.1 : INTRODUCTION

Having investigated the influence of instrumental parameters upon response (chapter 3) the next step in this work was to attempt to assess the dependence of response on the molecular structure of the analyte . Homologous series of organic compounds provided a useful probe in this respect , due to the relatively simple , well defined changes in molecular structure occurring between adjacent members of these series . The greatest variations in chemical and physical properties within an homologous series occur between the lower molecular weight members . Also , it is here that functional groups dominate the chemistry of the molecules . In view of these factors the members of the homologous series studied were those containing five or less carbon atoms .

In order to be able to assess properly the influence of various functional groups , it was first necessary to study the basic structure of all organic compounds i.e. the hydrocarbon skeleton . It is appreciated that there is considerable variability in both chemical and physical properties between even simple hydrocarbons and Wynne [12] has shown differences in response between ethane ethene and ethyne . However the objective of this study was to gain information about the affect of functional groups upon response . To facilitate this , the compounds studied were limited to those with saturated , straight chain hydrocarbon skeletons only .

4.2 : LOW MOLECULAR WEIGHT ALKANES

To date , many workers have studied the responses of sensors to methane or ethane , however only rarely have both been investigated simultaneously and no workers have yet compared the different responses obtained in relation to the possible sensing mechanisms . In this section the responses of the first five alkanes have been investigated (methane , ethane , propane , butane and pentane) with a view to understanding something about the nature of the response mechanisms occurring .

4.2.1 : Affects of Heater Voltage on Response

The importance of heater voltage was demonstrated in chapter 3 . The large variations in response observed made it necessary that heater voltage studies be carried out where optimum response was most important .

To simulate normal analysis conditions it was desirable that the five compounds be studied together , therefore the choice of chromatographic conditions was important . Because of the influence of the chromatographic conditions observed in chapter 3 it was considered undesirable to use temperature programming , also because of the skewness of the response at low heater voltages it was necessary to have good separation , whilst minimising the analysis time to get good peak height response to the heavier homologues . The result of the above was that compromise conditions were employed for the alkane chromatographic separation . those used in this investigation were :

COLUMN	1 m x 4 mm activated alumina
COLUMN TEMPERATURE	100°C
CARRIER GAS	air
CARRIER FLOW	55 ml min ⁻¹
INJECTOR	1 ml gas sampling valve
INJECTOR TEMPERATURE	20°C
DETECTOR	TGS 813
DETECTOR TEMPERATURE	110°C

The average peak height responses , from five injections of

50 vpm each in air of the alkane mixture , were determined . at various heater voltages between 4.75 and 6.25 V , using a computing integrator (HP 3390A) . It would have been preferable , because of the peak broadening during separation , to have measured peak areas . However this was not possible because the skewness of the peaks at low voltages would have caused false optima (in terms of analytically useful response) to be observed . The skewed nature of the peaks obtained at low heater voltages also affected the lower limit of the range of heater voltages that could be studied . since under the compromise separation conditions , the methane and ethane peaks were not sufficiently resolved to avoid response interference .

Typical chromatograms from each voltage studied are shown in figures 4.2.1 - 4.2.5 and figure 4.2.6 shows the peak height response - heater voltage profiles obtained for the alkanes .

From the data obtained it was possible to make a number of observations . Firstly the the chromatograms showed a variable dependence of skew factor upon heater voltage and analyte . Methane , for example , tended to be highly skewed at low voltage (figure 4.2.1) whilst at higher voltages (figure 4.2.5) a much more symmetrical peak was observed with a skew factor of approximately unity . In contrast butane skew factor was much less affected by heater voltage . Table 4.2.1 shows measurements of the skew factors of propane butane and pentane at 4.75 V and 6.25 V . The table confirms the observation that the dependence of skew factor on heater voltage reduced as molecular weight increased and that there was also a general increase in skew factor with molecular weight .

FIGURE 4.2.1 :
A TYPICAL CHROMATOGRAM OBTAINED FROM THE SEPARATION OF THE
LOW MOLECULAR WEIGHT ALKANES DETECTED BY A TGS 813
OPERATED AT A HEATER VOLTAGE OF 4.75 V

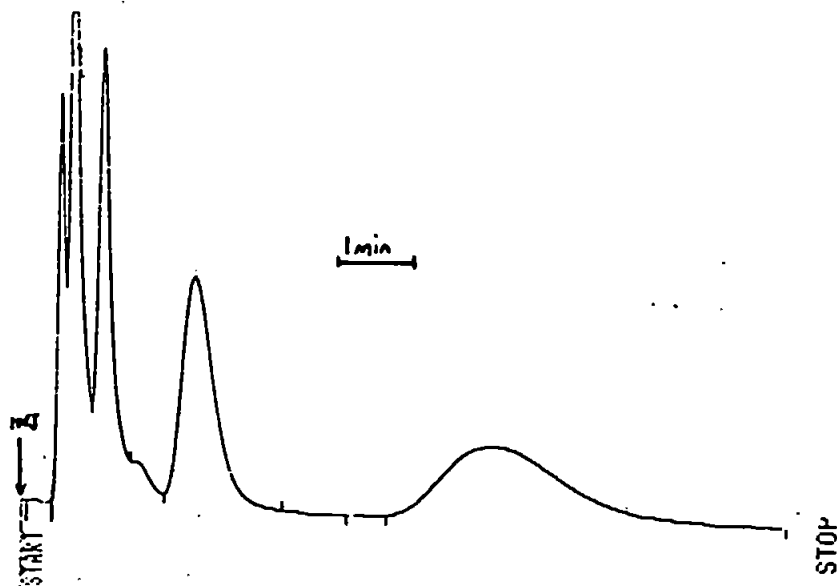


FIGURE 4.2.2 :

A TYPICAL CHROMATOGRAM OBTAINED FROM THE SEPARATION OF THE
LOW MOLECULAR WEIGHT ALKANES DETECTED BY A TGS 813
OPERATED AT A HEATER VOLTAGE OF 5.0 V

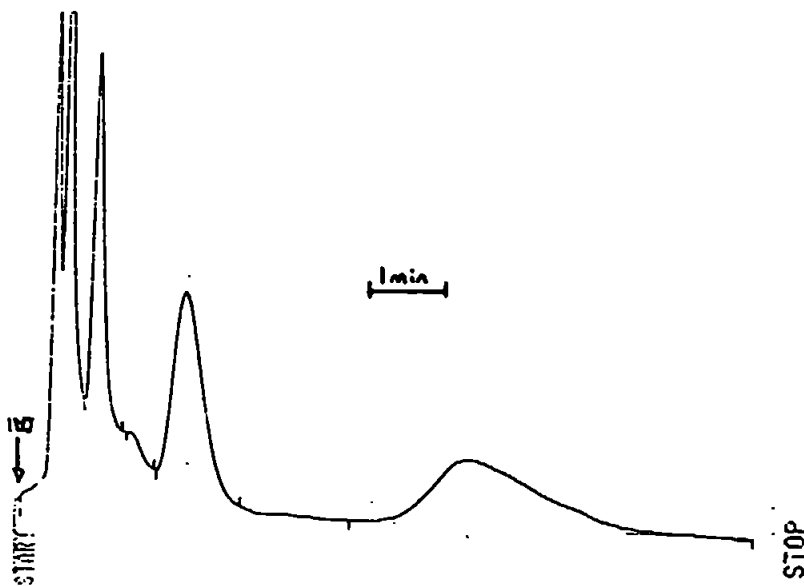


FIGURE 4.2.3 :

A TYPICAL CHROMATOGRAM OBTAINED FROM THE SEPARATION OF THE
LOW MOLECULAR WEIGHT ALKANES DETECTED BY A TGS 813
OPERATED AT A HEATER VOLTAGE OF 5.5 V

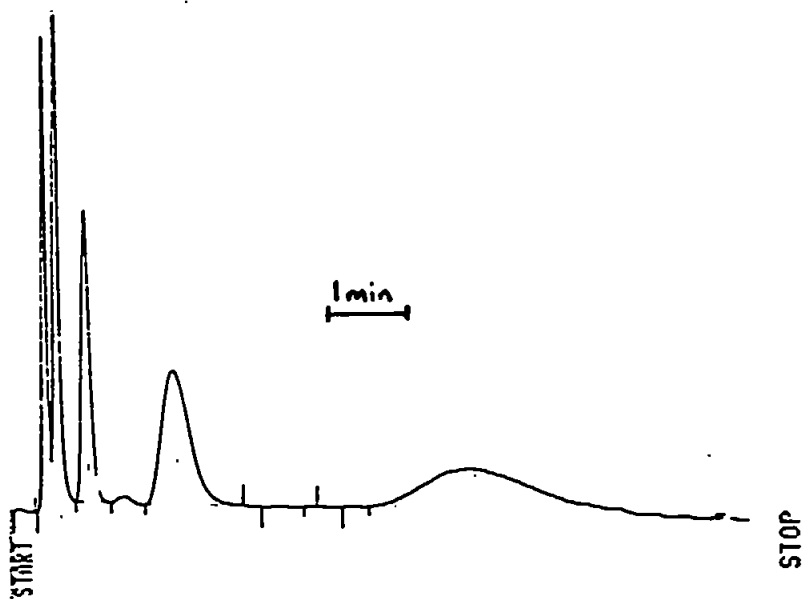


FIGURE 4.2.4 :

A TYPICAL CHROMATOGRAM OBTAINED FROM THE SEPARATION OF THE
LOW MOLECULAR WEIGHT ALKANES DETECTED BY A TGS 813
OPERATED AT A HEATER VOLTAGE OF 6.0V

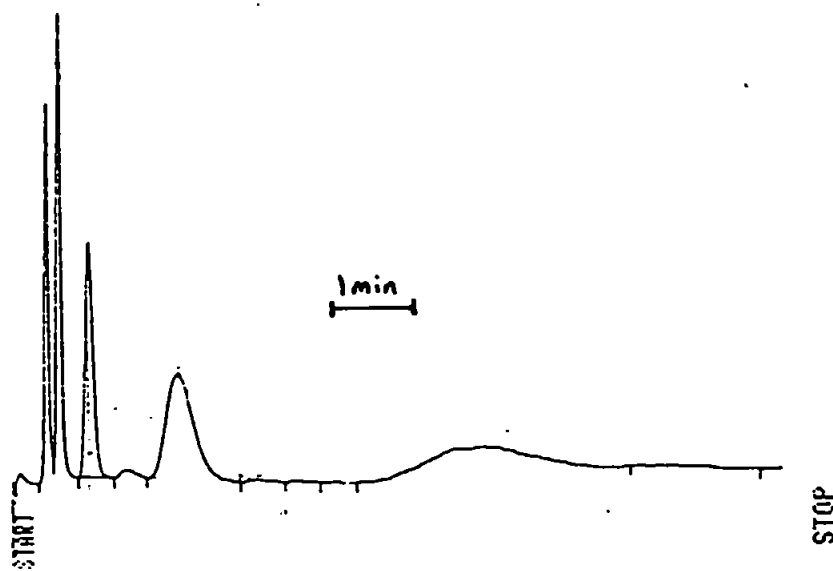


FIGURE 4.2.5 :

A TYPICAL CHROMATOGRAM OBTAINED FROM THE SEPARATION OF THE
LOW MOLECULAR WEIGHT ALKANES DETECTED BY A TGS 813
OPERATED AT A HEATER VOLTAGE OF 6.25 V

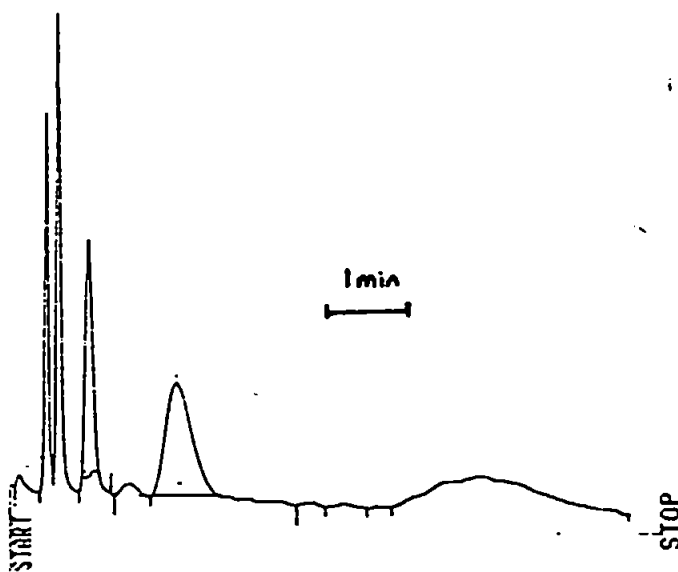


FIGURE 4.2.6

THE AFFECT OF HEATER VOLTAGE ON PEAK
HEIGHT FOR LIGHT ALKANES ON A TGS813

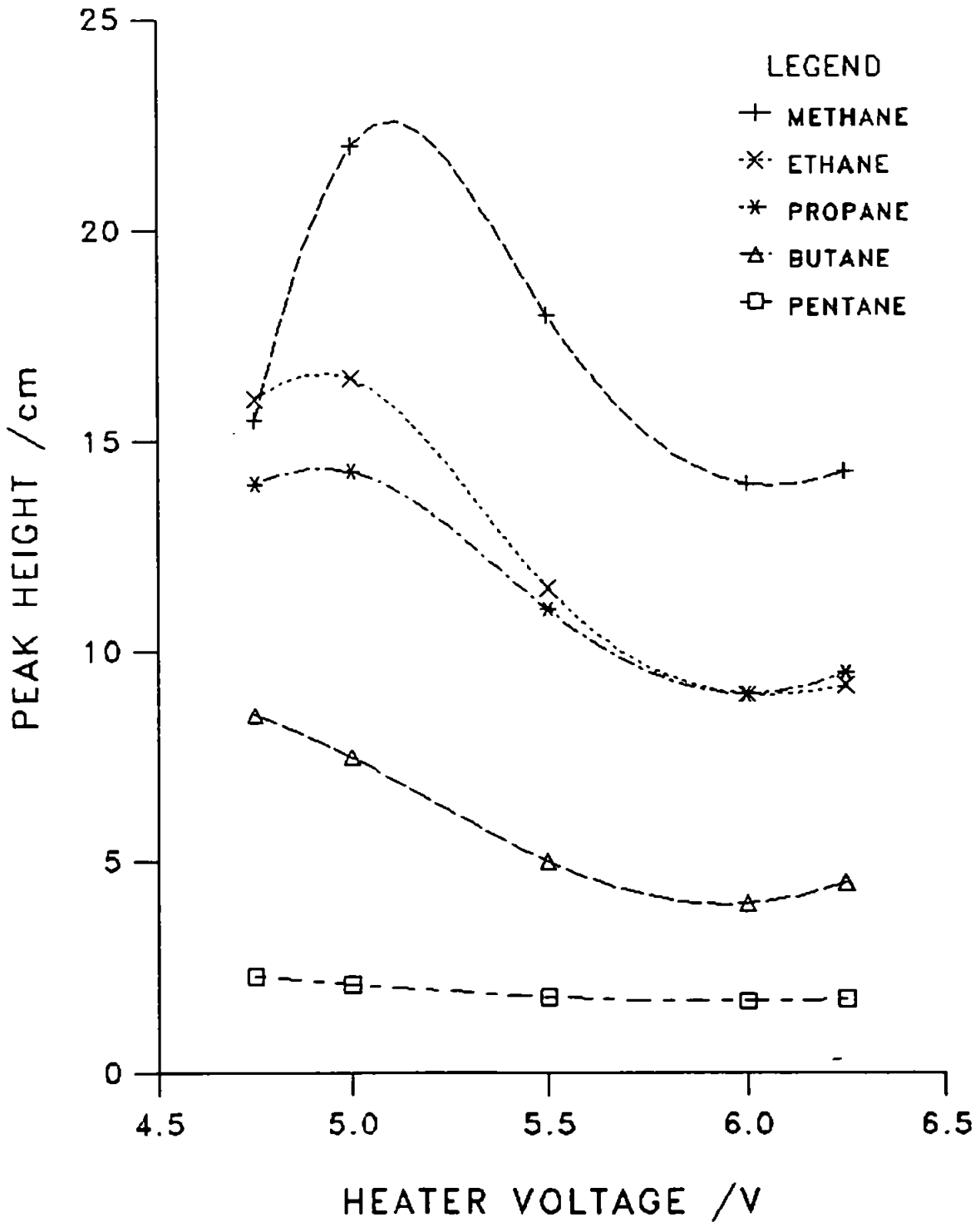


TABLE 4.2.1 : COMPARISON OF SKEW FACTORS OF PROPANE ,
BUTANE AND PENTANE WITH RESPECT TO HEATER VOLTAGE

COMPOUND	HEATER VOLTAGE /V	
		4.75
PROPANE	1.5	1.0
BUTANE	1.4	1.33
PENTANE	1.6	1.6

Figure 4.2.6 shows the dependence of peak height upon heater voltage . It shows that separate optima exist for methane ethane and propane and , from the gradients of the butane and pentane profiles , suggests that distinct optima also exist for these higher molecular weight analogues . Unfortunately , however these could not be observed because of the limitation on minimum voltage described above . The trend shown was that optimum voltage (for peak height) reduces with increasing molecular weight but appears to tend to a limit .

4.2.2 : Response Relationships between Compounds

The true measure of chromatographic response is based upon peak area . The reason for this is that as retention time increases a peak becomes broader and peak height reduces , peak area however remains constant . The fundamental principles behind this process are discussed in most chromatographic texts [56] .

It was noted previously that excessively skewed peaks lacked analytical utility and could cause biased response relationships to be observed . However it is essential that direct comparisons of response can be made . For this reason heater voltages of 5.5V and greater only , are used in this section . This meant that because acceptable peak shapes were obtained , confidence in peak area measurements was possible .

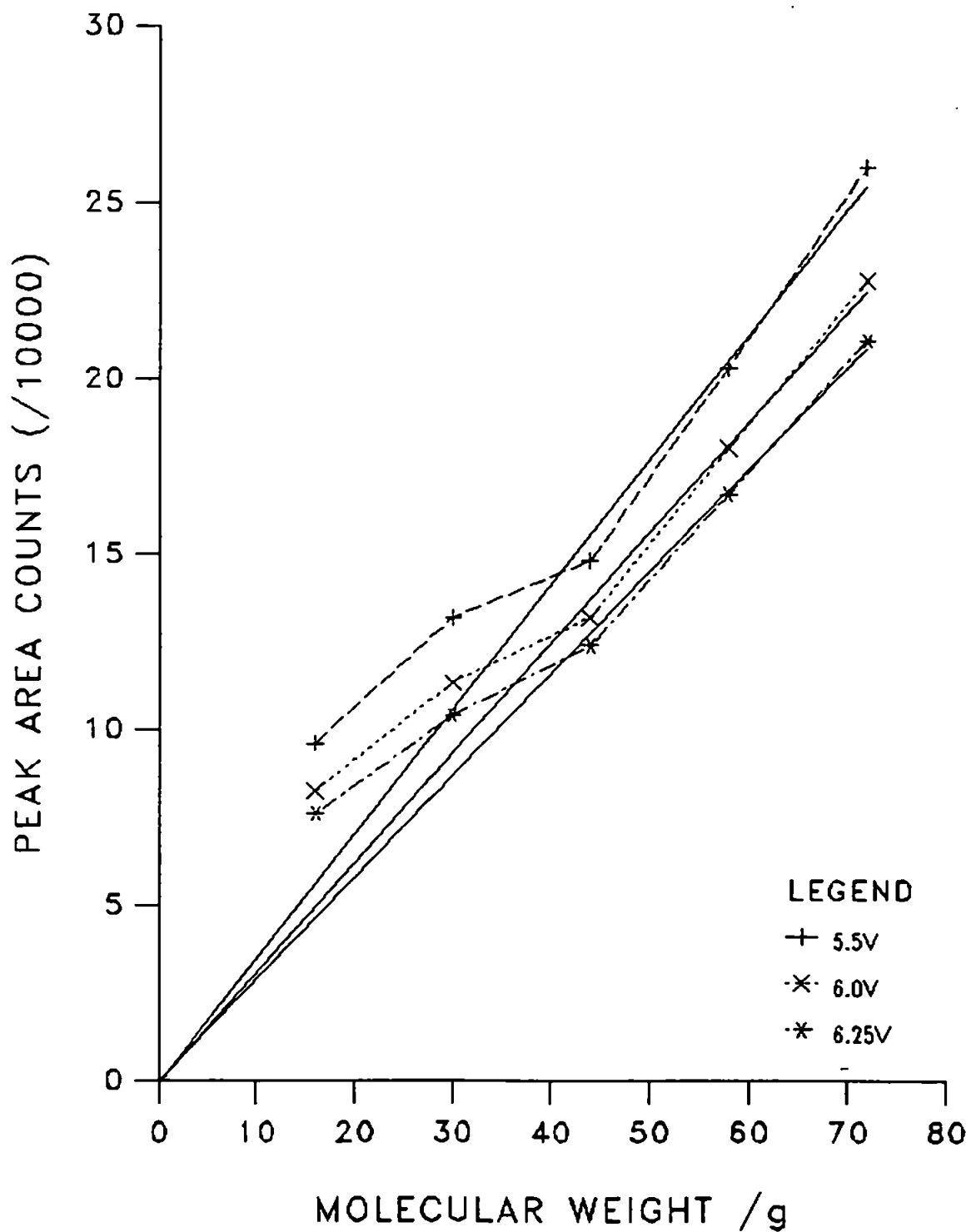
To facilitate mechanistic comparisons it was preferable to consider molar response relationships . The use of volume ratio gas mixing proved convenient in this respect since it allowed molar relationships to be measured directly .

Figure 4.2.7 shows the peak area responses with respect to molecular weight , at voltages between 5.5 and 6.25 V . Peak area measurement was performed using the computing integrator (HP 3390A) and areas quoted are the average values determined from five 1 ml injections of a 50 vpm alkane in air mixture . It is observed from figure 4.2.7 that :

1. peak area decreased with increasing heater voltage ;
2. peak area and hence molar sensitivity increased with molecular weight ;

FIGURE 4.2.7

THE PEAK AREA RELATIONSHIPS OBSERVED
BETWEEN THE LIGHT ALKANES



3. the relationship between propane , butane and pentane was linear and could be extrapolated to the origin , whilst methane and ethane did not conform to this relationship giving higher than expected peak areas .

4.2.3 : Discussion

The observations made from the responses of the Taguchi sensor to the alkanes raised a number of points worthy of further consideration .

Firstly discrete optimum heater voltages for each of the alkanes together with a general decrease in optimum with increasing molecular weight was observed . The implication of these observations is that the molecular structure of the analyte does affect the response of the sensor . Furthermore the reduced optimum heater voltages for higher molecular weight homologues was considered significant . The explanation of these observations most probably lies in the activation energies for the sensing processes . According to Harrison and Maunders [45] the activating reaction for ethane relies upon the abstraction of a hydrogen atom . Data such as the homolytic bond dissociation energies for alkanes (table 4.2.2) tend to suggest that hydrogen abstraction becomes easier with increasing alkane molecular weight . Also the homolytic bond dissociation energies show that the ease of hydrogen abstraction tends to a minimum as molecular weight increases - in direct agreement with the observed optimum heater voltage , molecular weight trend . It appears therefore that the response maxima could be dependant on the activation energy of the homolytic fission of a carbon to hydrogen bond .

The observation of a variation in skew factor with molecular weight and heater voltage was also significant since it gave information about the recovery of the sensor after interaction with a reducing gas . The sensing mechanism may be considered to

TABLE 4.2.2 : HOMOLYIC BOND DISSOCIATION ENERGIES FOR ALKANES

REACTION				H / Kjmole ⁻¹
CH ₄	----->	CH ₃ ·	+ H·	435
CH ₃ CH ₃	----->	CH ₃ CH ₂ ·	+ H·	410
CH ₃ CH ₂ CH ₃	----->	CH ₃ CH ₂ CH ₃ ·	+ H·	410
CH ₃ CH ₂ CH ₃	----->	CH ₃ ·CHCH ₃	+ H·	397

consist of the following processes :

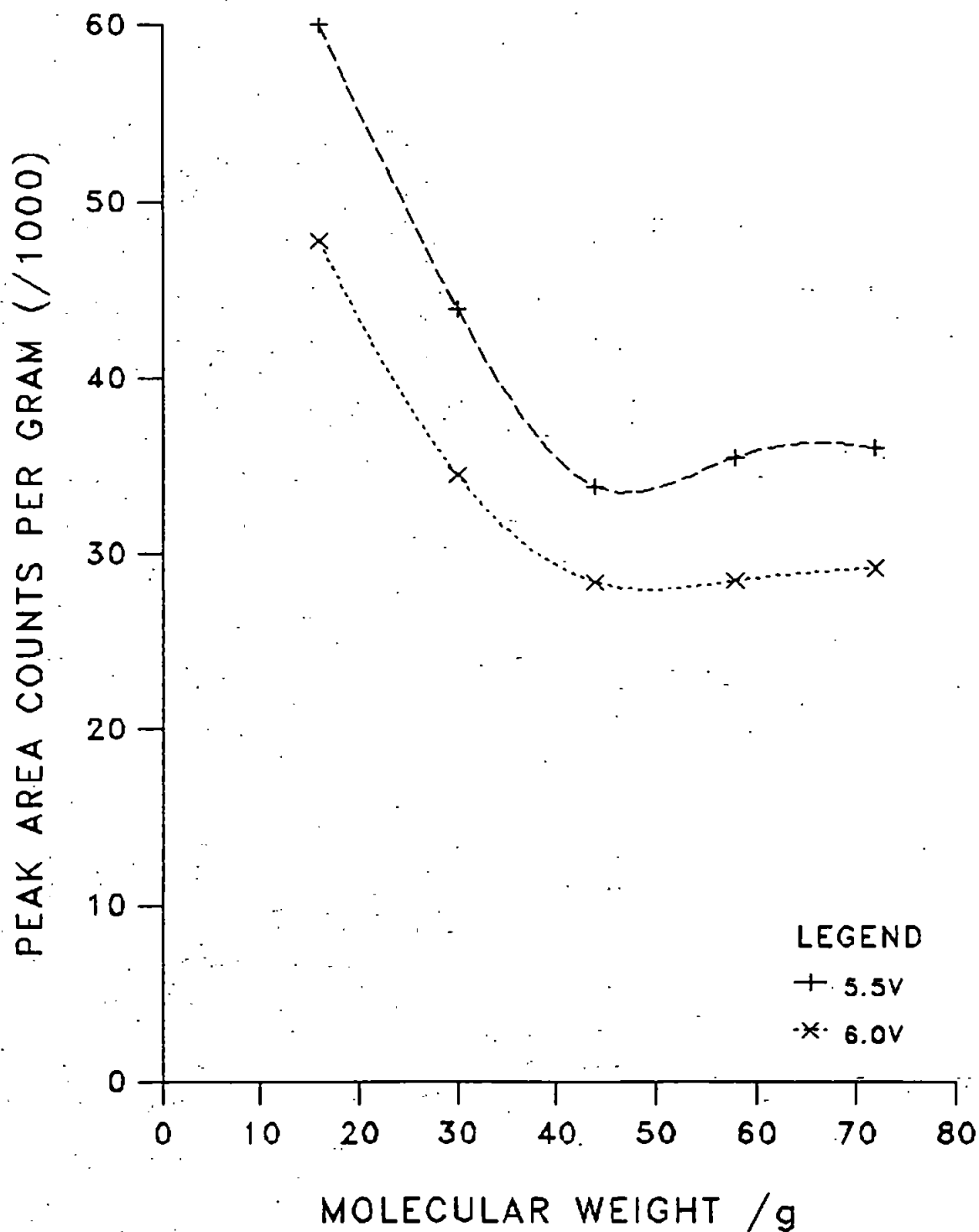
1. interaction of the analyte gas with the sensor surface involving oxidation of the analyte ;
2. desorption of the oxidised analyte ;
3. oxidation of the sensor surface by oxygen from the sensor's surrounding atmosphere .

Previously it was uncertain whether step 2 was involved in the rise in conductivity (the sensing mechanism) or was part of the recovery mechanism . The observation of a variable temperature and molecular weight dependence of the recovery process (indicated by the skew factor of the peaks) suggests that step 2 is involved in the recovery process . The reasoning behind this is that step 3 alone could not possibly explain the observed variations in skew factor with heater voltage and molecular weight . Further- more it ^{is} likely that step 2 is the rate determining step in the recovery since step 3 is likely to be a very fast process due to the relatively very high oxygen concentration in the carrier gas .

The observations from the peak area measurements were also relevant . Peak area was seen to increase with increasing molecular weight showing that molar sensitivity improved with molecular weight . Figure 4.2.8 shows the mass sensitivity of the Taguchi sensor , i.e. the the response per gram of analyte . This graph suggests that there could be two different mass sensitivity functions . Firstly , a large decreasing sensitivity per gram exhibited by methane and ethane contrasted with , secondly , a

FIGURE 4.2.8

THE PEAK AREA RESPONSE PER GRAM OBTAINED
FOR THE LIGHT ALKANES



small general increase in mass sensitivity with molecular weight for propane butane and pentane . The difference between the alkanes is that , in propane butane and pentane there are secondary hydrogen atoms where none exist in methane or ethane . The decrease in sensitivity could thus be explained by the decreasing mole fraction of hydrogen in the molecules tempered by the existence of the secondary hydrogen atoms in the higher molecular weight homologues . The change in hydrogen mole fraction between the alkanes is large for the smaller molecules but decreases rapidly with increasing molecular weight leading to lower mass response as molecular weight increases . However as molecular weight increases so does the ratio of secondary to primary hydrogen atoms . This could explain the observed increase in sensitivity between propane butane and pentane since the homolytic bond dissociation energies show that requires less energy to abstract a secondary hydrogen atom than a primary one . The differences observed in the homolytic bond energies appear to be small , however it should be remembered that they could be significant in the exponential term of the Arrhenius equation causing relatively large differences in reaction rates and hence sensitivity to be observed .

Finally , the observation of a linear sensitivity function for propane , butane and pentane which intercepts the origin is also worthy of discussion . It is significant for a number of reasons . From a mechanistic point of view a linear molar sensitivity function suggests that , for straight chain alkanes , the sensitivity is dependent upon molecular weight . This means that each molecule must undergo a number of interactions related



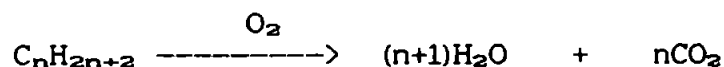
to its molecular weight with the sensor surface . Furthermore , this suggests that the degree of oxidation of the alkane by the tin oxide is constant . It is not likely to be 100% since in order to explain the observed skew factor - molecular weight dependence the post oxidation desorbing species must be different for each alkane . 100% oxidation would leave only CO₂ and H₂O on the surface and thus could not account for the differences in recovery observed . It is likely therefore that the straight chain alkanes undergo partial but reproducible oxidation .

The results presented in this section are by no means conclusive , however , they do suggest that the sensing mechanisms are much more complex than some workers conclude from measurements on only a few compounds . For example , in a recent paper , McAleer et.al. [52] suggested that the response of a tin oxide sensor to gases containing hydrogen could be entirely attributed to the affects of water vapour produced by combustion close to the sensor surface . The work herein shows two major contradictions with this water vapour theory :

1. the dependence of skew factor on molecular weight as discussed above cannot be explained by water vapour interactions alone ;
2. if water vapour , produced by combustion , were responsible for the sensing , then two features would have been observed in the molar sensitivity function :
 - a. the molar sensitivity function would have been linear for all the alkanes ;

b. the molar sensitivity function would have intercepted the response axis at a point representing the molar sensitivity to water .

Point b. can be explained by examining the general combustion equation for alkanes :



Therefore in terms of response and concentration :

$$[H_2O] = \text{RESPONSE} = (1 + n(C_nH_{2n+2})) \times S_{\text{water}}$$

where ,

$$S_{\text{water}} = \text{molar water vapour sensitivity}$$

And therefore the sensitivity function dependent on water vapour would not pass through the origin , contrary to the observation above .

Since the features outlined above were not observed in the molar sensitivity function produced in this work , it is likely that , at least for the Taguchi sensor used here , that the response mechanism relies upon direct interaction of the analyte with the sensor surface .

4.2.4 : Applications

The final part of this section was to examine the analytical figures of merit for the determination of straight chain alkane concentrations using the sensor . In order to achieve the above and to assess the potential of the sensor as a GC detector a sample of natural gas was analysed .

Calibration of the sensor was achieved using the standard alkane gas mixture described in chapter 2 .

Natural gas consists of approximately 95% v/v methane and it was therefore necessary to be able to dilute the natural gas to ensure that the methane concentration would lie within the calibration range . It was decided that the best method of achieving this was to use the gas blender . However as stated earlier the input pressure of sample and diluent gases must be at least 30psi for the blender to function properly . Since the normal pressure of natural gas in the laboratory was only approximately 10psi it was necessary to purchase a cylinder of natural gas compressed at 2000psi and then to use a two-stage regulator to step down the supply pressure to 30psi . The carrier gas (air) was used to dilute both the natural gas and the alkane standard .

The chromatographic conditions employed were the same as those for the previous studies in this chapter . The heater voltage used was 5.5V , chosen as a compromise between maximum sensitivity and minimum skew factor .

Calibration points were determined by the average peak heights from five injections of the diluted alkane gas standard . Theoretical peak height detection limits were calculated from

three times the standard deviation of the lowest concentration calibration point which was injected ten times in order to be statistically significant .

Figures 4.2.9 to 4.2.13 show the calibration curves obtained . Linearity was observed up to 500vpm for methane (where the point differed from the calibration line by 5%) . It was observed that the upper limit of linearity improved as the alkane increased in molecular weight . This was probably due to the effective dilution of the analyte by diffusion during the separation which was also responsible for the apparent reduction in sensitivity shown by the gradients of the peak height calibration lines .

Table 4.2.3 shows the theoretical detection limits obtained . It was observed that the detection limits showed a greater deterioration in sensitivity with molecular weight than the calibration line gradients . The explanation for this again lay in the peak broadening during separation , which reduced the peak heights and thereby reducing the precision of the peak height measurement and thus having a multiplicative affect on the detection limit determination . It was not considered relevant at this point to improve the detection limits for the more massive alkanes using temperature programming . The reason for this was to ensure that the measurements had been carried out under identical sensor operating conditions .

Table 4.2.4 shows the results of the natural gas analysis , the results obtained were compared with a typical analysis obtained by British Gas [66] . The table shows that good agreement was obtained , once again demonstrating the analytical

viability of the sensor for gas chromatographic detection .

FIGURE 4.2.9

THE CALIBRATION CURVE OBTAINED FROM A
TGS 813 FOR METHANE CONCENTRATION

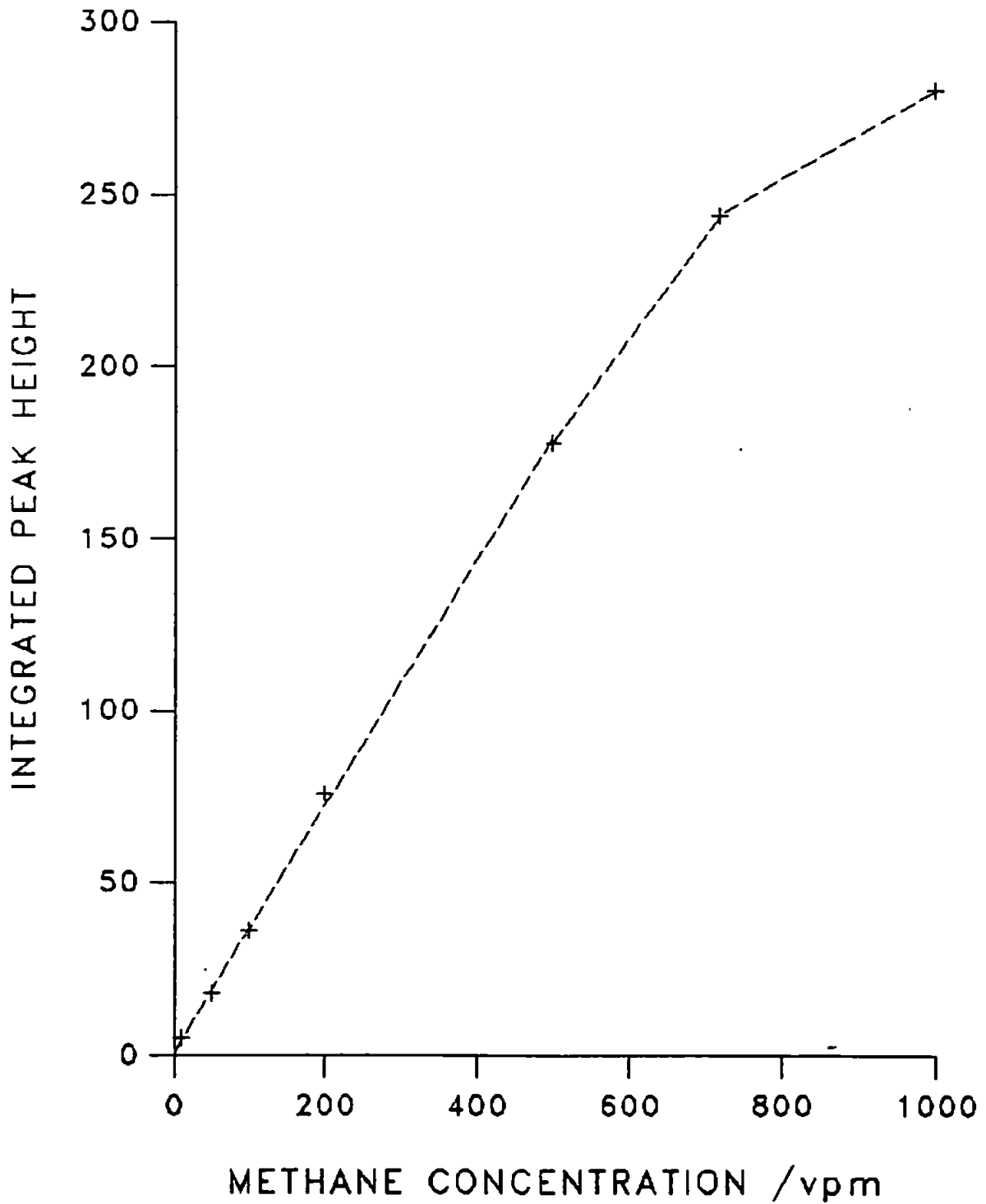


FIGURE 4.2.10

THE CALIBRATION CURVE OBTAINED FROM A
TGS 813 FOR ETHANE CONCENTRATION

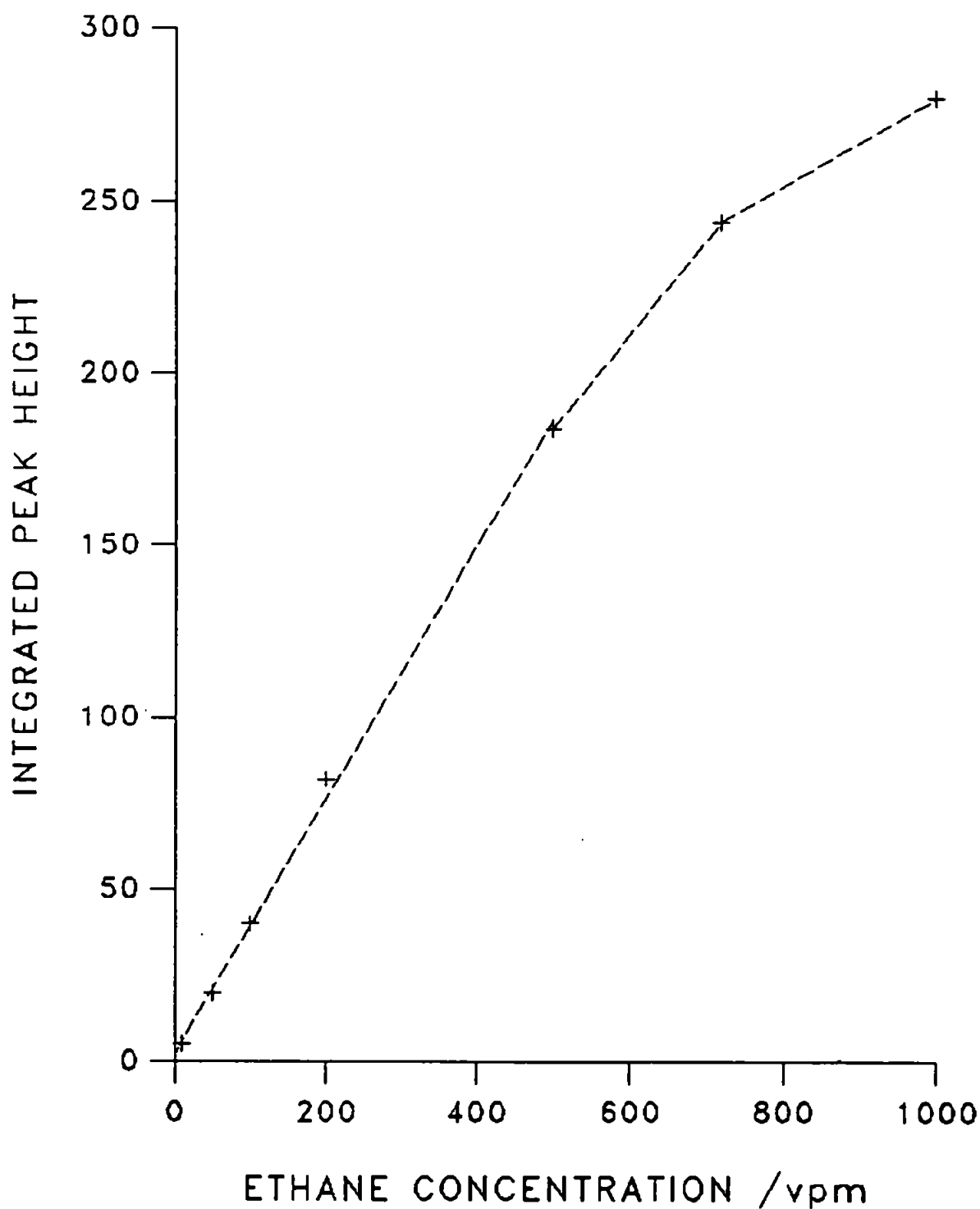


FIGURE 4.2.11
THE CALIBRATION CURVE OBTAINED FROM A
TGS 813 FOR PROPANE CONCENTRATION

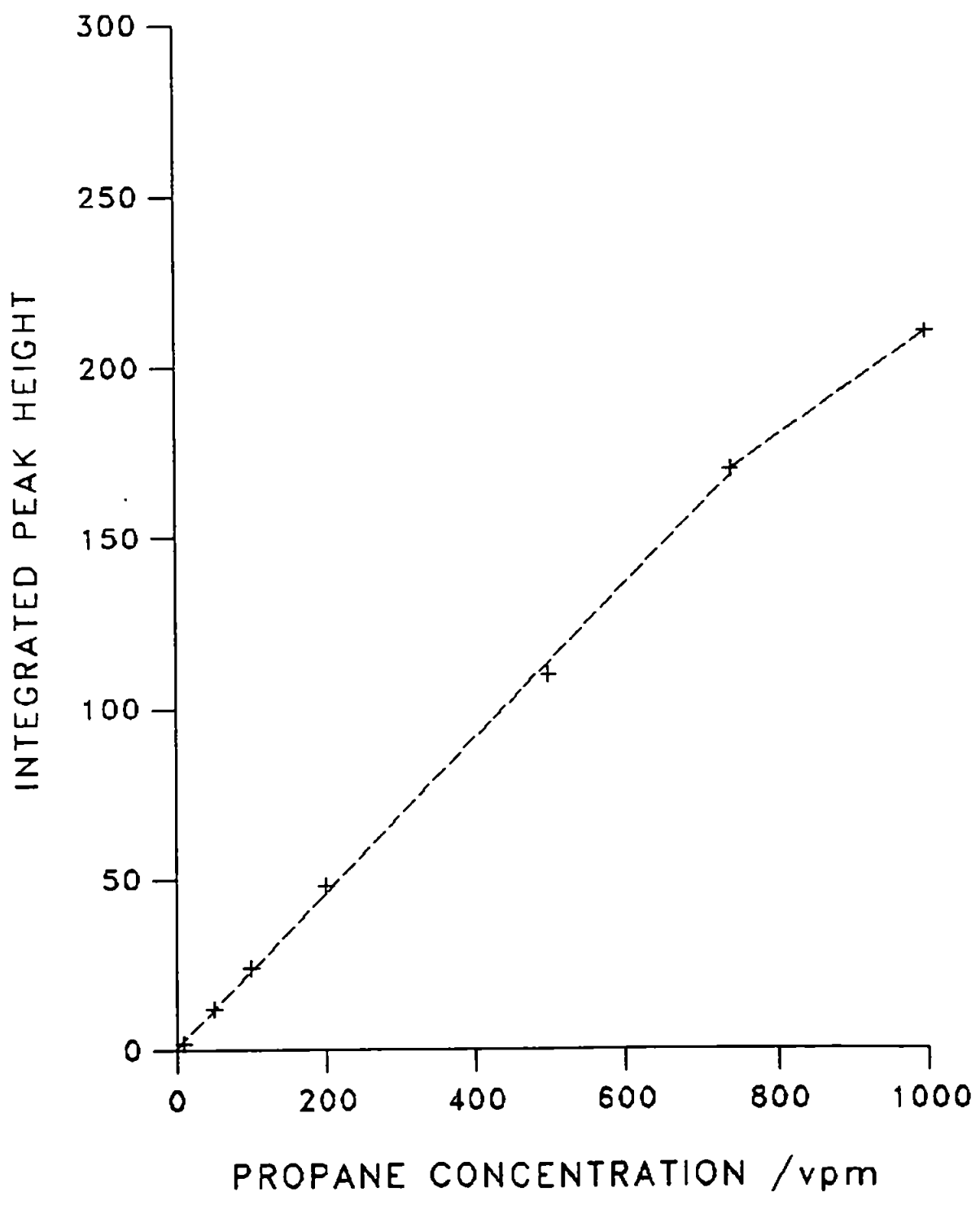


FIGURE 4.2.12

THE CALIBRATION CURVE OBTAINED FROM A
TGS 813 FOR BUTANE CONCENTRATION

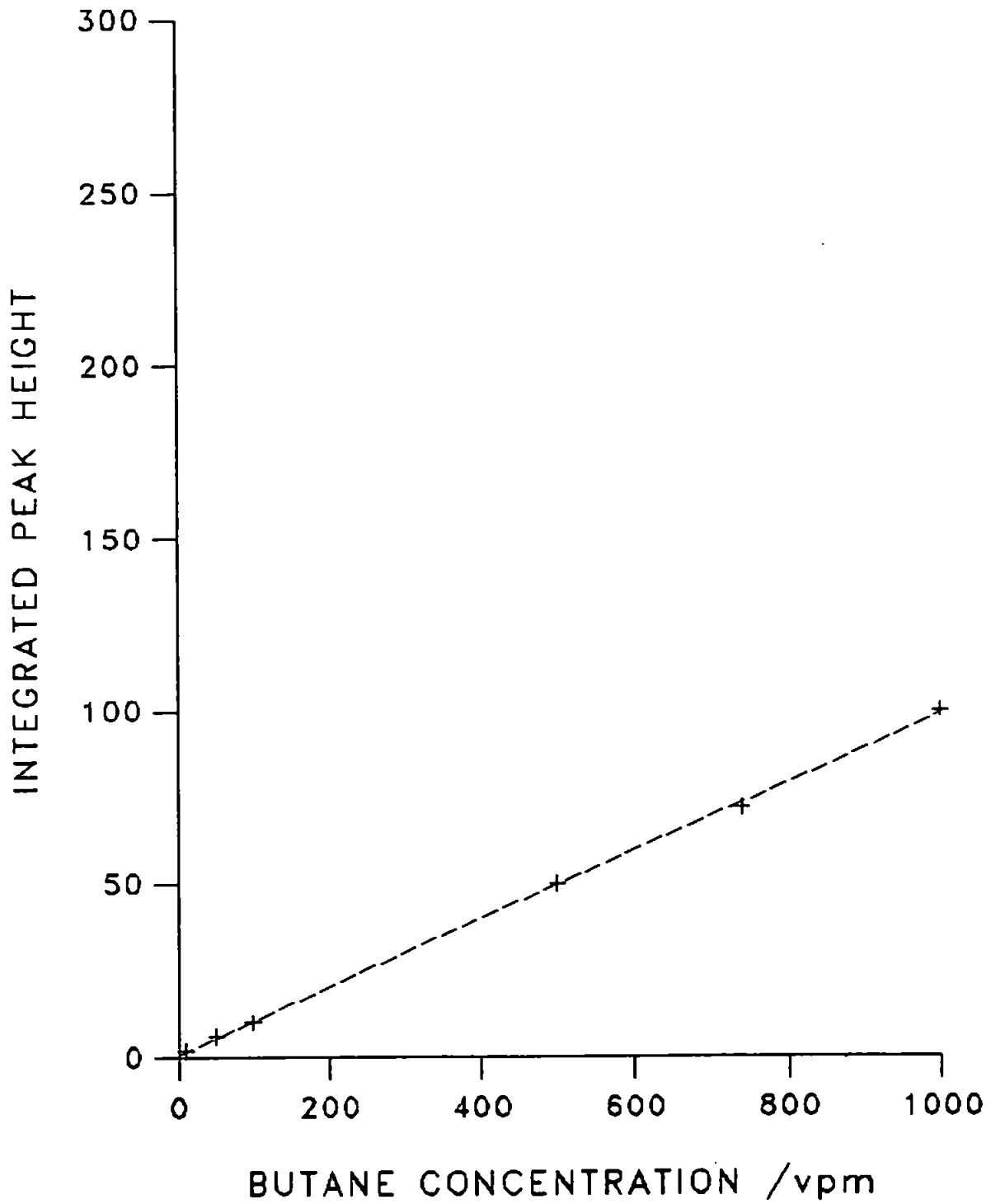


FIGURE 4.2.13

THE CALIBRATION CURVE OBTAINED FROM A
IGS 813 FOR PENTANE CONCENTRATION

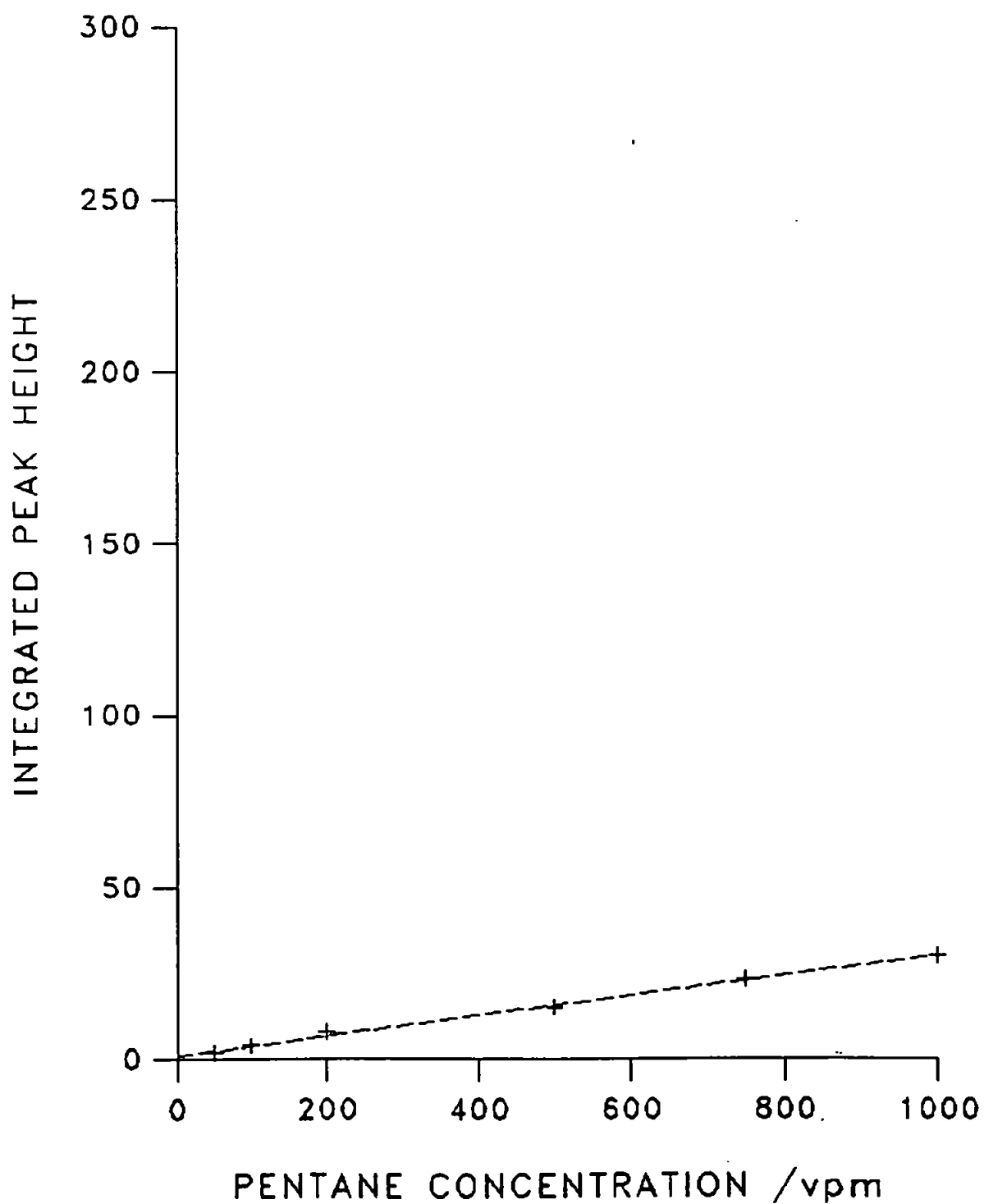


TABLE 4.2.3 : THEORETICAL PEAK HEIGHT DETECTION LIMITS
FOR THE LOW MOLECULAR WEIGHT ALKANES

COMPOUND	DETECTION LIMIT /vpb
METHANE	100
ETHANE	100
PROPANE	150
BUTANE	300
PENTANE	1000

TABLE 4.2.4 : DETERMINATION OF METHANE , ETHANE , PROPANE ,
BUTANE AND PENTANE CONCENTRATIONS IN A SAMPLE OF
NATURAL GAS

ANALYTE	FOUND / %v/v	TYPICAL ANALYSIS [66] / %v/v
METHANE	95 ± 2	93.6
ETHANE	3.5 ± 0.1	3.25
PROPANE	0.62 ± 0.02	0.69
BUTANE	0.20 ± 0.01	0.15
PENTANE	0.10 ± 0.04	0.09

4.3 : ANALYTICAL FIGURES OF MERIT FOR THE DETECTION OF ALCOHOLS , ALDEHYDES AND KETONES

This section of work was designed to investigate further two areas of the application of Taguchi gas sensors to gas chromatographic detection . Firstly the affects on response of some common oxygen-containing functional groups would be assessed . Secondly this section was used to investigate the applicability of the sensor to capillary column gas chromatographic detection .

The use of capillary columns presented number of possible challenges to the sensor application . Firstly capillary column stationary phases are generally much more sensitive to oxygen in the carrier gas than packed columns . Secondly the carrier gas volume flow rate is much less than for packed columns and lastly capillary columns require a much smaller sample volume than packed columns .

Perhaps the most serious of the above challenges was the preclusion of the use of air as carrier gas . However , it had already been recognised that the use of an oxygenated carrier gas would severely limit the range of applications of the sensor due to the problem of column compatibility . In fact it was considered that the use of capillary columns was a possible way of overcoming the above limitation . The reason for this lies in the second of the challenges defined above . The low volume flow rate of capillary columns meant that the oxygen required by the sensor for recovery could be supplied via an air auxiliary flow into the detector with minimum dilution , sensor cooling and gas

usage . The carrier gas could thus be inert without severely affecting the sensor performance . Also the much greater efficiency of capillary columns (in terms of peak broadening) would contribute to the minimisation of of the sample dilution problem described in chapter 3 . The last of the challenges described above was also considered to be possibly beneficial to the sensor performance , since it would reduce the probability of saturation of the sensor surface by the sample arising from liquid sampling , coupled with high column efficiency . This conclusion may be best illustrated with the aid of an example :

assume density of water is 1 g ml^{-1}

therefore 1 mole water (18 g) is 18 ml

if a typical packed column liquid sample size is $5 \mu\text{l}$

then the No. moles of water would be $5/18000$ in a typical injection

since 1 mole of water occupies approx. 22.4 l at STP. and from $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ at 200°C (a typical injection temperature)

1 mole of water would occupy 38.8 l

therefore the equivalent gaseous injection to $5\mu\text{l}$ of liquid water would be $\frac{5}{18000} \times 38\ 800 = 10.7 \text{ ml}$

THUS LIQUID SAMPLING UNDER NORMAL CONDITIONS REPRESENTS A TENFOLD INCREASE IN SAMPLE VOLUME FROM THAT USED FOR GAS SAMPLING

HOWEVER a typical capillary column injection size is 1 μ l using split injections with a minimum ratio of 20:1 the effective injection volume is 0.05 μ l following the above an equivalent gaseous injection at 200°C would be only : $\frac{0.05}{18000} \times 38\ 800 = 0.107$ ml

THUS CAPILLARY COLUMN LIQUID SAMPLING UNDER NORMAL CONDITIONS REPRESENTS A TENFOLD REDUCTION IN SAMPLE VOLUME FROM THAT COMMONLY USED FOR GAS SAMPLING WITH PACKED COLUMNS

The above calculation shows that sensor surface saturation would be much less likely to occur using capillary columns . This was considered to be highly important when the nature of the samples was taken into account . Previously the research was conducted using gaseous samples of relatively low concentration . The balance of the gaseous samples was made up with nitrogen or air , since there was virtually no conductivity changes from the interaction of these gases with the sensor , no problems associated with 'solvent front' effects were observed . The use of liquid sampling , preferred due to the nature of the samples used in this section , meant that sensor surface saturation by the solvents was likely . Saturation of the sensor surface immediately prior to analysis could have caused significant affects on the response of the sensor . Consequently , the reduction in sample volume allowed using capillary columns was considered advantageous . The only possible disadvantage from

reducing sample volume lay in terms of a deterioration in detection limit . However it was felt that this potential problem would be (at least partly) overcome by the higher efficiency of capillary columns over packed columns , leading to greater sample concentrations at the detector thus producing more easily detectable peaks . The above point was especially relevant to the analysis of more highly retained species .

It was concluded that the use of capillary column technology could actually prove advantageous to the application of a Taguchi gas sensor to gas chromatographic detection .

In this section of work the focus of the research was shifted slightly away from the study of the sensor surface reaction to a more practically oriented study of the analytical applicability of the sensor to the determination of the compounds chosen .

There were two reasons for this shift in emphasis . Firstly, preliminary work showed the response characteristics of the compounds , to be similar to those of the corresponding alkane . Secondly , at the time this work was carried out there was considerable interest in the immediate potential of the sensor for commercial application (The most prominent of which was for it's possible use in a portable GC.) . This meant that the analytical applicability needed to be more widely assessed .

4.3.1 : Instrumental Considerations

Once again the major consideration in the choice of operating conditions was the sensor heater voltage . In view of the different priorities of this section it was decided that it would be more practical to operate the sensor at a fixed voltage . The results of chapter 3 showed that it was likely that most compounds would have different optimal heater voltages . However , as discussed previously , changes in heater voltage required considerable equilibration periods and were thus undesirable in commercial application of the sensor . The voltage chosen for this work was determined by matching the final flow rate through the detector housing (i.e. the capillary column flow rate plus the make-up gas flow rate) with that used in the packed column analyses of the alkanes . The heater voltage was varied to give the same baseline conductivity as that used for the alkane analysis . Using this method it was ensured that the surface environment of the sensor would be similar to the optimum determined for the alkanes . The actual voltage determined (5.25 V) was found to be quite similar to that used previously (5.5 V). The most probable explanation for the difference between the two figures was that the flow rate coming from the jet in the detector housing was higher for the packed column application than for the present study . The higher flow rate was aimed at the sensor element and probably cooled the sensor slightly more efficiently than the relatively diffuse flow caused by passing the majority of the detector flow through the oxidant channel of the detector . Since the cooling of the detector was less efficient it was found that a lower voltage was sufficient to

maintain the same surface temperature .

In using capillary columns it was quickly found that they were much better suited to temperature programming than the packed columns used previously . It was realised that this must have been due to the lower volume flow rate through the capillary column (the auxiliary gas flow was not affected by changes in column temperature) . Previously , in packed column separations , temperature programming had been problematical . This was due to the difference in the cooling properties of the carrier gas , caused by its varying flow rate and temperature during the temperature program . The variance in the cooling of the sensor by the carrier gas caused the chromatographic baseline to drift . In capillary column separations , however , it was observed that the the chromatographic baseline was much more stable . This , as stated above , could be explained by the small influence of the carrier gas on the general cooling properties of the flow across the detector . Temperature programming was therefore used in the subsequent capillary column separations where appropriate .

It was noted above that one of the reasons for the change in emphasis of this section was a commercial interest in the potential of the sensor as a GC. detector . One of the requirements of the company involved was that the sensor response should be applicable to peak area measurement . It has been noted previously that there was concern over the validity of peak area measurement , due to the skewed nature of the sensor response . It was decided that peak area response could only be considered representative of the analytically useful response if the skew factor was small . A value of 2 or less was selected as the limit

for representative peak area measurement . This apparently arbitrary skew factor maximum was based upon the reproducibility of peak area determinations . It had been observed that the precision of peak area measurement (using an integrator) degraded as skew factor increased . The reason for this was probably that peak termination became increasingly difficult for the integrator electronics to identify as skew factor increased . Fortunately the compounds studied in this section all exhibited skew factors below the maximum value specified .

It was indicated earlier that capillary column analyses could be more favourable for liquid sampling due to the reduced sample volume required . The reason for this was that it was undesirable to saturate the detector with the solvent immediately prior to the analysis of the compounds of interest . This was particularly so in the work carried out in a project such as this due to the lack of knowledge of the mechanisms of the sensing reactions . The result of this was that the sample size was kept to a minimum . Also a split injection system was used to further reduce the sample size . Unfortunately it was felt that discrimination in terms of favouring high boiling point compounds may occur in the split injector . Consequently there was a desire to minimise sample size but to also keep the split ratio to a minimum . The result of this was that very small samples were used . One of the consequences of using very small sample volumes (~0.1ul) is that it is very difficult to ensure reproducibility of the injected volume . It was considered that there was two choices for improving the sampling reproducibility : firstly an internal standard could have been used to correct for variances

in sample volume or , secondly to try to keep the injection procedure identical for each sample by using an autosampler . Under normal circumstances the former or both are preferred . However , due to the lack of knowledge of the sensing behaviour , it was desirable to use the simplest possible samples . Therefore the second option was selected . The use of an autosampler (PU 4700 , Philips Scientific) standardised the injection routine and thereby improved the sampling reproducibility for the small volumes involved .

4.3.2 : Alcohols

Following the philosophy outlined in the introduction to this chapter , only alcohols consisting of five or less carbon atoms have been studied . Furthermore , the study concentrated on the primary alcohols due to the continuity available from methanol to pentan-1-ol . Propan-2-ol was also briefly studied to enable comparison between primary and secondary alcohols . Tertiary alcohols were not included because no response data was available for branched hydrocarbons and therefore the alcohol functional group's contribution to the response could not have been assessed .

The five primary alcohols studied were determined at concentrations ranging from 50 vpm to 1% (v/v) in hexane . This equated to on-column injections of between 0.1 and 20ng when the injection volume and split ratios were taken into account .

The column selected for this application was a high polarity capillary column (BP20 , 25m x 320 μ m (i.d.) x 5 μ m film thickness) obtained from Philips Scientific . The chromatographic conditions were optimised to give adequate separation in minimum analysis time . The conditions employed were :

COLUMN	BP20 (25 m x 320 μ m x 5 μ m film)
COLUMN TEMPERATURE	initial 30°C x 4 min ramp 15 C min ⁻¹ final 110°C x 0 min
CARRIER GAS	white spot nitrogen
CARRIER FLOW	2.2 ml min ⁻¹
INJECTOR	0.1 μ l x 40:1 split ratio

INJECTOR TEMPERATURE	200°C
DETECTOR	TGS 813 x 5.25 V heater voltage
DETECTOR TEMPERATURE	110°C
AUXILIARY GAS	40 ml min ⁻¹ air

Peak area measurement was achieved using a computing integrator (PU 4810, Philips Scientific). The choice of chromatographic conditions was such that methanol and ethanol tended to lie on the tail of the solvent peak. It was found that reproducible peak areas could be obtained for methanol and ethanol by using the tangent skimming facility of the integrator.

Table 4.3.1 shows the average peak areas obtained from five injections of the primary alcohol mix at each concentration studied. Also quoted are the sensitivities in area counts per gram and area counts per mole together with the correlation coefficients for the least squares best fit straight line calibration curves obtained. To retain continuity with the work on alkane responses, peak height detection limits were used. These, as before, were calculated on twice the standard deviation of ten injections of the lowest concentration standard and are also included in table 4.3.1.

As mentioned above one secondary alcohol was investigated. This was studied using a solution of equal concentrations of propan-1-ol and propan-2-ol in butan-1-ol solvent. Butan-1-ol was used as the solvent in this analysis to remove any possible effects of the solvent front on the analysis. The small injection volume used prevented the butan-1-ol from saturating

**TABLE 4.3.1 : RESULTS OBTAINED FOR THE DETECTION OF
PRIMARY ALCOHOLS USING A TAGUCHI 813**

CONCENTRATION / %v/v @20°C	MEAN PEAK AREA COUNTS ($\times 10^4$)				
	METHANOL	ETHANOL	PROPANOL	BUTANOL	PENTANOL
1	1480	1570	1150	920	900
0.5	780	870	610	470	430
0.125	220	270	176	110	120
0.1	180	180	130	92	95
0.05	91	93	66	51	52
0.025	44	46	31	27	25
0.0125	23	24	16	15	13
0.01	19	20	13	13	11
0.005	10	11	7	6	6
SENSITIVITY					
AREA COUNTS $g^{-1}(\times 10^{14})$	9.0	9.5	6.5	5.0	5.1
AREA COUNTS $mole^{-1}$ ($\times 10^{14}$)	290	440	400	370	450
CORRELATION COEFFICIENT					
	0.998	0.999	0.999	0.996	0.999
LIMIT OF DETECTION / vpm					
	0.36	0.33	0.42	0.48	0.41

the column . No changes in the propan-1-ol retention time was observed , also . the observed sensitivity to the propan-1-ol was the same as for the primary alcohol mix , this meant that the tail of the hexane peak had no measurable affect on the alcohol sensitivity . The average peak area ratios from five injections of the propanol mix were determined , the application of the ratio to the propan-1-ol sensitivity gave the propan-2-ol sensitivities which were :

$$1.5 \times 10^{14} \text{ area counts g}^{-1} \text{ or}$$

$$8.9 \times 10^{15} \text{ area counts mole}^{-1}$$

4.3.3 Aldehydes and Ketones

In this section the response of the sensor to a selection of aldehydes and ketones was investigated . As before , the types of compound studied were limited to those of straight chain carbon skeletons containing no more than five carbon atoms . The compounds studied were : ethanal ; propanal ; butanal ; propanone and butanone . In this section methanol proved to be a useful solvent .

Chromatographic separation was based on two different columns . Propanal and butanal were readily separated from each other and the solvent on the BP20 column using the same conditions as those for the alcohol measurements with the exception that an isothermal separation at a column temperature of 130°C was possible . The separation of ethanal from the methanol solvent proved difficult using the BP20 column , a much better separation was achieved using a Poraplot Q column (Chrompack ltd) . The two ketones : propanone and butanone were also well separated on the Poraplot Q column and were studied in conjunction with ethanal . The chromatographic conditions employed for the separation of ethanal , propanone and butanone were :

COLUMN	Poraplot Q
	25 m x 320 μm x 10 μm film
COLUMN TEMPERATURE	initial 50°C x 2 min
	ramp 5 C min ⁻¹
	second 120°C x 1 min
	ramp 10 C min ⁻¹
	final 200°C x 9 min

CARRIER GAS	white spot nitrogen
CARRIER FLOW	2.6 ml min ⁻¹
INJECTOR	0.1 μ l x 32:1 split ratio
INJECTOR TEMPERATURE	200°C
DETECTOR	TGS 813 x 5.25V heater voltage
DETECTOR TEMPERATURE	110°C
AUXILIARY GAS	40 ml min ⁻¹ air

Peak areas for all of the aldehydes and ketones studied were measured using the same PU 4810 computing integrator used for the alcohol studies . Again peak areas quoted are the average values from five injections at each concentration level in the calibration series . The sensitivities and correlation coefficients and obtained are shown in table 4.3.2 .

TABLE 4.3.2 : FIGURES OF MERIT OBTAINED FROM THE STUDY OF
THE RESPONSE OF A TAGUCHI 813 TO ALCOHLS , ALDEHYDES
AND KETONES

COMPOUND	SENSITIVITY		CORRELATION COEFFICIENT
	AREA COUNTS		
	per g $\times 10^{14}$	per mole $\times 10^{16}$	
METHANOL	9.0	2.9	0.998
ETHANOL	9.5	4.4	0.999
PROPANOL	6.5	4.0	0.999
BUTANOL	5.0	3.7	0.996
PENTANOL	5.1	4.5	0.999
PROPAN--2--OL	1.5	0.89	---
ETHANAL	4.8	2.1	0.997
PROPANAL	3.6	2.1	0.998
BUTANAL	2.6	1.9	0.997
PROPANONE	3.6	2.1	0.999
BUTANONE	2.7	1.9	0.996

4.3.4 : Discussion

As indicated earlier in this section the focus of the work was shifted towards the assessment of the potential analytical performance of the detector . The main reason for this being the encouraging results obtained from the hydrogen and alkane analyses .

This part of the study examined a number of different aspects of the sensor's potential using three different homologous series of compounds . The major interest here was the sensitivity , linearity and reproducibility of response that could be obtained . However , the study also showed the use of capillary column separation and peak area response measurement .

Sensitivity was found to be similar to that exhibited by the alkanes . This was best illustrated by the comparison of the detection limits between the alcohols (table 4.3.1) and the alkanes (table 4.2.3) . The tables showed that the detection limits were comparable for the C₃ analogues . The main difference was the uniformity of detection limit obtained for the alcohols . This was undoubtedly due to the higher efficiency of the capillary column used than for the packed column used for the alkane separation . It is likely that similar results would have been obtained for the aldehydes and ketones since their sensitivities were of the same order of magnitude as those measured for the alcohols .

All of the compounds showed good linearity of response across the range of concentration studied . This indicated two things : firstly that the calibration of the sensor was convenient and secondly that the measurement of peak area

response was representative of concentration . Both of the above were considered to be of paramount importance to the analytical potential of the sensor .

Reproducibility of response (as already discussed) is also vital if the sensor is to be a useful analytical tool . This parameter was monitored by observing the relative standard deviation (RSD) obtained from the peak area measurements for each set of repeat injections at each concentration level studied . It was observed that reproducibility was slightly improved in the current study over that found initially (chap.3) . The RSDs obtained were always less than 2.5% in contrast with the earlier work where 3% RSD was common . It is possible that the reproducibility could have been improved by the use of internal standards and/or larger injection volumes , although these were not used here for the reasons described earlier . It is also interesting to note that increased injection volumes could have improved the detection limits .

The study also showed that the sensor was equally well suited to capillary column or packed column application . In fact , there were a number of advantages discovered for capillary column separation . Perhaps the most important of these was the ability to use an inert gas (nitrogen in this case) without adversely affecting the sensor response . This was important due to the increased availability of stationary phases (and hence applications) that were not degraded by the carrier gas . Also the improved temperature programming available with capillary columns significantly widened the range of potential application .

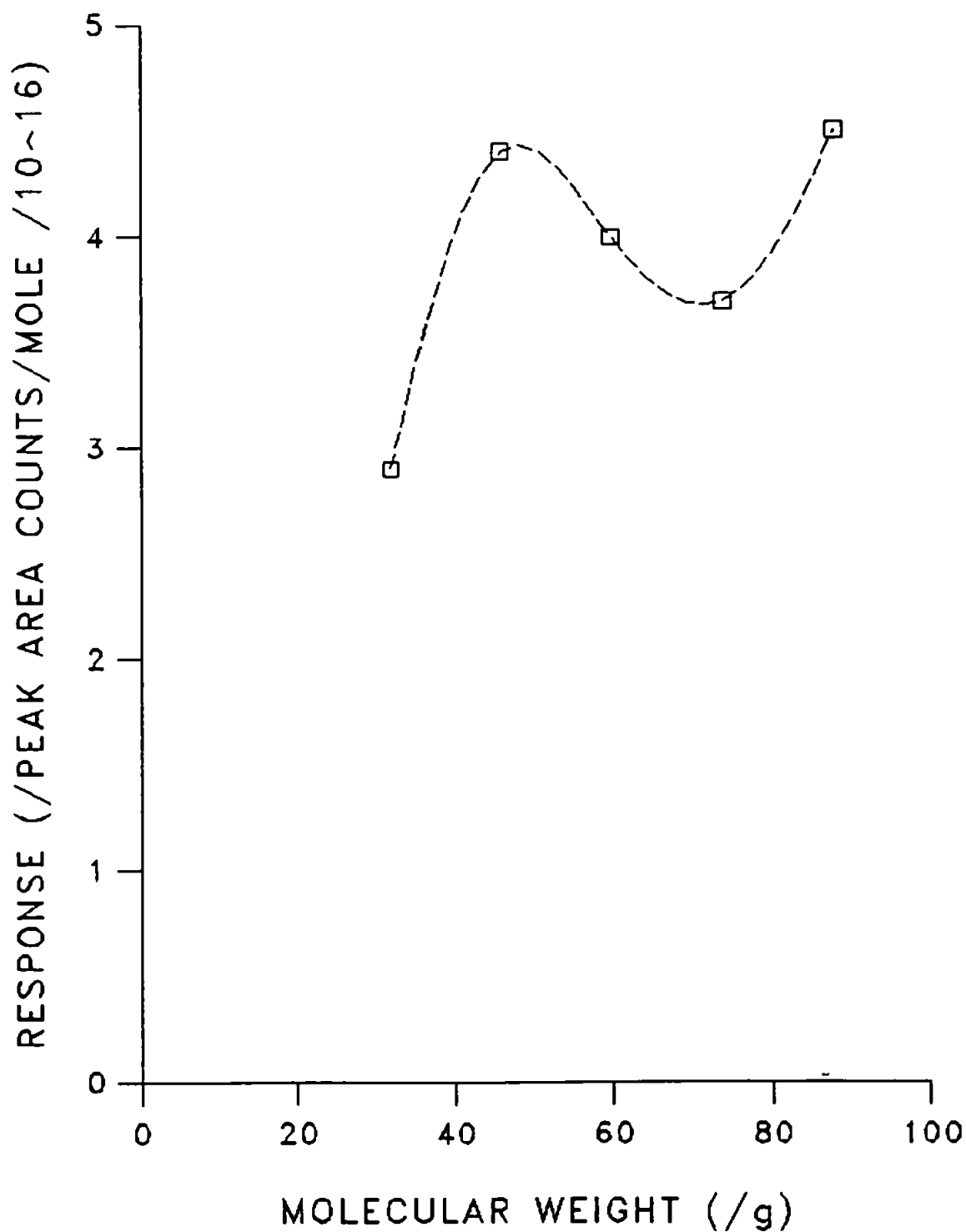
Although the focus of this section was on the evaluation of the analytical performance/potential of the sensor, the data obtained indicated a number of interesting mechanistic details.

In terms of the study of sensing mechanisms, the most useful data obtained in this section were the peak area molar sensitivity factors. The reasons for this were that the peak areas are directly related to the response (i.e. are independent of retention time) and, that the molar sensitivity relates the response at the molecular level. Thus interpretation of the peak area molar sensitivities in conjunction with the chemical properties of compounds may lead to improved mechanistic understanding.

Figure 4.3.1 is a plot of peak area molar sensitivity versus molecular weight for the alcohol series. A simple consideration of the chemistry of the primary alcohols shows that each successive homologue corresponds to the addition of a $-\text{CH}_2-$ unit. On this basis it might have been expected that the sensitivity / molecular weight plot might have been similar to that obtained for the alkanes (figure 4.2.7). Comparison of the two curves shows a difference in the minimum point, propane for the alkanes in comparison with butan-1-ol for the alcohols. A possible explanation of this difference in the two curves lies in considering the affect of the functional group on the alcohol molecules. It is well known that the influence (i.e. inductive effect) of a functional group decreases rapidly with distance, and that there is very little affect at greater than three atoms away [67]. It is therefore probable that the differences observed between the alkane and alcohol sensitivity curves was

FIGURE 4.3.1

THE PEAK AREA RESPONSE RELATIONSHIPS
OBSERVED FOR LIGHT ALCOHOLS ON A TGS 813



due to the changing inductive effect of the alcohol group . This reasoning is supported by the sensitivity ratios . Table 4.3.3 shows the relative sensitivities (normalised on the C₅ homologue) for both alkanes and alcohols . From table 4.3.3 it is observed that the C₄ figures are very similar , whereas the others differ markedly . These observations suggest that as the alcohol series is ascended the relative sensitivities become more dependant on the addition of the -CH₂- unit than on the changing influence of the functional group .

Because the data for the alcohols and alkanes was collected under entirely different analytical conditions it was not considered wise to compare directly the absolute sensitivities obtained . In order therefore , to make a comparison in absolute sensitivity a number of C₆ hydrocarbons including hexane were assessed . In all four compounds were studied : hexane ; cyclohexane ; hex-1-ene and benzene . The four compounds were determined using the conditions defined below :

COLUMN	PLOT alumina/KCl 25 m x 320 μm x 10 μm film
COLUMN TEMPERATURE	initial 50°C x 0 min ramp 30 C min ⁻¹ second 130°C x 4 min ramp 10 C min ⁻¹ final 190°C x 6 min
CARRIER GAS	white spot nitrogen
CARRIER FLOW	2.6 ml min ⁻¹
INJECTOR	0.1 μl x 28:1 split ratio
INJECTOR TEMPERATURE	200°C

TABLE 4.3.3 : NORMALISED SENSITIVITY RATIOS FOR THE
ALCOHOLS AND ALKANES

CARBON NUMBER	ALCOHOLS	ALKANES
1	0.64	0.42
2	0.97	0.69
3	0.88	0.55
4	0.82	0.82
5	1.00	1.00

DETECTOR	TGS 813 x 5.25 V heater voltage
DETECTOR TEMPERATURE	110°C
AUXILIARY GAS	40 ml min ⁻¹ air

Table 4.3.4 shows the sensitivity values obtained . from this it was immediately observed that the three types of functional group (alcohol , aldehyde and ketone) had a large positive affect on sensitivity (c.f. tables 4.3.1 and 4.3.2) . Comparing the absolute sensitivity values obtained , and assuming that the hexane sensitivity would at least have been of the same order as the pentane and lower molecular weight alkanes , the increase in sensitivity obtained for the aldehydes , alcohols and ketones from that of the corresponding alkane was at least 2 orders of magnitude . The mechanistic explanations of this increase in sensitivity are as follows :

1. a chemical affect , whereby the functional groups activate other atoms in the molecule e.g. increasing the acidity of the hydrogen atoms close to the functional groups .
2. a catalytic affect whereby the functional groups formed strong interactions with the sensor surface holding the molecules close to the tin oxide where oxidation could take place .

It is very likely that both mechanisms actually contribute to the increase in sensitivity observed , although the sensitivities observed tend to indicate that 2. may have been more important . This is due to the similarity between the aldehyde and ketone sensitivities i.e. since aldehydes have more

TABLE 4.3.4 : SENSITIVITY VALUES OBTAINED FOR THE DETECTION
OF HEXANE , HEX-1-ENE , CYCLOHEXANE AND BENZENE

BY A TAGUCHI 813

COMPOUND	SENSITIVITY	
	/AREA COUNTS g^{-1}	/AREA COUNTS $mole^{-1}$
HEXANE	2.5×10^{12}	2.2×10^{14}
HEX-1-ENE	1.1×10^{13}	9.2×10^{14}
CYCLOHEXANE	3.4×10^{12}	2.9×10^{14}
BENZENE	3.7×10^{12}	2.9×10^{14}

acidic protons than ketones the chemical affect would have caused differences to be observed . Also it has been reported that both aldehydes and ketones form similar surface carboxyl species with tin oxide [68] which would lead to very similar chemical environments for both types of compound and hence similar sensitivities would be expected . The catalytic mechanism can also be assumed for the alcohols although the surface species formed are somewhat different . Thornton and Harrison [34] observed the formation of surface methoxy for methanol . The assumption that the other alcohols form alkoxy groups could then account for the observed difference in sensitivity between the aldehydes and ketones compared to the alcohols .

Another point of interest , particularly to the potential of the sensor for future commercial use in gas chromatographs was the observation that the peak shapes did not appear to be adversely affected by the formation of relatively strong bonds between analyte and sensor surface . In fact , similar skew factors were observed for all of the compounds studied . From this observation it could be hypothesised that the chemisorbed species may be similar in all cases i.e. that hydrocarbons , alcohols , aldehydes and ketones all eventually become chemisorbed to the tin oxide surface via. for example , a carboxyl-type bond . Absolute sensitivity would then depend upon the ease with which the analyte species form the chemisorbing interaction . The data in reference [34] tend to support this view , the authors report that the surface methoxy groups formed from the methanol can be oxidised to surface formate . Furthermore they report that both ethanal and propanone form

surface carboxylates . Formation of a carboxylate species is also possible for hydrocarbons , where the initial interaction is likely to be formation of the alkoxy species followed by oxidation to carboxylate in a similar manner to that observed for alcoholic alkoxy groups . In order for the relative sensitivity figures to make sense the formation of a surface alkoxy group from a hydrocarbon must be less likely than that from an alcohol . Thornton and Harrison [34] proposed the a mechanism for alcohols whereby the alkoxy group was formed by dissociative chemisorption shown in figure 4.3.2 .

A similar mechanism for the hydrocarbons would be unlikely due to the absence of a polarising oxygen atom . The possible mechanism for hydrocarbon alkoxy group formation probably depends upon the presence of reactive surface species and in some cases the prior abstraction of a hydrogen atom from the hydrocarbon as shown in figure 4.3.3 . Reactions such as those shown in figure 4.3.3 would be possible , however , they could not be as likely as the alcoholic alkoxy formation shown in figure 4.3.2 which could therefore account for the decreased sensitivity observed for the hydrocarbons .

The principal reason for studying the C₆ hydrocarbons was in order to compare alkane sensitivity with that to the alcohols aldehydes and ketones under similar operating conditions . However since this was necessary the opportunity was taken to gain a brief insight into the affects of double bonds (and hence C:H ratios) on sensitivity . This resulted in the inclusion of the other three compounds in the experiment . The sensitivities measured produced some interesting results . It had been expected

FIGURE 4.3.2 :

A POSSIBLE REACTION SCHEME FOR THE FORMATION OF A SURFACE
ALKOXY GROUP BY DISSOCIATIVE CHEMISORPTION

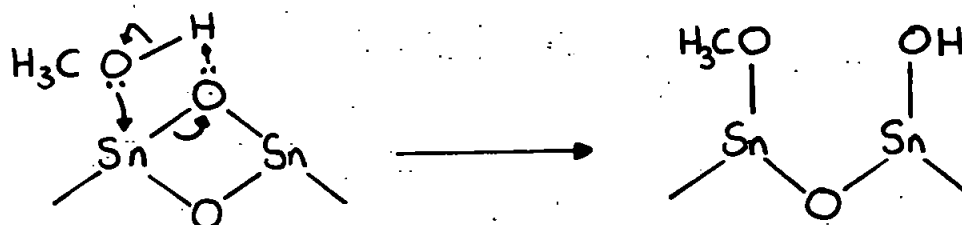
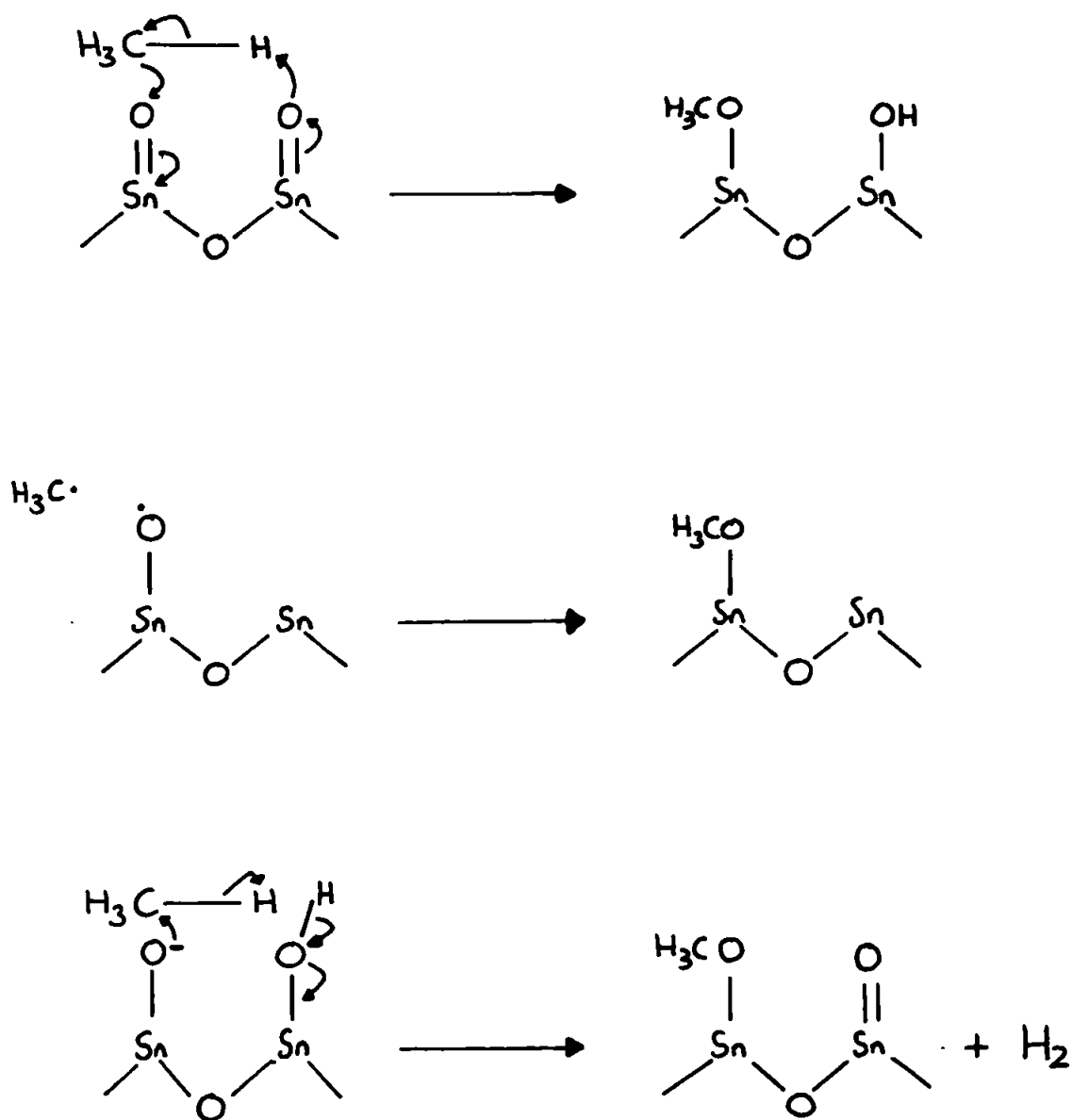
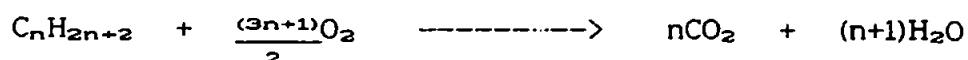


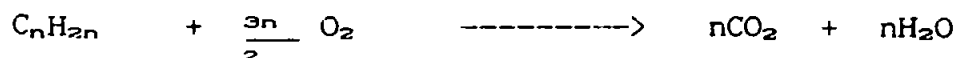
FIGURE 4.3.3 :
A POSSIBLE REACTION SCHEME FOR THE ABSTRACTION
OF A HYDROGEN ATOM FROM AN ALKANE



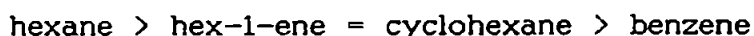
from consideration of the oxidation (combustion) of the hydrocarbons that sensitivity would be reduced as the degree of unsaturation increased . The reason for this was that for each double bond , one less water molecule was produced in combustion and hence one less oxygen atom was required by the combustion leading to less oxygen atoms being desorbed from the tin oxide surface i.e. for alkanes :



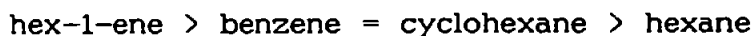
whereas for alkenes :



The reduction in the number of oxygen atoms released from the tin oxide would mean that less electron density would be released into the tin oxide bulk to change the conductivity and hence the sensitivity per mole would be reduced . From the consideration above it might be expected that the sensitivity order would be :



However , the observed sensitivities showed a quite different order :



It was therefore clear that the sensitivities were not entirely dependant upon the C-H ratio , this was particularly revealed by the difference in sensitivity between hex-1-ene and cyclohexane .

The close similarity between hexane and cyclohexane indicated that sensitivity was relatively unaffected by the cyclic structure of the compound . It was therefore believed that the presence of the double bond in hex-1-ene was responsible for its increased response . This was supported by the similarity between benzene and cyclohexane despite the difference in C-H ratio . The work on alcohols aldehydes and ketones suggested that the efficiency of chemisorption played a significant role in determining sensitivity . With this knowledge it could be hypothesised that the double bonds present in hex-1-ene and benzene were responsible for the difference between their expected and observed sensitivities . The mechanism being that the double bonds improved the chemisorption efficiencies in a similar manner to that observed for compounds containing oxygen atoms . The physical interaction involved was hypothesised when the additives in the tin oxide were considered . It has been previously mentioned that metal atoms such as platinum and palladium are added to the tin oxide to improve sensitivity and or selectivity . Both Pt and Pd are well known adsorbers of hydrogen and are thus added to promote hydrocarbon sensitivity by forming bonds with the hydrocarbon analyte thereby holding them close to the tin oxide where the sensing reactions occur . However it is also likely that the Pt and/or Pd are responsible for the enhanced sensitivity shown by compounds containing double bonds . Another well known property of these metals is their ability to form bonds with unsaturated organic molecules through the overlap of partially filled d-orbitals with the pi-electron system of the organic compound e.g. the Pd catalyst used in the Wacker

process [69] . This interaction represents a route for the chemisorption of an unsaturated organic analyte which would lead to stronger binding with the surface than through the physisorption available to alkanes . Hence this leads to a greater binding efficiency and hence greater sensitivity .

In this chapter the analytical potential of the sensor has been assessed for a range of common compounds and data has been collected indicating that there are a number of different mechanisms by which chemical structure can influence the response of the sensor . However , it has generally been shown that the sensor responds well and has much potential as a GC detector with either packed or capillary column separations .

It has also been shown that the presence of other metals in the tin oxide lattice could modify sensitivity . The only factor that caused concern was the skewed nature of the chromatographic peaks with the possible affects on peak area measurement and column resolution . It was felt that these latter points were worthy of further study .

CHAPTER 5 : HALOGENATED COMPOUNDS

5.1 INTRODUCTION

Much of the work reported in chapter 4 was carried out in response to the interest in the tin oxide sensor for gas chromatographic detection expressed by a commercial chemical company . The results obtained in chapter 4 demonstrated the potential of the sensor used in this application . As a direct result of these encouraging results it was requested that some work on chlorofluorocarbons be undertaken . Coincidentally this request combined readily with the direction in which the research was intended . At the end of chapter 4 . it was noted that the unsymmetrical nature of the chromatographic peaks obtained (ie. the tailing) was one of the few factors that might curtail the future development of a G.C detector based on tin oxide . Thus any further work on the sensor in this application required an in depth study of the nature and degree of the peak tailing that could be encountered . The connection between peak tailing and halogenated compounds had already been observed in preliminary work involving chloromethanes and therefore halogenated compounds provided an excellent opportunity for studying the nature and degree of tailing as required .

In the course of this work a number of parameters were identified that had possible influence on the nature of the sensing reaction . It was assumed that these parameters could therefore also affect peak tailing . The parameters identified were :

1. heater voltage ;
2. column flow rate ;

3. carrier gas composition ;
4. make-up gas flow rate ;
5. make-up gas composition ;
6. presence and nature of sensor bead additives ;
7. sensor bead morphology ;
8. analyte species composition and structure .

It was therefore felt that the study of peak tailing undertaken should be designed to take account of all of the parameters identified above . However this was not possible for a number of reasons . First it was considered necessary to keep the chromatographic conditions constant . The reason for this was so that the retention time could be kept constant . It was essential to keep the retention time constant in order to avoid possible complication of the peak shape measurement by the diffusion processes occurring before detection . In fact these chromatographic considerations fixed a number of the potential variables defined above . Firstly it was decided to use a single stationary phase for all of the compounds studied , the column material (supplied by I.C.I. Research and Technology Centre , Runcorn . Cheshire . U.K.) used was 25% E301 on "Chromosorb" . This was packed in-house into a 1 m stainless-steel 4 mm (i.d.) column . The stationary phase was oxygen sensitive and therefore nitrogen was used as the carrier gas . Consequently it was necessary to use air as the make-up gas in order to supply the required oxygen to the sensor . The net result of these requirements was to fix three of the parameters identified above :

Carrier gas composition ;

Carrier gas flow rate :

Make-up gas composition .

The remaining parameters , listed above , were used as variables in the study .

Throughout the previous parts of this work the measure of peak shape used has been skew factor , and this was maintained for it's simplicity in this study . The effects of each of the identified potential contributors to skew factor were compared . However because it was recognised that sensitivity is also of major importance to a detection system and that a compromise between this and peak shape might have to be made the affect on peak height response was also assessed .

The studies of heater voltage and analyte composition were relatively straightforward consisting of measuring skew factor and peak height for a number of different voltages for each compound studied . The means of studying sensor bead composition and morphology presented the most problems . Perhaps the best way to have studied this may have been to fabricate sensors with different levels of activating agents under different conditions to give varying surface characteristics . Unfortunately this was not possible , the only available alternative was to use different Taguchi sensors and then compare the results obtained in relation to a study of the composition of the sensors used . In this section three different Taguchi sensors were employed :

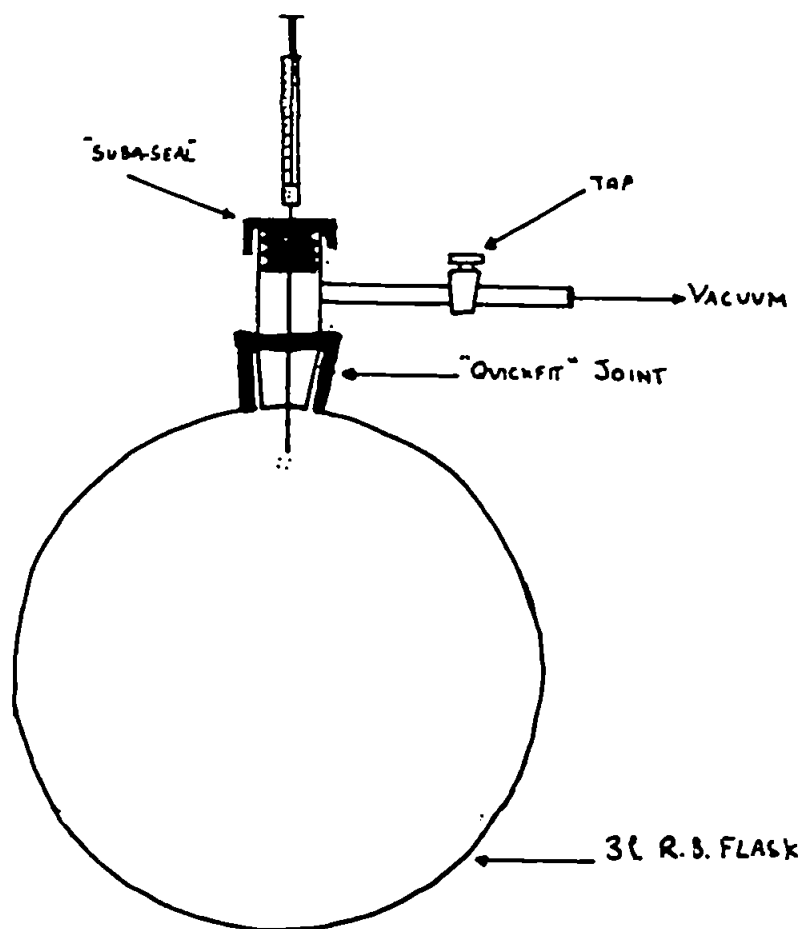
1. T.G.S. 813 - the sensor used to date ;
2. T.G.S. 822 - a sensor reported to be alcohol sensitised ;
3. T.G.S. 831 - a sensor reported to be sensitised to
chlorofluorocarbons .

Thus in essence this section consisted of studying peak height and skew factor at a number of different heater voltages for a number of different compounds on a number of different sensors .

The remaining parameter from the list above was make-up gas flow rate , this was treated as a chromatographic variable , an optimisation was performed on one of the compounds studied and then set at the optimum found for the rest of the study .

One of the problems that occurred during the course of this chapter was the method of sampling the compounds used since most were liquids . In chapter four the sampling of liquids in this work was discussed , it was noted that , for the purposes of this study , it was not desirable to introduce liquid samples . The reason for this was that liquid samples were much more likely to saturate the detector and thereby give unrepresentative results . In chapter four this was overcome by the use of small samples and a split injector . Unfortunately the split injection port and autosampler (required to give reproducible results with small (<1 ul) samples) were not available during this section of the study . Therefore it was necessary to produce vapour standards from the liquid samples . This was achieved using the apparatus shown in figure 5.1.1 which consisted of a 3l round-bottomed flask with a single "quickfit" neck , the flask was sealed with a "quickfit" adaptor to which an evacuation line with a tap had been added , the top of the adaptor was sealed with a rubber "suba-seal" which was used as a septum for withdrawing samples with a gas-tight syringe . To make a standard the flask was first evacuated three times to a pressure less than 3torr , flushing

FIGURE :5.1.1
THE APPARATUS USED TO PREPARE VAPOUR STANDARDS
FROM VOLATILE LIQUIDS



with air between evacuation steps . With the flask evacuated the sample was introduced through the septum . The flask was then allowed to fill by opening the tap and admitting air , to prevent loss of sample . the tap was closed before the pressure had fully equilibrated , final equilibration of pressure was achieved by rapid cycling of the tap until no further gas could be heard entering the flask through the evacuation line .

In an attempt to ensure reproducibility of mixtures the sample liquid was placed in an ice bath before making the vapour standard , also the atmospheric pressure at the time the standard was made was recorded and the nominal concentration corrected with respect to 760torr pressure . The only parameter that could not be accurately controlled was the temperature of the rooms in which the standards were prepared and used . however the temperatures were observed to remain constant to within $\pm 5^{\circ}\text{C}$ during the period for which each of the standards were used .

5.2 MAKE-UP GAS FLOW RATE OPTIMISATION

Carrier gas composition and flow rate were discussed in the introduction to this chapter . it was also noted that the decision to keep these mainly chromatographic variables constant, affected the choice of make-up gas . The nitrogen carrier and air make-up system used in the previous chapter had proven successful and was therefore retained in this study , the remaining chromatographic variable , the make-up gas flow rate was also to be kept constant throughout the peak shape study . Because the chromatographic conditions were different from those used in the previous chapter , and because packed columns were used here there was a large difference in the carrier gas flow rate . Consequently it was considered necessary to re-optimize the make-up gas flow to take account of these changes . In optimizing the make-up gas flow rate there were two considerations : firstly there was the choice of sensor to use ; and , secondly was the choice of sample gas to use . In fact the choice of sensor was straightforward , since all of the previous work had been concerned with the T.G.S. 813 , this was the natural reference point from which to begin . The choice of sample gas was less simple . Since the make-up gas was to be optimized for the whole study it was considered best to choose a sample gas which would be representative of the type of compounds likely to be encountered in the study . For this reason the sample gas used was one of those requested by the initiators of this section of the work . "Arcton 22" (Difluorochloromethane ; CF_2HCl) this compound was considered an ideal choice since it contained most of the constituent atoms likely to occur in a

potential analyte . The optimisation was carried out by injecting samples of Arcton 22 at different flow rates of air . The chromatographic conditions used were :

COLUMN	1 m x 4 mm (i.d.) 25% E301 on "Chromosorb"
CARRIER GAS	40 ml min ⁻¹ Nitrogen
COLUMN TEMPERATURE	55°C
DETECTOR TEMPERATURE	130°C
HEATER VOLTAGE	6.5 V

For convenience the make-up gas flow was set using a pressure regulator operating "upstream" of a "type B" restrictor (Philips Scientific) . The make-up flow rate was then quoted in terms of the pressure at the regulator in psi (pounds per square inch) . The range of pressures studied 0-10 psi corresponded to flow rates of approximately 0-30 ml min⁻¹ through the detector housing . As in all of the experiments carried out in this study both peak height and skew factor were measured . output from the detection circuit was fed to a line chart recorder and measurements made by hand . The results of the optimisation are shown in figures 5.2.1 and 5.2.2 . The skew factor versus gas pressure plot (figure 5.2.1) shows a minimum at between 2 and 3 psi whilst the peak height versus gas pressure plot showed a gradual increase in sensitivity with increasing gas pressure . The optimum pressure selected was 3 psi . The reason for this was that although sensitivity was observed to increase with increasing pressure the observed skew factor was much higher than the value set in chapter 4 for accurate peak area measurement .

FIGURE 5.2.1

THE AFFECT ON SKEW FACTOR FOR ARCTON 22
OF AN AUXILIARY DETECTOR GAS FLOW

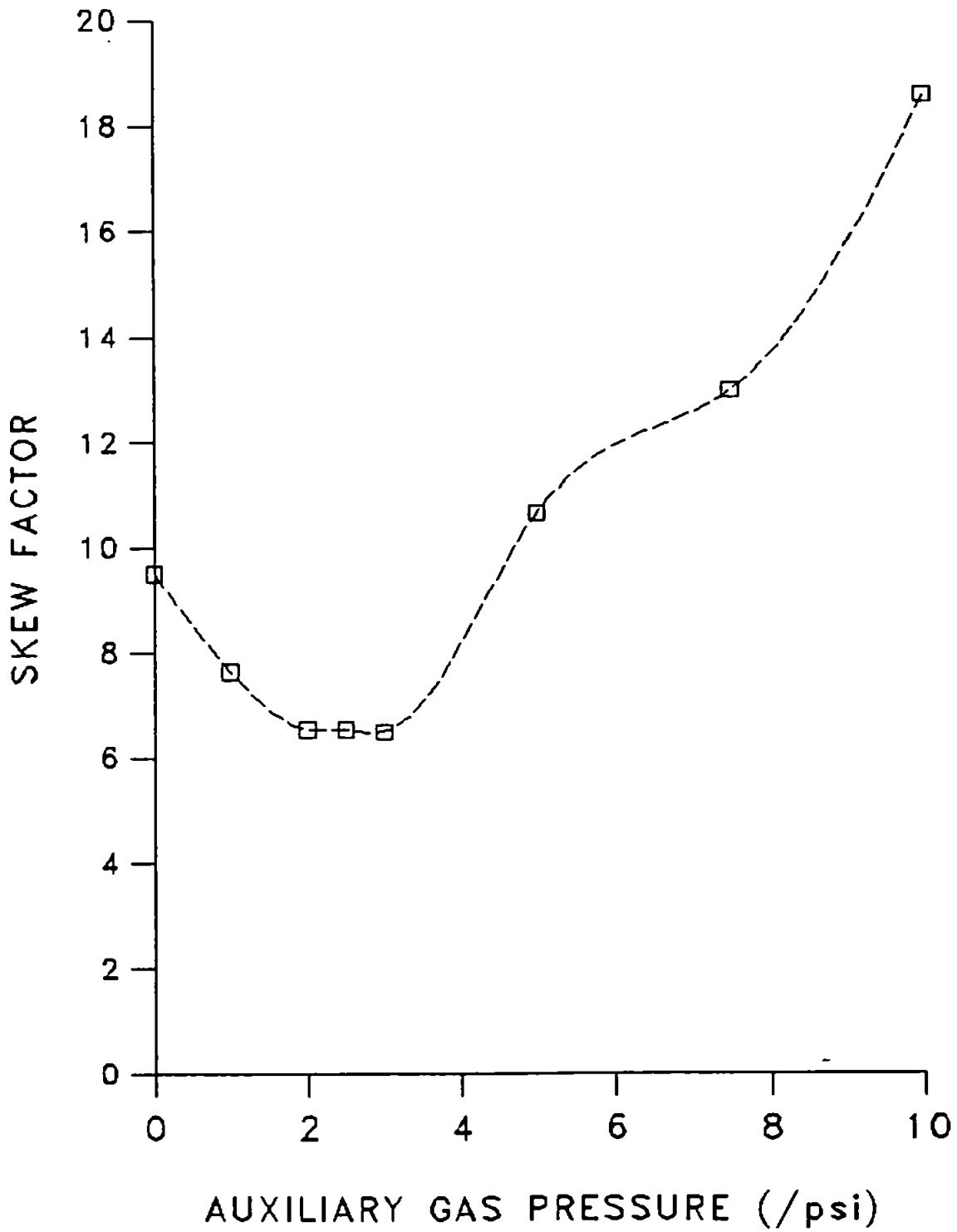
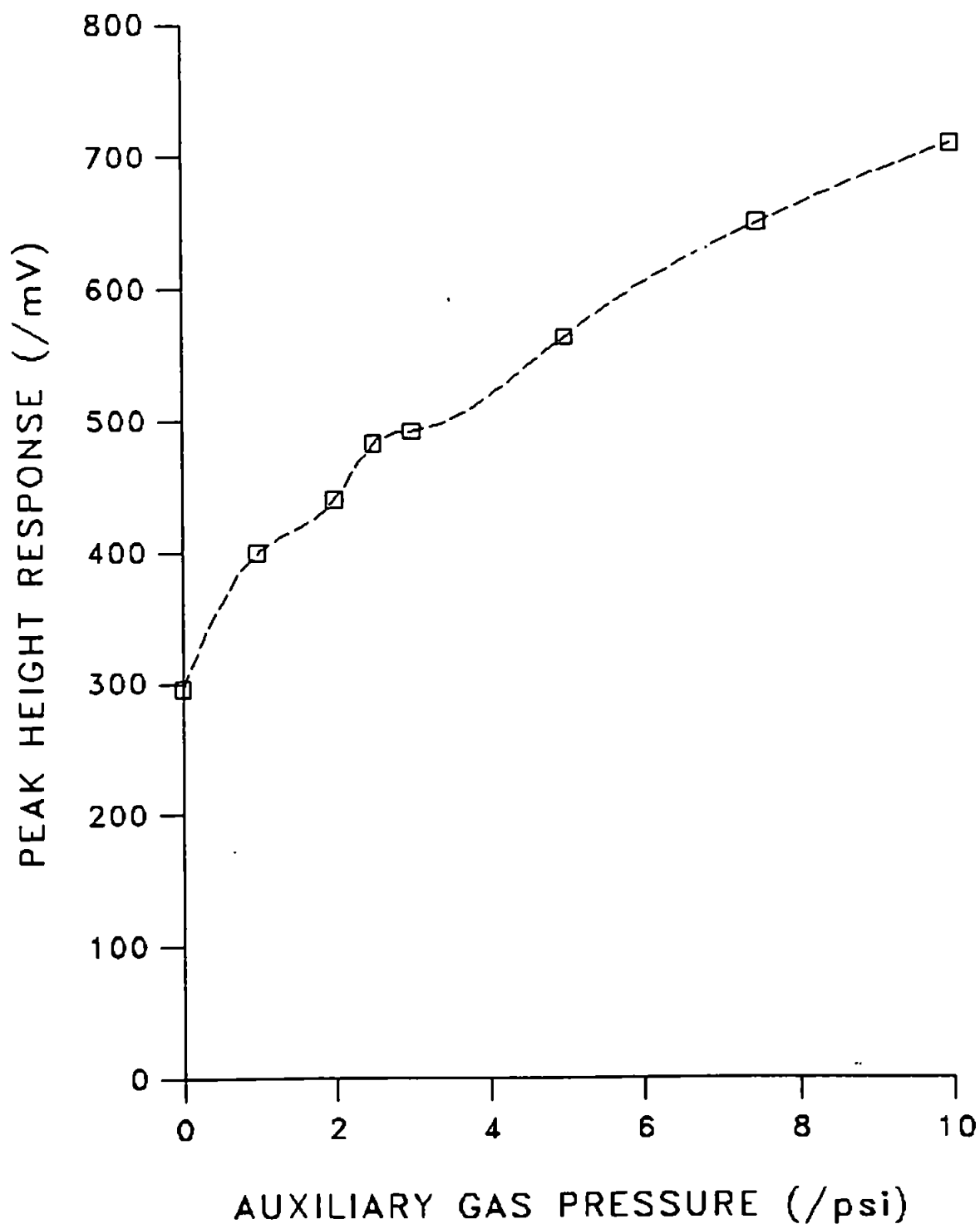


FIGURE 5.2.2

THE AFFECT ON PEAK HEIGHT FOR ARCTON 22
OF AN AUXILIARY DETECTOR GAS



5.3 HEATER VOLTAGE RANGE

In the introduction to this chapter the work to be carried out here was summarised as measuring peak height and skew factor at a number of different heater voltages for a number of different compounds on a number of different sensors . Previous experiments have shown that the range of potentially useable voltage lies between 4.5 and 8V . The 3.5V range described by these limits is very large when compared with the change in response previously observed for changes in heater voltage of as little as 0.25V . The consequence of this observation was that a very large number of voltages would have had to have been studied in order to have been confident that the optimum voltage had been covered . This would obviously have been extremely tedious and time consuming . However , the work on related compounds , e.g. alkanes , had shown that the heater voltage optima occurred over only a relatively small proportion of the working range of the sensor . Therefore it was considered reasonable that an experiment should be carried out to find the approximate range over which the optimum heater voltage should be found and thereby limit the number of voltages that had to be studied .

In fact two experiments were carried out to determine the optimum voltage range . The first experiment used Arcton 22 as the sample gas on the TGS. 813 . This experiment did not attempt to cover all of the available voltage range . All of the previous observations of peak tailing had indicated that high heater voltages were required with samples which exhibited significant peak tailing . This experiment therefore concentrated on the

upper end of the voltage range . Again , both skew factor and peak height were measured . The voltage range across which the experiment was carried out was from 6.5V to 9.0V . It may be observed that the upper end of the voltage range studied was actually higher than that specified above as the normal useful range . The upper limit specified above corresponds to the limit at which reversible response i.e. lower voltages exhibit the same response before and after the higher voltage had been applied , can be observed .

It was decided that the experiment should go beyond the specified range in order to check that no further improvement in skew factor could be achieved . The sensor used in this experiment was then discarded .

Figures 5.3.1 and 5.3.2 show the the results obtained in this experiment . Figure 5.3.2 , the peak height versus heater voltage plot , shows that a marked decrease in response was observed as the voltage was increased . Figure 5.3.1 however , the skew factor versus heater voltage plot showed only a gradual improvement as heater voltage was increased . The results obtained in this first experiment were not encouraging , they showed that very high heater voltages were necessary for acceptable peak shapes to be obtained . It was decided that , before destroying a large number of sensors by operating at high heater voltages, another compound should be studied to ensure that the results obtained were representative of the range of voltage likely to be required . The second compound used , Arcton 11 (Trichlorofluoromethane : CFCl_3), was another of those supplied by ICI for use in this investigation .

FIGURE 5.3.1

THE AFFECT OF HIGH HEATER VOLTAGES ON
PEAK HEIGHT FOR CHLOROFLUOROCARBONS

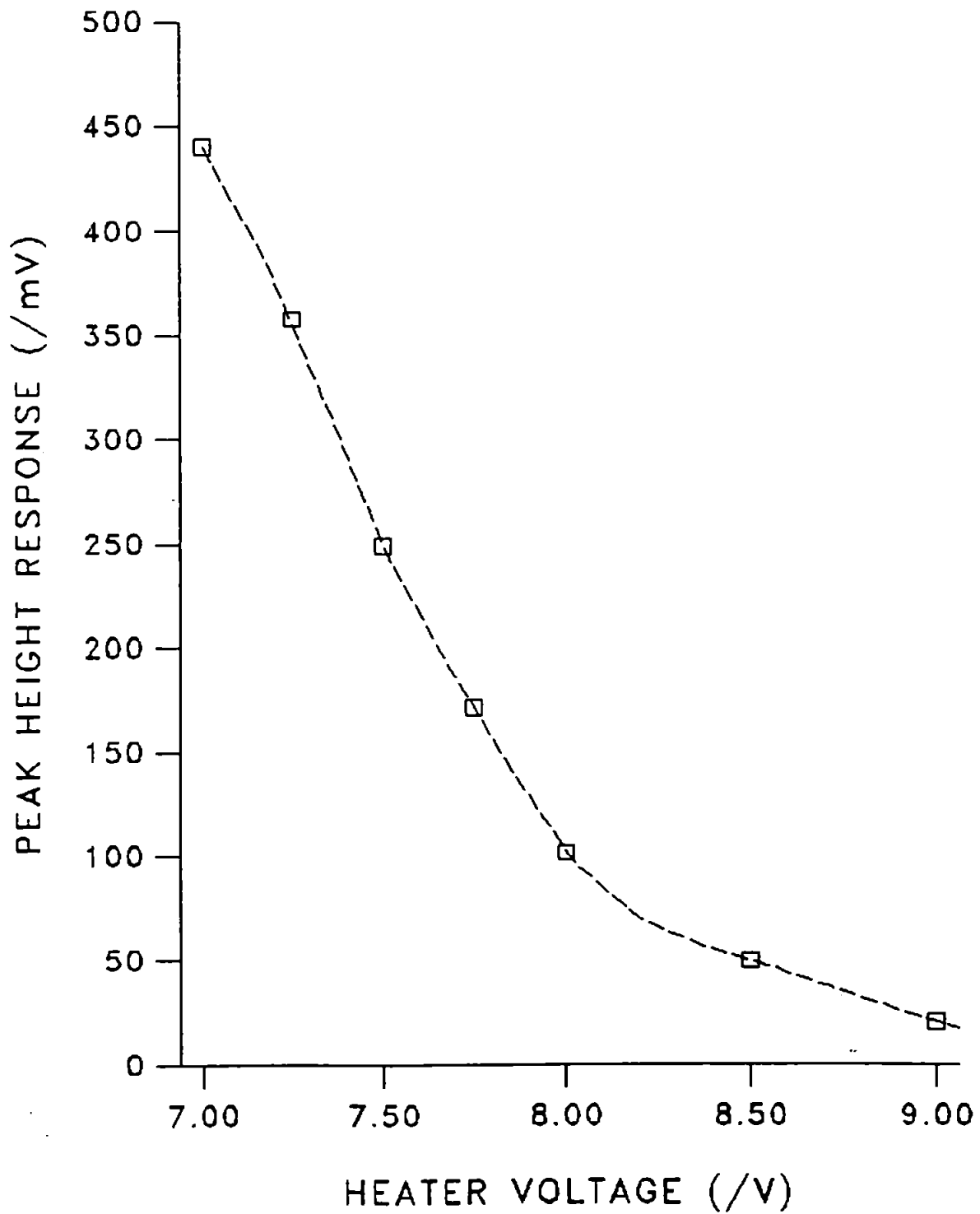
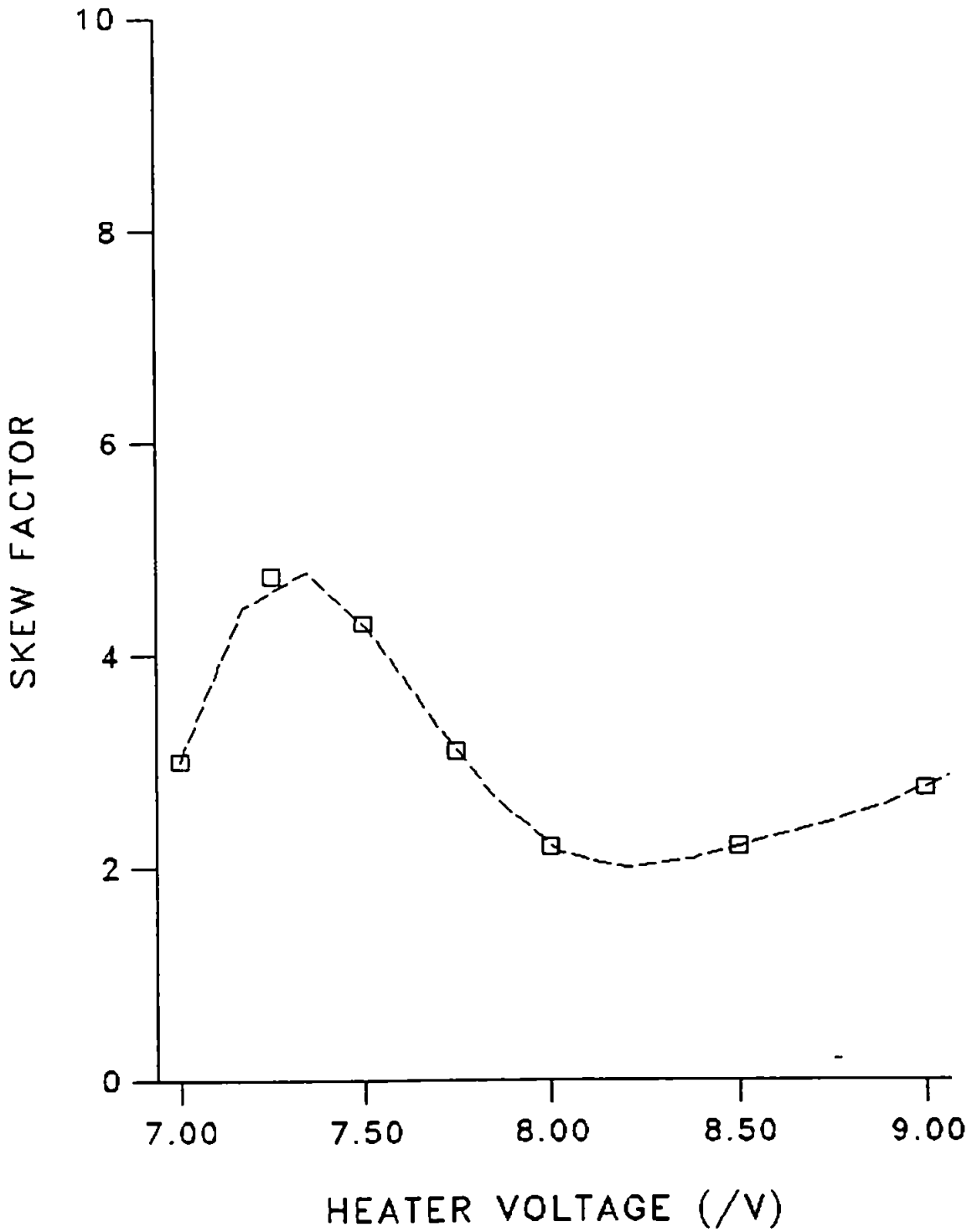


FIGURE 5.3.2

THE AFFECT OF HIGH HEATER VOLTAGES ON
SKEW FACTOR FOR CHLOROFLUOROCARBONS



This experiment was carried out in a similar manner to the first experiment in this section . the voltage range however , was slightly different to the above , it was hoped that a slightly lower range could be used and therefore the initial voltage was 6.0V instead of the 6.5V used above . The upper limit of the experiment was determined during the experiment when the peaks were observed to be penetrating the baseline and no further improvement in either peak shape or response was being observed . Figure 5.3.3 shows typical chromatograms obtained from each of the voltages studied in this experiment . The chromatograms show the significant changes which occurred over the voltage range . Figures 5.3.4 and 5.3.5 are the relevant plots of skew factor and peak height against heater voltage which also demonstrate the marked change observed . These results were much more encouraging than those from Arcton 22 especially when the relatively small reduction in peak height between 6.25 and 6.5V is compared with the improvement in skew factor . Although skew factor did improve between 6.5 and 6.75V it was observed that penetration of the baseline had occurred , which was analytically unacceptable .

The two experiments performed in this section demonstrated that heater voltage could have a very large affect on the peak shapes obtained . The inference from this observation was that the voltages to be studied should cover a large proportion of the working range of the detector . This had to be combined with the second inference that significant changes in response could be observed between different compounds . The compromise reached in order to be able to study a number of compounds was that three different voltages should be studied for each compound on each

FIGURE 5.3.3 :

CHROMATOGRAMS SHOWING THE AFFECT OF A NARROW HEATER VOLATGE
RANGE ON THE RESPONSE OF A TGS 813 TO ARCTON 11

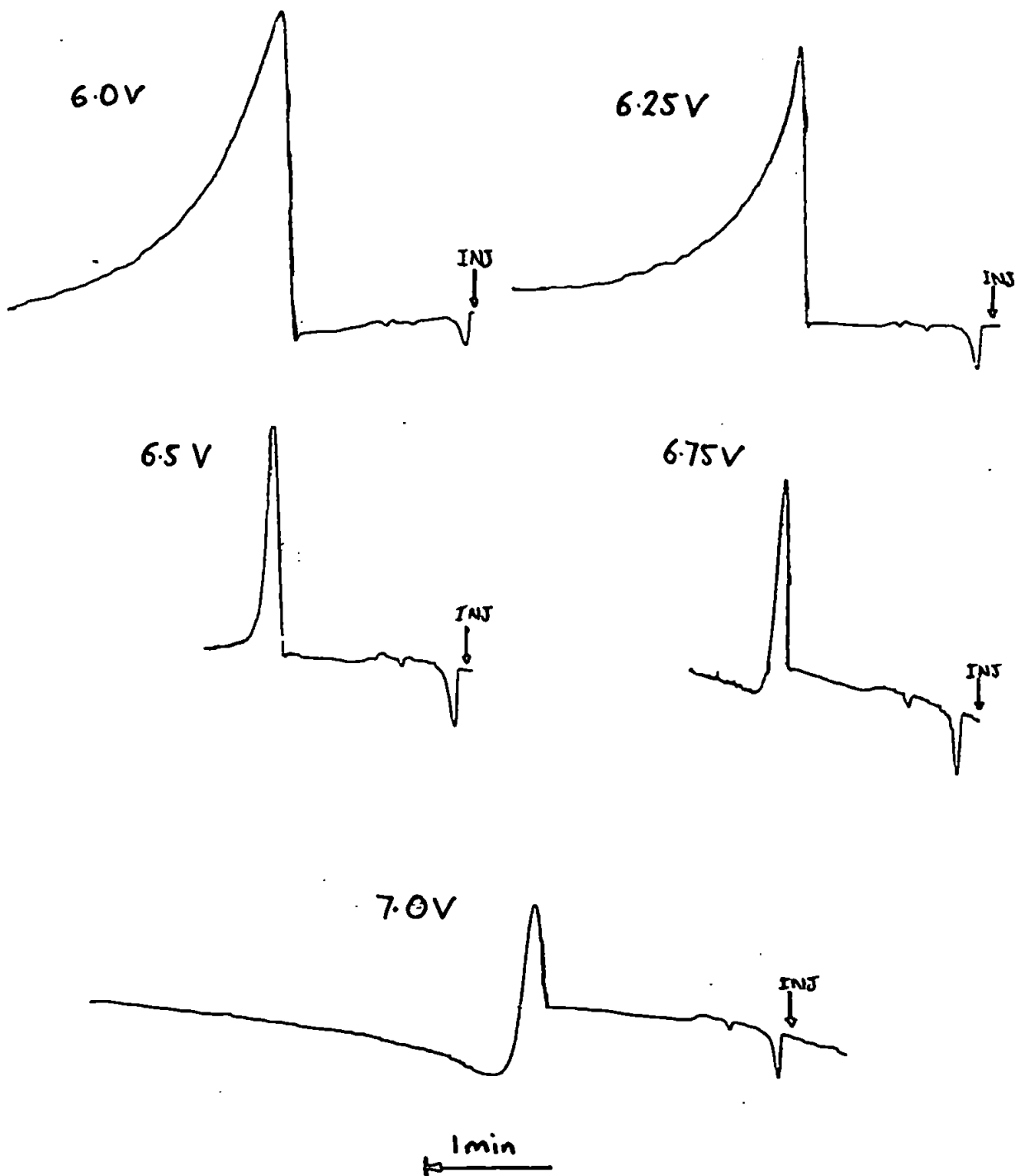


FIGURE 5.3.4

THE AFFECT OF HEATER VOLTAGE ON SKEW
FACTOR TO ARCTON 11 BETWEEN 6.0 AND 7.0V

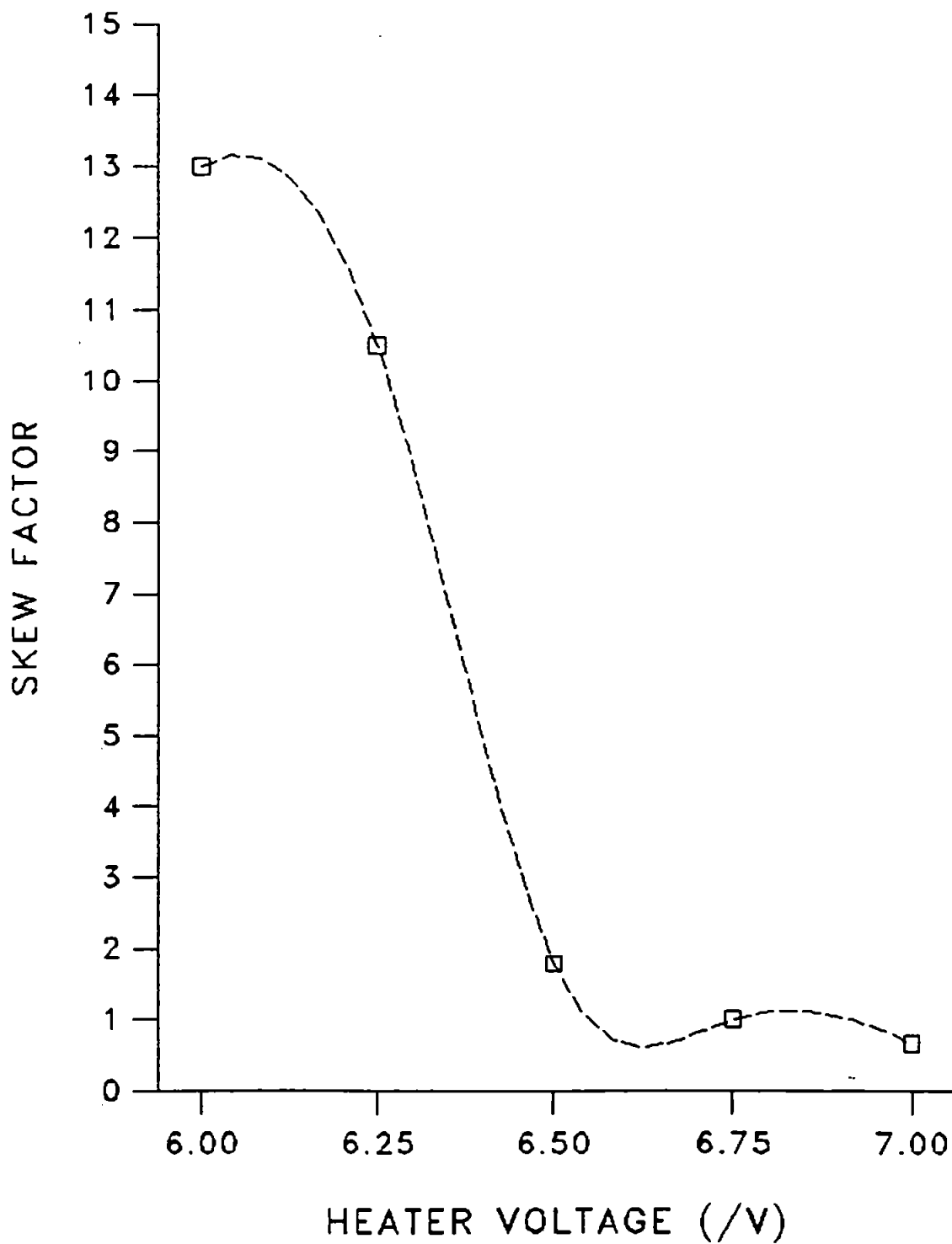
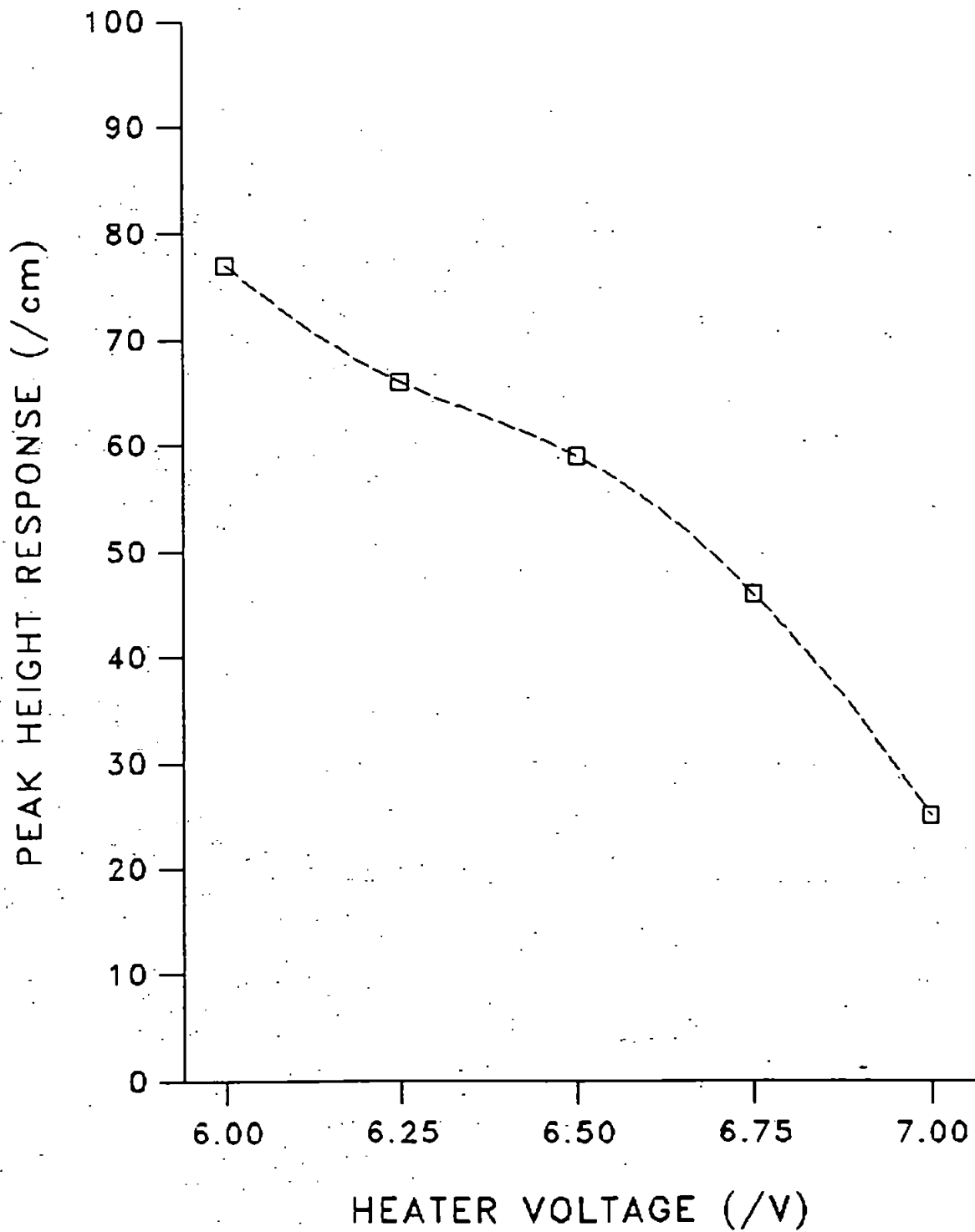


FIGURE 5.3.5

THE AFFECT OF HEATER VOLTAGE ON PEAK
HEIGHT FOR ARCTON 11 BETWEEN 6.0 AND 7.0V



of the three sensors . As described above it was necessary that the three voltage points chosen covered a relatively large proportion of the range available . Therefore the three points chosen were : 5.75V : 6.25V and 6.75V .

5.4 : CHLOROMETHANES

The first group of compounds to be studied in this chapter were the chloromethanes : Dichloromethane ; Trichloromethane and Tetrachloromethane . These three compounds were chosen to examine the affect of increasing the number of halogen atoms in an analyte molecule on the response and peak shape of the sensors . It might have been preferable to have included Chloromethane in this section in order that the full range have been studied . However chloromethane is a gas at 0°C and it was therefore difficult to produce a vapour standard in the same manner as the other three chloromethanes . This meant that there would have been doubt about the relative sensitivity of chloromethane when compared with its homologues . On balance therefore , chloromethane was not included in this section .

As described above this section consisted of measuring skew factor and peak height for each compound on each sensor at three different heater voltages . Vapour standards were prepared for each compound using 10ul of liquid sample in the flask , gaseous injections of 0.5 cm³ of the standards were used . Five injections were made at each voltage and the averages of both peak height and skew factor recorded . As before at least 30 minutes was allowed for equilibration between changes in voltage , also in this section when sensors were changed they were allowed to equilibrate at 5.25V (the low voltage point) overnight .

The results from this section are shown in Tables 5.4.1 to 5.4.6 . A number of general observations can be made from these tables :

TABLE 5.4.1 : SKEW FACTORS OBTAINED FROM INJECTION OF
DICHLOROMETHANE

SENSOR	SKEW FACTORS		
	5.75V	6.25V	6.75V
TGS 813	4.6	2.9	1.9
TGS 831	7.6	6.5	4.6
TGS 822	6.5	5.6	6.6

TABLE 5.4.2 : PEAK HEIGHTS OBTAINED FROM INJECTION OF
DICHLOROMETHANE

SENSOR	PEAK HEIGHT (mV)		
	5.75V	6.25V	6.75V
TGS 813	742	577	264
TGS 831	506	485	325
TGS 822	2770	2640	2300

TABLE 5.4.3 : SKEW FACTORS OBTAINED FROM INJECTION OF
TRICHLOROMETHANE

SENSOR	SKEW FACTORS		
	5.75V	6.25V	6.75V
TGS 813	N.R	3.7	1.6
TGS 831	3.6	2.9	1.7
TGS 822	N.R	N.R	13.3

N.R. : BASELINE NOT FULLY RECOVERED AFTER 10 MINUTES

TABLE 5.4.4 : PEAK HEIGHTS OBTAINED FROM INJECTION OF TRICHLOROMETHANE

SENSOR	PEAK HEIGHT (mV)		
	5.75V	6.25V	6.75V
TGS 813	314	250	88
TGS 831	58	56	28
TGS 822	1072	1010	835

TABLE 5.4.5 : SKEW FACTORS OBTAINED FROM INJECTION OF
TETRACHLOROMETHANE

SENSOR	SKEW FACTORS		
	5.75V	6.25V	6.75V
TGS 813	N.R	2.5	NEG.
TGS 831	NEG.	NEG.	NEG.
TGS 822	27	36	N.R

N.R. : BASELINE NOT FULLY RECOVERED AFTER 10 MINUTES

NEG. : NEGATIVE PEAKS OBTAINED

TABLE 5.4.6 : PEAK HEIGHTS OBTAINED FROM INJECTION OF
TETRACHLOROMETHANE

SENSOR	PEAK HEIGHT (mV)		
	5.75V	6.25V	6.75V
TGS 813	133	75	NEG.
TGS 831	NEG.	NEG.	NEG.
TGS 822	632	550	388

NEG : NEGATIVE PEAKS OBTAINED

1. Peak height reduced as heater voltage increased :
2. Skew factor reduced as heater voltage increased :
3. Sensitivity reduced as chlorine content increased :
4. skew factor increased as chlorine content increased :
5. Sensitivity decreased in the order 822 , 813 , 831 :
6. Skew factor decreased in the order 822 , 831 , 813 .

Table 5.4.7 summarises the affects of both heater voltage and increasing chlorine content on the sensitivity of the each sensor . The table shows the percentage reduction per volt observed for each compound on each sensor . The calculation of percent reduction was simply :

$$\frac{PH-PH''}{PH} \times \frac{100}{V''-V}$$

WHERE : PH'' = PEAK HEIGHT AT HIGHER VOLTAGE (mV)

PH = PEAK HEIGHT AT LOWER VOLTAGE (mV)

V'' = HIGHER VOLTAGE (V)

V = LOWER VOLTAGE (V)

The interpretation of Table 5.4.7 is that low values indicate relatively small changes in sensitivity as heater voltage increased . It can be observed from Table 5.4.7 that increasing heater voltage caused a reduction in sensitivity . Furthermore , however Table 5.4.7 shows that the TGS 822 was least affected whilst TGS 813 was affected severely by increasing voltage also the table shows that increasing the chlorine content of the analyte causes the reduction in sensitivity observed with increasing heater voltage to be greater . The only function that Table 5.4.7 does not summarise is the relative sensitivities

TABLE 5.4.7 : PERCENTAGE REDUCTIONS IN PEAK HEIGHT OBSERVED
WITH INCREASING HEATER VOLTAGE FROM 5.75 V TO 6.75 V
FOR THE CHLOROMETHANES

SENSOR	REDUCTION (%V ⁻¹)		
	CH ₂ Cl ₂	CHCl ₃	CCl ₄
TGS 813	64	72	116
TGS 831	36	52	--
TGS 822	17	22	38

observed between each analyte on each sensor . This data is contained in Tables 5.4.2 , 5.4.4 and 5.4.6 , and as identified above shows that sensitivity decreased in the order : TGS 822 ; TGS 813 ; TGS 831 for each of the analytes studied . The actual differences observed between sensors was significant and increased with both chlorine content and heater voltage .

The data from the skew factor measurements is somewhat different from that observed from the sensitivities . Tables 5.4.1 5.4.3 and 5.4.5 show the relationships between skew factor , heater voltage and sensor type . As described above the tables show that in almost every case skew factor improved with increasing voltage but deteriorated with increasing chlorine content . The analytical significance of the values for skew factor must be measured by comparison with the limit , set in chapter 4 , for use with peak area measurement , of 2.0 . It is noted that only the TGS 813 satisfies this requirement for both dichloromethane and trichloromethane and that none of the sensors used do so for tetrachloromethane . However , it must be remembered that this section was not an exercise in determination of analytical application but rather an attempt to identify some of the parameters that lead to peak tailing . In fact all of the parameters suspected , have been shown to affect peak tailing to a greater or lesser extent .

During the course of this section two unexpected phenomena were observed . Firstly was the observation that in some cases "incomplete recovery" of the baseline occurred . In all but one case the "incomplete recovery" was observed at low voltages , the exception being for tetrachloromethane on the TGS 822 at 6.75V

and in this case the two observed skew factors at the lower voltages were very large and increasing with voltage . There are two possibilities that could explain the observation : the first is that the sensor surface becomes irreversibly changed during the sensing interaction and the second and more likely is that recovery was very slow in these cases and that the ten minutes allowed between interaction and subsequent injection was not long enough for full recovery to be observed . In fact upon leaving a TGS 822 at 6.75V after interaction with trichloromethane full recovery was observed after approximately 2 hours . It was noted that the TGS 822 seemed particularly prone to slow recovery .

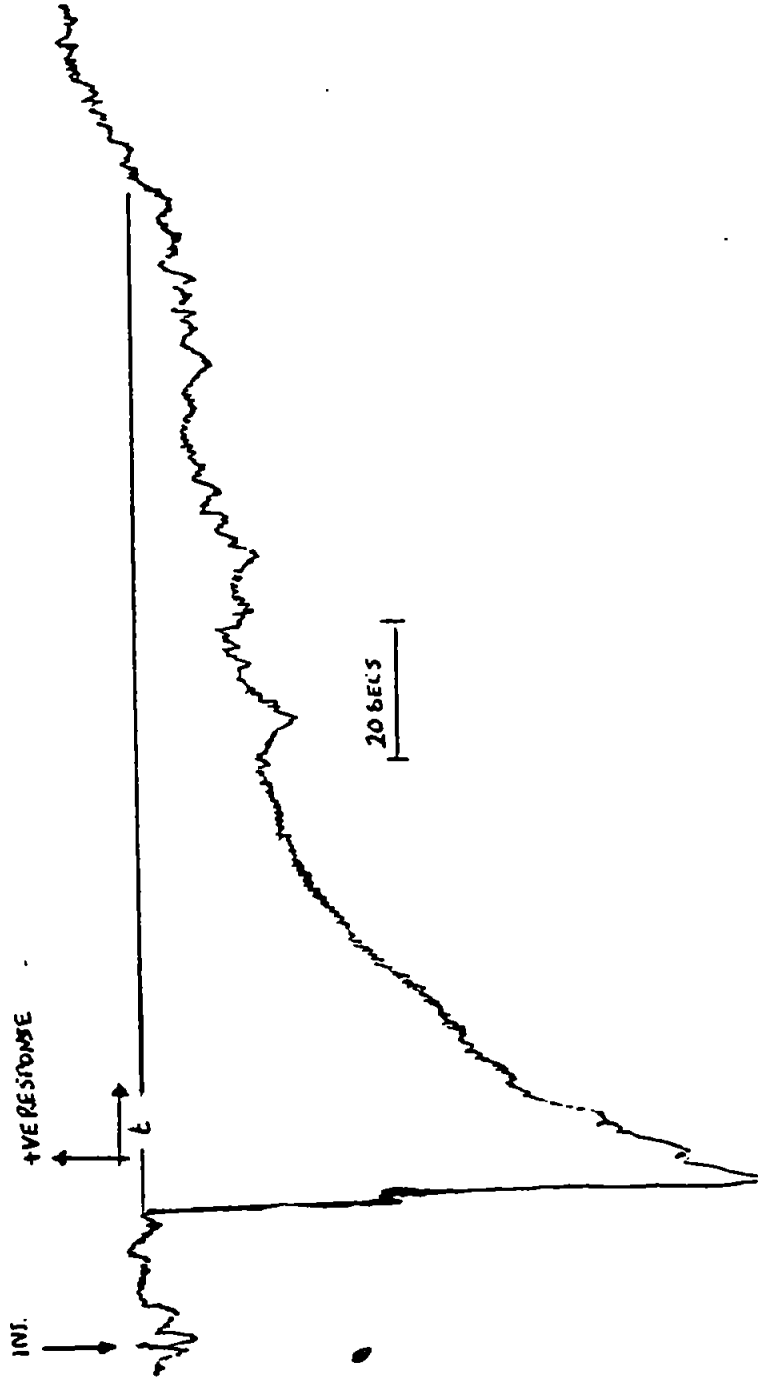
The second "unexpected" observation made during this section was that of negative response to tetrachloromethane by both the TGS 813 and TGS 831 . There are again two possible explanations for such phenomena :

In the current theory of response mechanism , changes in conductivity are based upon interactions of the analyte gas with reactive surface-chemisorbed oxygen species leading to breakage of the chemisorbing bond allowing previously immobilised conduction band electrons to carry current . Therefore , the first explanation is that interaction of an analyte containing chlorine with the sensor surface leads to formation of a species better able to immobilise the electron density from the conduction band of the tin oxide than the chemisorbed oxygen species . The result of such an interaction would be a net withdrawal of electron density from the conduction band thus leading to a negative peak . The second possibility is that the analyte gas cools the sensor bead more efficiently than the

carrier gas and make-up gas . the sensor would then behave more like a thermal conductivity detector . Cooling of a semiconductor leads to demotion of the conduction electrons to the valence band thus reducing electrical conductivity . One of the most conclusive pieces of evidence to support the former view comes in looking at the shape of the negative response "peak" . Figure 5.4.1 shows a typical "negative peak" . it is observed that the baseline recovery is slow in comparison with the disturbance . the significance of this is that a purely physical interaction such as thermal conduction should give a symmetrical shape . So there are theoretically two possibilities : firstly that the column efficiency was poor and that the "tailing" was due to voids etc. in the column packing , or , that there had been a chemical interaction with the sensor surface . However since very good peak shapes had already been obtained with similar compounds using the same column it was much more likely that there had been chemical interaction between tetrachloromethane and the sensor surface .

FIGURE 5.4.1 :

A TYPICAL EXAMPLE OF THE NEGATIVE RESPONSE OF A TAGUCHI GAS
SENSOR TO TETRACHLOROMETHANE



5.5 : MONO-HALOMETHANES

Section 5.4 showed the affect on skew factor and response of changing the number of chlorine atoms in the analyte molecule . This section was designed to investigate the affect of changing the halogen atom on the two figures of merit .

The monohalomethanes were selected for this study . the reason for this was the considered advantage of keeping the molecules relatively simple . It could be argued perhaps that the tetra- halomethanes would be more representative of the affect of changing the halogen atom . However , as observed for tetrachloromethane in the previous section the more halogen atoms present the more seriously response and skew factor are affected and the less measurements can be made which are representative of the "normal" interaction between analyte and sensor .

Unfortunately the use of the mono- homologues also affected the range of analytes available for study . The reason for this was the differing physical nature of the required analytes (fluoro- and chloromethane are gases at room temperature) and as described above the use of gaseous compounds was effectively prohibited by the nature of the sampling system . The net result of the above considerations was that this experiment was limited to a comparison between bromomethane and iodomethane . It should be noted here that bromomethane is also a gas at room temperature (20°C) although it was possible to sample bromomethane satisfactorily by cooling the bottle in an ice bath before taking the sample .

As in the previous experiments in this chapter both peak

height and skew factor were measured for five injections of each analyte at a number of different voltages on the three sensors used . The stabilisation periods between changes in sensor or heater voltage were also similar to those used previously .

The results from this section are shown in Tables 5.5.1 and 5.5.2 . Table 5.5.1 shows the affect of changing the halogen atom on skew factor . The table has a number of interesting features :

skew factor appears worse for bromomethane than iodomethane on the TGS 813 ;

very little difference can be observed between analytes on the TGS 831 ;

skew factor appears better for bromomethane than iodomethane on the TGS 822 ;

heater voltage does not appear to affect skew factor as much as for the chloromethanes cf. Table 5.4.1 ;

in general skew factor appears lowest on TGS 813 and highest on TGS 822 .

Also included in Table 5.5.1 are the results obtained from the dichloromethane study , whilst it was appreciated that the results were not strictly comparable in terms of absolute values of skew factor , it was thought that the general trends observed should have been similar . There are some similarities , eg. that the skew factors decrease in order 822 > 831 > 813 , however the affect of heater voltage is markedly different for both TGS 813 and 831 in that the improvement in skew factor is much larger for dichloromethane than either bromomethane or iodomethane although the TGS 822 showed very little heater voltage

TABLE 5.5.1 : SKEW FACTORS OBTAINED FROM INJECTION OF
BROMOMETHANE AND IODOMETHANE

COMPOUND	SENSOR	SKEW FACTORS		
		HEATER VOLTAGE		
		5.75V	6.25V	6.75V
IODOMOMETHANE	TGS 813	1.8	1.4	1.6
	TGS 831	2.1	1.8	1.9
	TGS 822	5.6	5.3	5.1
BROMOMETHANE	TGS 813	2.1	1.8	1.9
	TGS 831	2.0	1.9	1.8
	TGS 822	4.3	4.5	4.5
DICHLOROMETHANE	TGS 813	4.6	2.9	1.9
	TGS 831	7.6	6.5	4.6
	TGS 822	6.5	5.6	6.6

TABLE 5.5.2 : PEAK HEIGHT RESPONSES OBTAINED FROM
INJECTION OF BROMOMETHANE AND IODOMETHANE

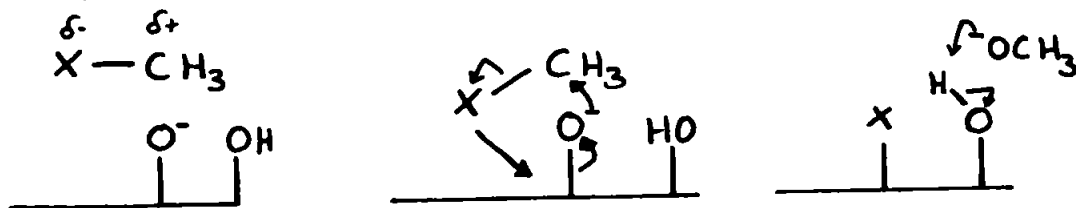
COMPOUND	SENSOR	RESPONSE (mV ug ⁻¹)		
		HEATER VOLTAGE		
		5.75V	6.25V	6.75V
IODOMOMETHANE	TGS 813	707	634	291
	TGS 831	744	660	428
	TGS 822	1667	1500	1590
BROMOMETHANE	TGS 813	1152	1081	771
	TGS 831	287	316	245
	TGS 822	1852	1813	1494
DICHLOROMETHANE	TGS 813	369	287	131
	TGS 831	252	241	162
	TGS 822	1378	1313	1148

dependency .

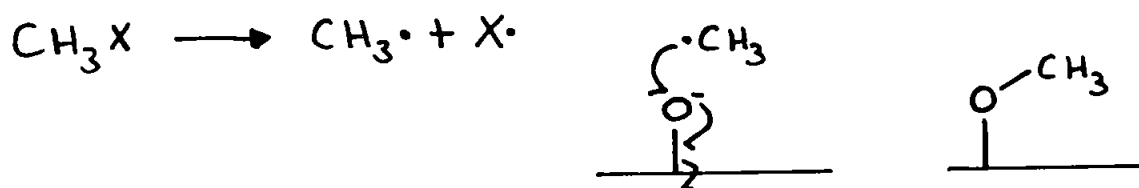
The general conclusion to be drawn from Table 5.5.1 is that as the halogen group is ascended the halomethane causes an increase in skew factor to be observed , although different sensors are affected to different extents , the TGS 822 being least affected and the TGS 831 most affected .

Table 5.5.2 shows the results obtained for the response of each sensor to the two different compounds at each of the voltages studied . It can be seen that the heater voltage dependence is similar to that observed for the chloromethanes whereby all of the responses decrease with increasing voltage to differing degrees with the TGS 813 most affected and TGS 822 least affected . Furthermore the sensitivity order is also similar to that for the chloromethanes with the TGS 822 most sensitive by a considerable margin with relatively little difference between TGS 813 and 831 , the TGS 831 being generally slightly less responsive than TGS 813 . The sensitivity order as might be expected shows a decrease as the halogen group is ascended . This is almost certainly due to the increasing electronegativity of the halogen atom and increasing homolytic bond dissociation energy of the halomethane . In the first instance polarisation of the halomethane molecule leaves an electron deficient alkyl group and an electron rich halogen , nucleophilic attack on the alkyl group by a surface O^- species cannot lead to electron density flowing back into the conduction band of the sensor (see below) similarly because of the differing electronegativity replacement of the surface O^- by the halogen atom / halide ion would cause a greater increase in conductivity

if the halogen were iodine as opposed to bromine or chlorine :

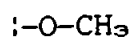


In the second instance free radical attack at surface O^- leads to the following reaction scheme :



the above scheme clearly shows electron density flowing into the tin oxide bulk and since homolytic bond dissociation energy increases from methyl iodide to methyl chloride it is seen that sensitivity must reduce in the order observed .

The above consideration of sensitivity relationships also sheds some light onto the possible cause of the poor peak shapes obtained using halogenated compounds . Examination of the possible surface species formed during the reaction shows that only the following are likely :



Of the above surface halide is most likely to cause the poor peak shapes since :

1. $:O-CH_3$ species were encountered in the previous chapter and did not lead to poor peak shape :

2. :-O-X species have greater electron withdrawing capacity than surface oxide and would therefore lead to peaks penetrating the baseline rather than giving slow recovery as observed .

5.6 : STUDIES OF SOME TYPICAL CHLOROFLUOROCARBONS

In this section three typical chlorofluorocarbons were examined for their affects on the three sensors . The three compounds used were :

1. ARCTON 11 (CFCl_3) Trichlorofluoromethane ;
2. ARCTON 12 (CF_2Cl_2) Difluorodichloromethane ;
3. ARCTON 22 (CF_2HCl) Difluorochloromethane .

As in the above experiments each compound was injected five times at the three heater voltages on the three different sensors . Again the equilibration times for changes in sensor voltage or between different sensors were kept to the values used in section 5.4 . Sampling of these three compounds was slightly more complicated than before since both Arctons 12 and 22 were gases . The two compounds (supplied by I.C.I. Research and Technology Centre , Runcorn . Cheshire . U.K.) were obtained in pressurised cylinders (2l) , however the pressure and volume of gas obtained was not suitable for us with the gas blender system used earlier in this work . also unfortunately the sensitivity of the sensors to the compounds was not high and it was therefore difficult to use the 3l flask described above . The sampling system used although probably not very accurate appeared to be consistent over the five injections made at each concentration . Sampling of the gases was achieved by connecting a thin rubber tube (1 cm i.d.) to the outlet of the gas cylinder , the gas was then allowed to flow down the tube at a flow rate of approximately 100ml min^{-1} (measured by a rotameter) after 2 minutes of flushing a 1ml gas sampling syringe ("pressurelok")

was inserted into the tube and a sample taken . Dilution of the sample taken was achieved by expelling some of the sample from the syringe and refilling with air from the laboratory . The third compound also presented a sampling problem since its boiling point (24°C) was very close to room temperature and as such it was difficult to obtain an accurate liquid sample since the vacuum created in drawing the sample into the syringe caused vaporisation leading to bubble formation in the syringe . This problem was circumvented by taking samples of the headspace using the gas sampling syringe . The result of the sampling problems was that it was considered unwise to compare quantitatively the response factors obtained , although it was felt that at least a qualitative response order for the three compounds could be determined .

The results obtained from this study are shown in Tables 5.6.1 and 5.6.2 which contain the skew factor and response data respectively . Taking Table 5.6.1 first , it is observed that significant problems were encountered with these compounds : Firstly it is observed that for both TGS 813 and 831 , with Arctons 11 and 12 , baseline penetration at the higher voltages was obtained ; Secondly that recovery times for the TGS 822 were longer than 10 minutes .

Figure 5.6.1 shows an example of a typical chromatogram obtained from a TGS 813 at 6.75V with Arcton 11 . It is observed from figure 5.6.1 that a normal "rise" side of the peak occurred , however during the recovery phase the conductivity was observed to decrease rapidly to a level below that of the normal baseline

TABLE 5.6.1 : SKEW FACTORS OBTAINED FROM THE ANALYSIS
OF THREE TYPICAL CHLOROFLUOROCARBONS

COMPOUND	SENSOR	SKEW FACTORS		
		HEATER VOLTAGE		
		5.75V	6.25V	6.75V
ARCTON 11	TGS 813	16.2	2.1*	0.66*
	TGS 831	7.6	9.2	3.8
	TGS 822	NR	NR	NR
ARCTON 12	TGS 813	3.5	6.5	1.5
	TGS 831	10.8	13.3	5.9
	TGS 822	NR	NR	NR
ARCTON 22	TGS 813	3.5	2.8	2.6
	TGS 831	3.1	2.3	1.7
	TGS 822	10.9	7.0	9.0

* - BASELINE PENETRATION ON RECOVERY OBSERVED
 NR - NO RECOVERY FOR 10 MINUTES AFTER INITIAL BASELINE
 DISTURBANCE

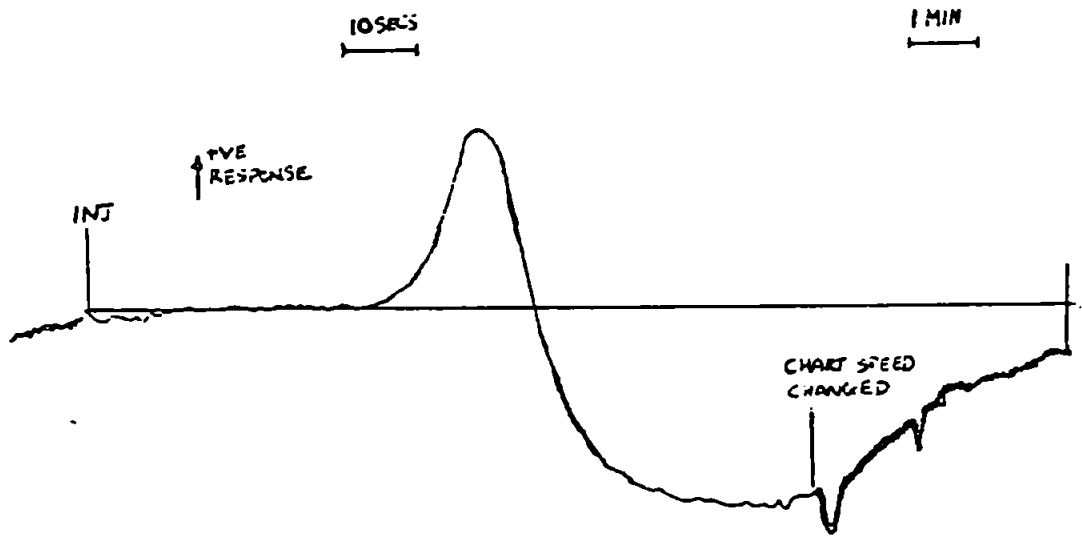
TABLE 5.6.2 : PEAK HEIGHT RESPONSES OBTAINED FROM
THREE TYPICAL CHLOROFLUOROCARBONS

COMPOUND	SENSOR	RESPONSE (mV ug ⁻¹)		
		HEATER VOLTAGE		
		5.75V	6.25V	6.75V
ARCTON 11	TGS 813	90	75	20
	TGS 831	6	5	4
	TGS 822	100	100	40
ARCTON 12	TGS 813	160	120	65
	TGS 831	8	7	7
	TGS 822	98	50	60
ARCTON 22	TGS 813	1700	2100	840
	TGS 831	35	25	15
	TGS 822	500	400	400

FIGURE 5.6.1 :

A TYPICAL CHROMTOGRAM DEMONSTRATING THE RESPONSE OF A TGS 813

TO ARCTON 11 WHEN OPERATED AT A HEATER VOLTAGE OF 6.75V



and then to gradually recover . This affect is further exemplified by the skew factor obtained at 6.75V of less than unity . Baseline penetration such as that observed is almost certainly due to the formation of surface species more electron withdrawing than the oxygen species normally present on the tin oxide surface . It is therefore probable that the penetration of the baseline is directly linked with the presence of fluorine in the two analytes due to its electronegativity . One factor which tends to betray this is that baseline penetration was not observed with Arcton 22 . However , although fluorine is present in Arcton 22 it is noted that the compound also contains hydrogen and it is probably the large response obtained from this moiety that overrides the mechanism causing baseline penetration . This view is supported by the fact that penetration was not observed with high sample concentrations . This indicates that the number of sites available for the mechanism causing penetration was limited . The result of this is that the affect would not have been observed at the lower chart recorder sensitivity required in order to measure the larger positive peaks .

As in section 5.4 a TGS 822 was left to recover fully after exposure to each compound that had caused severe tailing , again the sensor recovered to its baseline . In contrast with the previous section however the time taken to recover was longer by at least a factor of three .

Table 5.6.2 contains the peak height response data obtained for the three chlorofluorocarbons . The response is quoted in millivolts per microgram injected . The injection size (mass) has been calculated from the injected volumes assuming room

temperature of 25°C . pressure 760 torr . ideal gas behaviour and gaseous state for Arcton 11 . It was stated above that the values expressed should not be used quantitatively but should give at least an estimate of relative sensitivity between the three compounds . The table suggests that (as might be expected) Arcton 22 gives the higher response , this is undoubtedly due to the presence of the hydrogen atom in the molecule . The remaining two compounds (Arctons 11 and 12) show no real difference although if the various assumptions made above are considered it would be possible to say that the estimates for Arcton 11 are perhaps conservative and that consequently Arcton 12 is least active , giving in order of sensitivity :

Arcton 22 > Arcton 11 > Arcton 12

The order of sensitivity described above is consistent with the data from the earlier parts of this chapter in which it was observed that sensitivity decreases as the halogen group is ascended . It was encouraging to note that the order was consistent for all three sensors , and further that similar heater voltage dependence was observed to that found previously .

5.7 : CONCLUSIONS AND DISCUSSION

In this chapter a large amount of data has been obtained on the factors which affect both the peak shape and response from Taguchi sensors when exposed to halogen containing compounds . In this section it is attempted to bring the data obtained together in order to make some general comments about the mechanisms operating and their implications .

Perhaps the first point to make has been preempted by the choice of syntax in the paragraph above . Almost from the first experiment in this chapter it has been apparent that the range of affects between sensors , between heater voltages on the same sensor and between analytes , that have been observed would be difficult if not impossible to ascribe to one particular interaction . It seems clear that there are numerous ways in which the conductivity of tin oxide can be modulated . There are however a number of general principles that can be seen .

The parameter that has been observed , throughout this work , to have a major affect upon both sensitivity and peak shape is heater voltage . It is perhaps not surprising that heater voltage is so important as it is the voltage across the integral heating element of the TGS which controls the temperature of the tin oxide surface . The observed affects of heater voltage have been that peaks become more symmetrical as voltage (temperature) increases , and that there is an optimum voltage (temperature) for each different analyte . Furthermore from the results in this chapter it is apparent that for optimum peak shape sensitivity must be sacrificed . So far in this work it has not been necessary to know the temperature of the tin

oxide surface . However , in this chapter three different sensors have been compared with heater voltage a major parameter in the comparison . Since it is actually the temperature which is the critical factor affecting the rates of reactions occurring on the respective surfaces it is preferable that temperatures of the different sensor surfaces be available for comparison .

Surface temperatures of the three sensors were measured by attaching small thermocouples to the tin oxide bead . The temperature range involved (normally quoted as between 300 and 500°C) meant that a platinum/rhodium thermocouple was suitable for use . The thermocouples were attached to the tin oxide surfaces using a ceramic car exhaust repair paste . Errors arising from insulation of the thermocouple and oxide surface were kept to a minimum by using the ceramic paste sparingly . In order that the temperatures measured were representative of those of the sensors under the conditions used in the experiments the measurements were made with the sensor in the detector housing with the carrier and make-up gases flowing . Measurements of temperature were recorded for voltages applied between 0 and 7.5V , the usual time periods for equilibration were employed . Also the relative conductivities of the sensors were recorded at each voltage . Figures 5.7.1 to 5.7.3 show the heater voltage / temperature relationships and Table 5.7.1 shows the temperatures at the three voltages of interest 5.75 , 6.25 and 6.75V . It can be seen from Table 5.7.1 that there were only small differences between the temperatures measured , however these differences do tend to reflect the observed differences in sensitivity and peak shape between the sensors . The TGS 822 gave the lowest

FIGURE 5.7.1

THE SURFACE TEMPERATURE DEPENDENCE OF
A TGS 813 ON APPLIED HEATER VOLTAGE

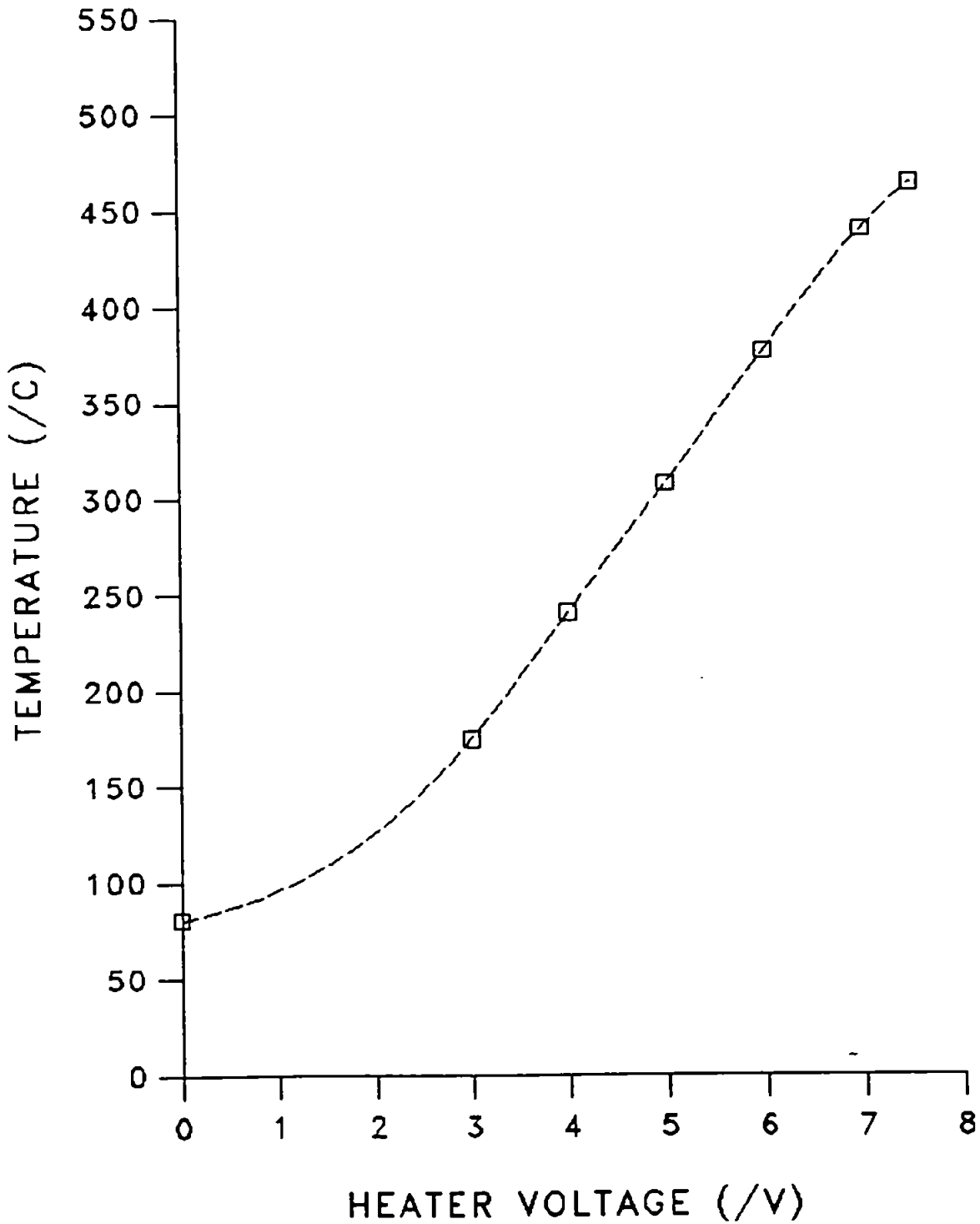


FIGURE 5.7.2

THE SURFACE TEMPERATURE DEPENDENCE OF
A TGS 822 ON APPLIED HEATER VOLTAGE

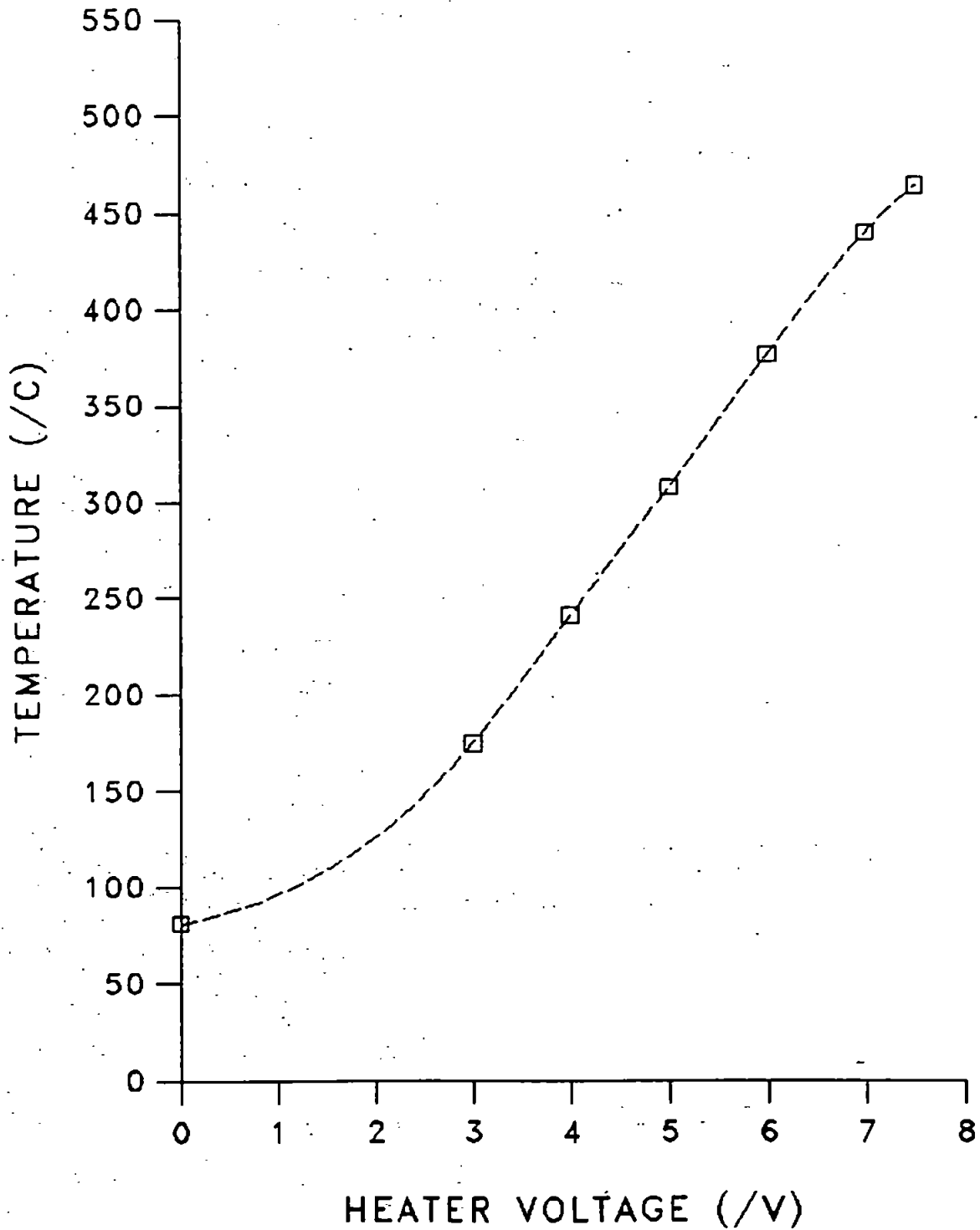


FIGURE 5.7.3

THE SURFACE TEMPERATURE DEPENDENCE OF
A TGS 831 ON THE APPLIED HEATER VOLTAGE

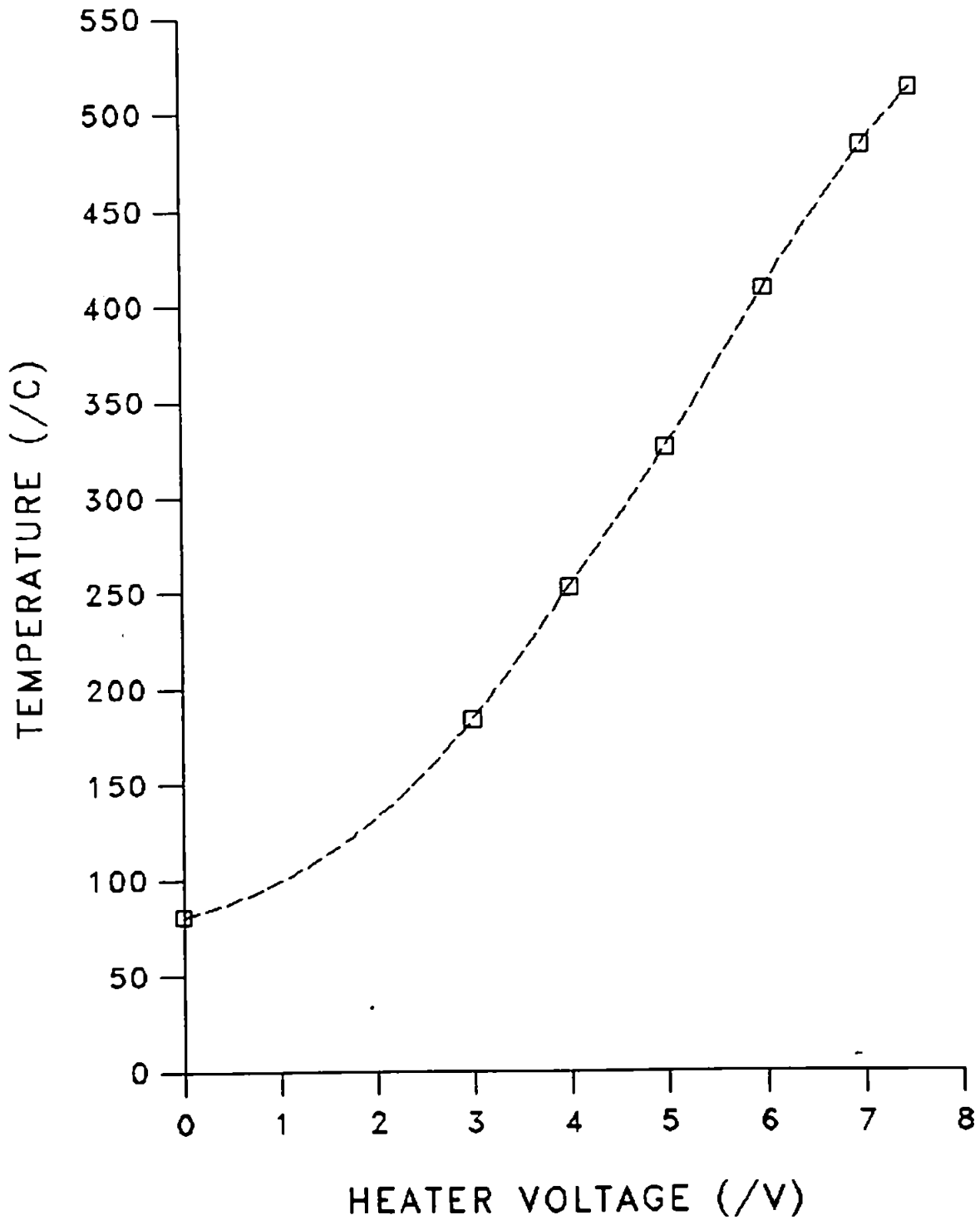


TABLE 5.7.1 : SURFACE TEMPERATURES FOR THE THREE SENSORS
AT THE HEATER VOLTAGES STUDIED

SENSOR	TEMPERATURE (/°C)		
TGS 813	358	390	424
TGS 831	388	424	462
TGS 822	340	370	402

temperatures reflecting the higher sensitivity and peak shape observed .the TGS 831 gave the highest temperatures reflecting its lower observed sensitivity . Although there are some significant differences between the temperatures it is unlikely that they could account for all of the observed affects . for example , the temperature difference between the TGS 822 and 813 is similar to that between TGS 813 and 831 yet the observed differences in performance between the TGS 822 and 813 are much greater than between TGS 813 and 831 . It therefore seems likely that although the temperatures were different other factors must have contributed to the differences in performance , temperature however remains the single greatest factor affecting sensor performance .

One of the other factors that could affect performance is the band gap of the tin oxide . Since the band gap is the energy difference between the conduction and valence bands the relative ease with which electrons can be promoted to carry current must at least affect sensitivity . From measurements of the chromatographic baseline at two different voltages it was possible to estimate the relative band gaps for the three sensors which , with respect to the TGS 813 were :

- TGS 813 1
- TGS 831 1.2
- TGS 822 1.3

It appeared that the TGS 813 had the lowest band gap and the TGS 822 the highest although all three were very similar . This was to be expected since all three sensors are the

same basic tin oxide . the intrinsic semiconductor . however it was necessary to know that this was actually true in this case . Despite the similarity of the results some links with the sensitivity / temperature data can be found . For example it was shown that the thermal band gap for the TGS 831 was larger than that for the TGS 813 . this fact coupled with the observed higher surface temperature suggests that sensitivity should be reduced for the TGS 831 - the result found in the majority of cases studied previously . However , and similar to the thermal considerations . the band gaps cannot account for the much greater sensitivity to the TGS 822 either.

The next consideration was the physical nature of the sensor surface . it was thought that the roughness of the sensor surface or rather the surface area of the tin oxide would have an affect on sensitivity . since there would be more sites for analyte gases to react with . Possibly the best way to have shown this would have been surface area determination by the nitrogen B.E.T. technique . The problem with this method was that only the tin oxide surface was of interest and since the tin oxide was physically inseparable from the ceramic former it would have been impossible to have confident in the specific areas determined for the three sensors . The alternative to surface area determination was microscopic inspection of the sensor surface . This was achieved using scanning electron microscopy (S.E.M.) . figures 5.7.4 - 5.7.6 show micrographs of the surfaces of the three sensors . The figures show that the surface of the TGS 822 was much rougher than either of the other two sensors used and that

FIGURE 5.7.4 :

ELECTRON MICROGRAPH OF THE SURFACE OF A TGS 813

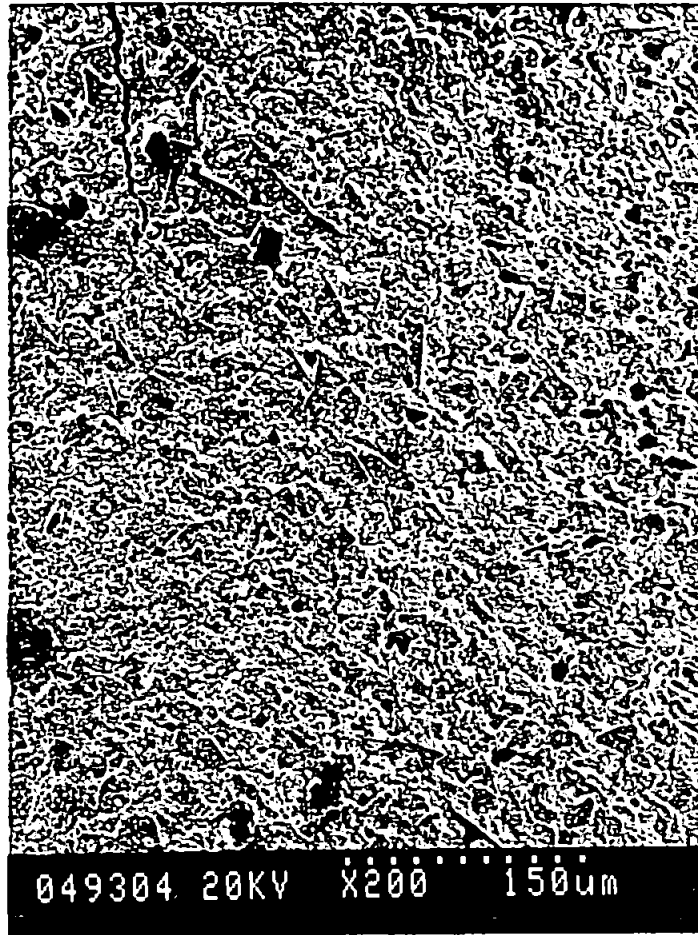


FIGURE 5.7.5 :
ELECTRON MICROGRAPH OF THE SURFACE OF A TGS 822

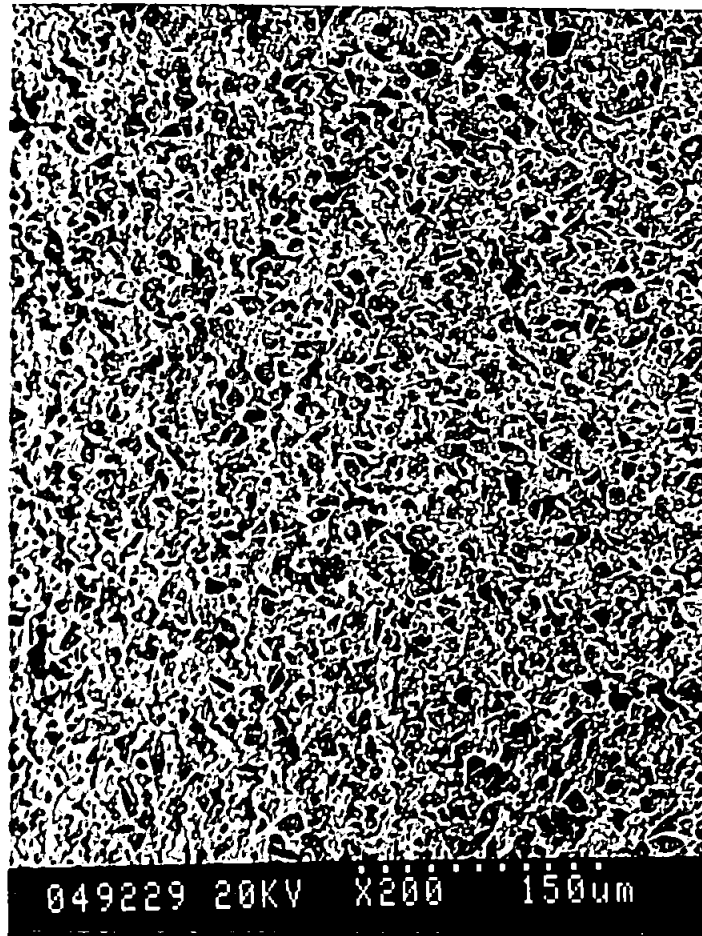


FIGURE 5.7.6 :

ELECTRON MICROGRAPH OF THE SURFACE OF A TGS 831



it could therefore be expected that the surface area of the tin oxide of the TGS 822 would be greater than the others and consequently it would be reasonable to expect greater response from the TGS 822 with respect to the other sensors . It is possible that this increased surface area for the TGS 822 could be responsible for its greater sensitivity especially when considered in conjunction with the lower surface temperature determined for the TGS 822 . It is unlikely however , that the physical nature of the tin oxide surface could account for the peak shape differences observed between the sensors .

The next parameter affecting sensor performance is the chemical environment in which the reactions take place . The chemical environment of a sensor basically depends upon three factors . firstly , the composition of the analytes secondly the type and number of active sites on the sensor surface and thirdly the composition of the carrier and make-up gases . For the purposes of this discussion however the third factor can be ignored since it was kept constant throughout these experiments . Also the first of these factors has been shown throughout this work to influence the sensitivity and peak shape and is shown by differing performance of a particular sensor to a range of different analytes and has been discussed earlier . It is the second of the chemical effects that is the most interesting at this time . The fact that the thermal and physical differences between the sensors could not fully account for the observed differences in performance meant that the chemical differences between the sensors must be significant . From the considerations above it is probable that the sensor chemistry has most of its

influence over the peak shape rather than the sensitivity although it cannot be discounted that other types of analyte may have different dependence on the various parameters . However the discussion here is of the affects on the performance of a sensor by its composition . It has already been mentioned that the Taguchi sensors differ by the type and amount of activating agents added to the tin oxide . In order that the affect of the various agents can be assessed it was necessary to know the composition of each sensor . There was a similar problem here to that above whereby it was difficult to separate the tin oxide from its substrate and that therefore no confidence was possible in the results from normal analysis . Also it was undesirable to destroy sensors unnecessarily , for these reasons a non-destructive technique was used for the analysis which could also be concentrated on the tin oxide portion of the sensor . The technique employed was energy dispersive x-ray fluorescence analysis using the electron beam from a S.E.M. as the excitation source . Figures 5.7.7 - 5.7.9 show the spectra obtained from the three sensors . The three spectra unfortunately showed no real differences between the sensors . It was possible that the reason for this was that the concentrations of the additives were below the limits of detection of the instrument . This was in fact quite likely since energy dispersive X-ray analysis in a SEM is not very sensitive having limits of detection at about the 1% level . Also most reports e.g. [70] indicate that the additives are present at concentrations of 3% or less . In order to overcome this problem it was necessary to attempt to separate the tin oxide layer from the remainder of the sensor . This was

FIGURE 5.7.7 :
ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTRUM OBTAINED FOR A
TGS 813 USING A SCANNING ELECTRON MICROSCOPE

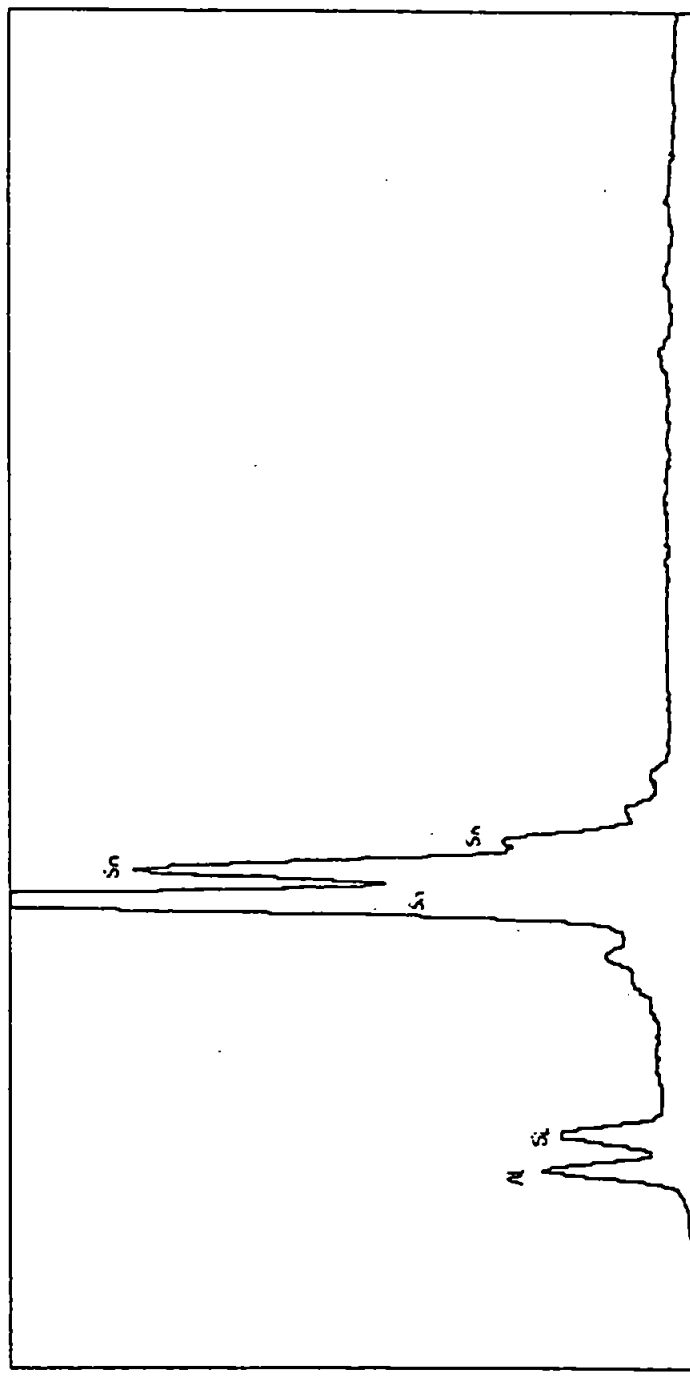


FIGURE 5.7.8 :

ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTRUM OBTAINED FOR A
TGS 831 USING A SCANNING ELECTRON MICROSCOPE

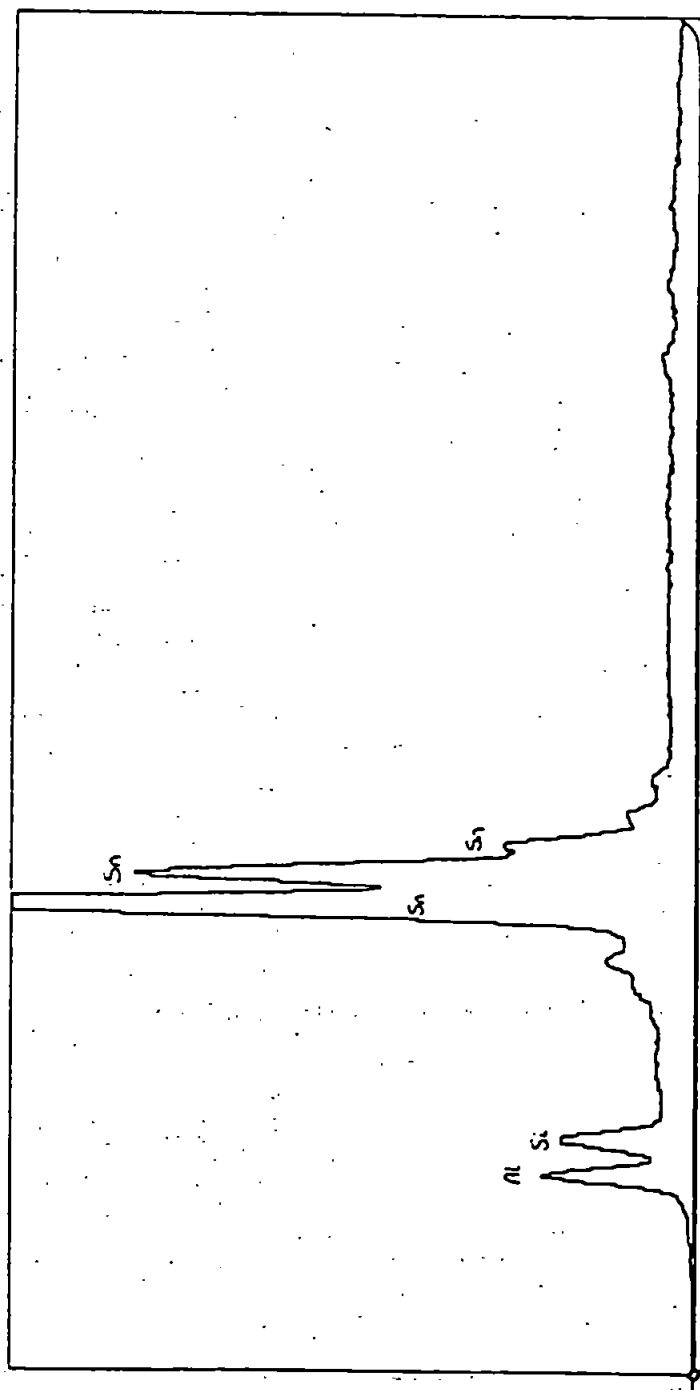
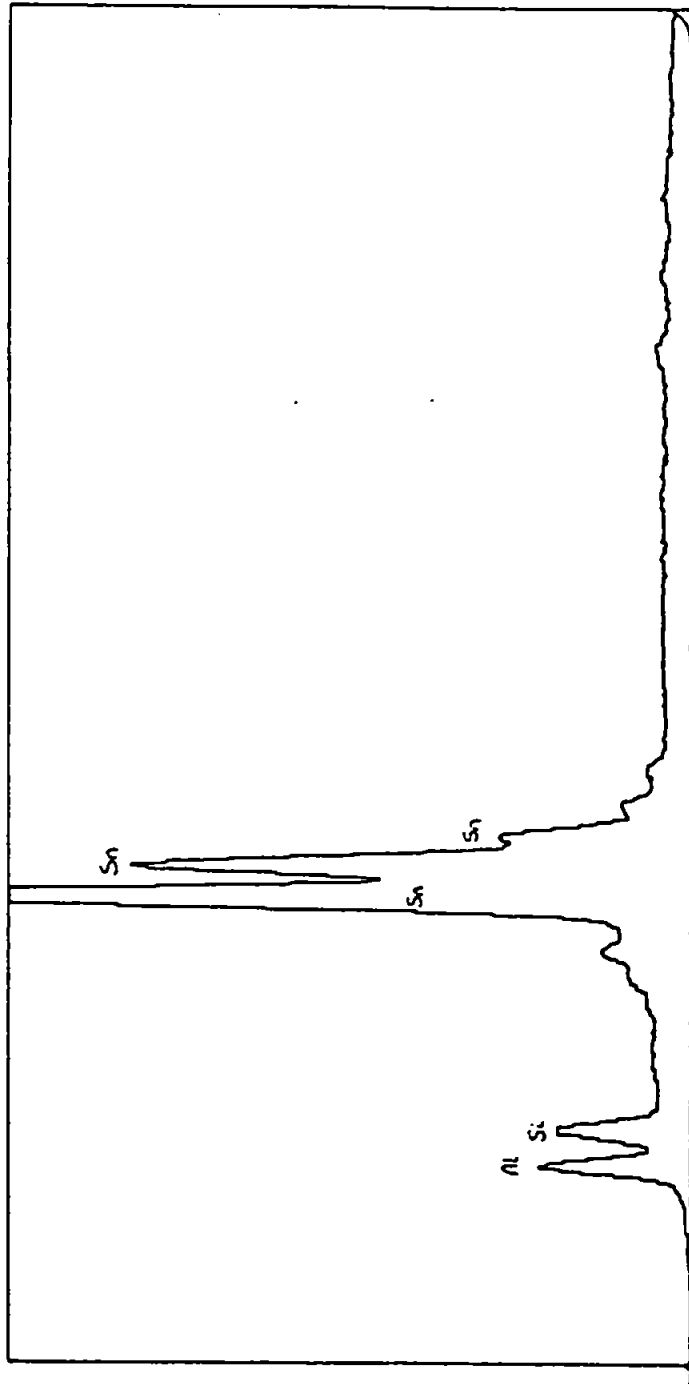


FIGURE 5.7.9 :
ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTRUM OBTAINED FOR A
TGS 822 USING A SCANNING ELECTRON MICROSCOPE



achieved by carefully scraping the oxide layer from the bead , a 10 mg sample was obtained from each of the three sensors and subsequently analysed by wavelength dispersive X-ray fluorescence spectrometry at the laboratories of ICI chemicals and polymers division . This is a more sensitive technique due to the greater excitation radiation flux obtainable . The concentrations were determined using the semiquantitative facility of the instrument . As had been expected it proved impossible to separate the tin oxide layer from the cylindrical former and contacts and the results obtained (Table 5.7.2) appeared to show that the platinum levels were equal in each of the sensors . It was observed from the table however that the two major components :

tin from the oxide layer and

aluminium from the cylindrical sensor former

differed between the three analyses . It was then recognised that the levels should be compared to the tin and aluminium (as oxides) within each analysis . Tables 5.7.3 and 5.7.4 show the calculated percentages relative to tin and aluminium oxide respectively . Table 5.7.3 was very useful since it was expected that the cylindrical former would be of constant composition with respect to the three sensors and that therefore elements from the former would have similar concentrations in this table allowing them to be eliminated from the consideration of the differences in response shown by the three sensors . The elements that could be considered part of the former were those whose concentrations did not differ by more than 0.1% from the average which included : Cl ; Ca ; Ni ; As and Zr . Also it is known that the

TABLE 5.7.2 : WAVELENGTH DISPERSIVE X-RAY FLUORESCENCE
ANALYSIS OF THE THREE SENSORS STUDIED

ELEMENT	CONCENTRATION (/%)		
	TGS 813	TGS 822	TGS 831
Al	16.90	22.38	16.74
Si	1.20	1.31	1.09
Cl	0.05	0.06	0.07
Ca	0.41	0.54	0.44
Ni	0.05	0.05	0.05
Cu	0.36	0.35	0.33
Zn	0.07	0.00	0.11
As	0.07	0.07	0.05
Zr	0.36	0.42	0.39
Sn	25.90	15.68	17.36
Pt	0.45	0.50	0.48
Au	3.05	3.21	2.40

TABLE 5.7.3 : WAVELENGTH DISPERSIVE X-RAY FLUORESCENCE
ANALYSIS OF THE THREE SENSORS STUDIED CALCULATED
WITH RESPECT TO TIN OXIDE

ELEMENT	CONCENTRATION (/%)		
	TGS 813	TGS 822	TGS 831
Al	51.2	112.0	76.0
Si	3.6	6.6	5.0
Cl	0.2	0.3	0.3
Ca	1.2	2.7	2.0
Ni	0.2	0.3	0.2
Cu	1.1	1.8	1.5
Zn	0.2	0.0	0.5
As	0.2	0.4	0.2
Zr	1.1	2.1	1.3
Pt	1.4	2.5	2.2
Au	9.2	16.1	10.9

TABLE 5.7.4 : WAVELENGTH DISPERSIVE X-RAY FLUORESCENCE
ANALYSIS OF THE THREE SENSORS STUDIED CALCULATED
WITH RESPECT TO ALUMINIUM OXIDE

ELEMENT	CONCENTRATION (/%)		
	TGS 813	TGS 822	TGS 831
Si	3.8	3.1	3.5
Cl	0.2	0.1	0.2
Ca	1.3	1.3	1.4
Ni	0.2	0.1	0.2
Cu	1.1	0.8	1.0
Zn	0.2	0.0	0.4
As	0.2	0.2	0.2
Zr	1.1	1.0	0.9
Sn	81.0	37.0	55.0
Pt	1.4	1.2	1.5
Au	9.5	7.6	7.6

electrodes under the tin oxide layer are gold allowing it to be eliminated . The remaining elements were :

- silicon ;
- copper ;
- zinc ;
- platinum .

The silicon present in the tin oxide is most probably due to the addition of a binder to improve the mechanical strength and stability of the sensor . The use of binders such as tetraethyl orthosilicate on the properties of tin oxide has been described by Yasunaga et.al. [71] . Its mode of operation is to bind the tin oxide particles to each other and the alumina substrate by the formation of interparticulate siloxane bridges . It is also mentioned that the binder could increase the activity of the sensor to hydrogen and Harrison and Maunders [45] observed large increases in surface hydroxyl species upon the exposure of ethane and ethene to a mixed tin oxide silica surface . It is therefore probable that the presence of silica has an affect on the sensitivity of the sensors possibly by abstracting hydrogen atoms from adsorbing species thus activating the molecules to further oxidation . The higher sensitivity of the TGS 822 might therefore (at least partially) be attributed to its higher silicon/silica content . The similarity between the TGS 813 and TGS 831 sensitivities however cannot be explained by the silicon/silica content and might be due to the other additives present .

Conflicting reports can be found in the literature regarding the properties of copper as an additive . Harrison and Thornton

observed that copper improved the adsorption of carbon monoxide on tin oxide [41] which would lead to enhanced sensitivity . they also noted that copper preferentially adsorbed CO to NO . Yamazoe . Kurokawa and Seiyama [70] however . have carried out experiments on a number of possible metal/metal oxide additives , including copper . by measuring their responses to carbon monoxide , hydrogen , methane and propane . They noted that copper had only small affects on the sensitivity and/or temperature optimum . The presence of copper in these sensors does suggest that it modifies the sensor sensitivity or selectivity to at least some degree and may well have a larger affect on other gases . The higher copper concentration in the TGS 822 suggests that copper may be added to improve the sensitivity/selectivity of sensors to more polar compounds such as the alcohols and in the case of the TGS 831 the chlorofluorocarbons . Again the differing concentrations do not explain the results obtained for the TGS 813 and TGS 831 . Unfortunately the authors of ref.[70] did not report the recovery characteristics of the powders they studied . It cannot therefore be discounted that copper is present as an agent to improve the recovery characteristics of sensors , although it is unlikely since the best recovery (lowest skew factor) was obtained from the TGS 813 which contained the least copper . Also the possible synergy between different additives cannot be discounted from the previous studies .

Perhaps the most interesting feature of the results obtained for zinc concentration is its absence from the TGS 822 which contains the greatest concentrations of the other additives

identified . Also the zinc concentration is significantly lower than for the other additives in both TGS 813 and 831 . Lastly zinc oxide is itself a semiconducting metal oxide sensitive to reducing gases [3] although lower temperatures are required for tin oxide sensors hence their greater usage [29] . The actual affect of zinc on the sensing properties is unclear but from its absence from the TGS 822 it may be that it has a detrimental affect on hydroxyl type adsorption adversely affecting alcohol sensitivity , but improving the sensor resistance to humidity variations .

Finally it was observed that platinum was present in all three sensors . The work of Yamazoe et.al. [70] showed considerable improvements in CO and H₂ sensitivity and reductions in optimum surface temperature for methane and propane with hydrogen showing the greatest differences . The action of platinum on other compounds may be similar to that described previously where the platinum performs the activation of analytes to oxidation by abstraction of hydrogen atoms and subsequent spillover to the oxidising tin oxide .

The general points to be made about the levels of the additives is that all were in the range indicative of response modulation via interaction at the surface with the additive . Additive concentrations were observed to be highest for the TGS 822 and lowest in the TGS 813 . The indications of this were that sensitivity was the factor most affected by surface additives . This was certainly true for the TGS 822 , however in a number of cases the TGS 813 proved more sensitive than the TGS 831 one possible explanation of this was that the TGS 813 used here was

that used in the earlier work . Yasunaga et.al. [71] noted the increased sensitivity of tin oxide sensors with time and it could be this that was responsible for the greater response observed . Finally it is observed that increasing amounts of additives might be associated with higher skew factors obviously detrimental to the use of Taguchi gas sensors for gas chromatographic detection .

CHAPTER 6 : DISCUSSION , CONCLUSIONS AND SUGGESTIONS FOR
FURTHER WORK

Discussion of the results obtained from each experiment has been attempted throughout this work . The purpose of this chapter is to bring together the sometimes contrary explanations to present a unified view in the light of all of the data produced and then to critically assess the contribution of this work . The areas in need of further study to elucidate more fully the potential and mechanisms of the sensors in their application as gas chromatographic detectors will be identified .

Perhaps the very first point that must be made is that all of this work has utilised the commercially available Taguchi gas sensors . The major usage of Taguchi gas sensors to date has been in systems for the rapid detection of hazardous gas concentrations i.e. in an alarm-type application and according to Yasunaga , Sunahara and Ihokura [71] more than 12 million gas detectors using a TGS are employed in Japan alone . It follows that the major development of tin oxide sensors has been biased towards reducing the time required to produce an alarm signal . Little attention has been paid to the recovery characteristics as this is unnecessary in the alarm application . In this work it has been shown many times that the major limiting factor to the application of the sensors to gas chromatographic detection lies in the relatively long recovery times required for many compounds . Chapter 5 of this work was mostly concerned with the peak shapes obtained from a number of compounds on some different Taguchi sensors . The chemical differences in sensor composition did not appear to be based on improving the recovery characteristics nor is it likely that they are from the reasons given above . Also the differences in the physical appearance of

the sensors are unlikely to have been the result of attempting to improve sensor recovery . Despite these considerations differences in the recovery characteristics of the three sensors were observed and were consistent . the TGS 813 showing the best recovery and the TGS 822 the worst . The probable reason for poor recovery was first implied in chapter 4 . where the three phases of a gaseous sensing interaction were described . It appears from the work done here that the recovery of the sensor relies upon both the desorption of the oxidised analyte species and subsequent re-oxidation of the sensor by atmospheric oxygen . The relatively massive oxygen concentrations in the sensor's atmosphere make it unlikely that the recovery process is limited by the re-oxidation reaction(s) although one possibility is that a proportion of the surface reactions involve loss of lattice oxygen atoms which are replaced more slowly than chemisorbed reactive oxygen species . This however , appears unlikely due to the different skew factors observed for different compounds . Therefore the more probable explanations lie in the desorption processes for the oxidised analyte . This view is enforced by considering the skew factors obtained for different compounds e.g. halogen containing compounds exhibited poor recovery whilst acceptable recovery was observed for compounds such as the alkanes . alcohols . aldehydes and ketones . In fact the similarity in recovery observed for the latter compounds reinforced the hypothesis that recovery was determined by the desorption of the analyte . since it was likely that all four types of compounds were chemisorbed to the surface by a similar chemisorption interaction such as a carboxylate . The desorption

of the oxidised analytes could be expected to be similar .
therefore leading to the observation of similar recovery rates .
Recently , Guest has observed acceptable recovery after
halocarbon interaction using a thin film tin oxide sensor [72]
and supposed that the improvement was due to the more uniform
surface (less rough) obtained in the fabrication process . This
view tends to support the hypothesis that the smoother surface of
the TGS 813 could contribute to its faster recovery . The reasons
for the observed improvement in recovery are unclear although it
might be possible that the presence of "inkpot" pore types in the
Taguchi sensors lead to diffusion limitation of the desorption
processes for a proportion of the chemisorbed analytes .

Whichever of the mechanisms described above are responsible
for the observed chromatographic peak shapes it seems clear that
any further work on the application of tin oxide gas sensors to
gas chromatographic detection should include an extensive study
of peak tailing . If , as it seems at present , the very rough
surfaces of the Taguchi type sensors severely affects their
recovery then work should be concentrated upon finding the
optimum configuration for chromatographic detection . One way of
achieving this would be to try to reduce the surface roughness of
the conventional TGS by reducing the amount of volatile agents
included in the tin oxide paste (usually waxes [20]) or by
modifying the drying and sintering process so that the
volatilisation of the organic proceeds slowly and does not
produce inkpot type pores . A third way to do this would be to
heat the paste using the sensor's integral heater leaving the
outer surface coolest and hence reducing the chances of inkpot

formation . These methods , however , do not appear practical in terms of the large volume of production required and it would appear that other methods might be better . Another possibility would be to use screen printing technology to produce "thick film" sensors , this technique would allow incorporation of the activators but may adversely affect the range of sensor designs obtainable requiring a flat surface for the printing . At least from a response point of view it might be desirable to move to thin film sensors in order to maintain an advantageous surface area to volume ratio whilst reducing the surface roughness . The problems that could be encountered with thin films would probably lie with the addition of the activators . This problem could however be outweighed by the flexibility allowed in terms of sensor design .

The development of thin film technology by the semiconductor industry in recent years might allow the Taguchi sensor to be effectively "turned inside out" i.e. produce a thin film of tin oxide on the inside of a capillary tube . The resultant detector would have a number of advantages over the current configuration including the possibility of greater sensitivity due to lower dilution of the column effluent in the detector housing , lower dead volume in the detector housing and reduced thermal mass . Since it is envisaged that the major usage of tin oxide GC detectors would be based around portable chromatographs this latter point is highly significant . The reduced thermal mass would require less power to heat the tin oxide surface which would mean that one of the most problematical areas of portability , the weight of the batteries required for power ,

would be eased . Also this design would reduce the space required for the detector possibly enabling the integration of the detector and column heating systems .

The application of and design of compact , low cost and lightweight portable gas chromatographs based on tin oxide detectors is another major area for further work . This study has shown the high potential of the tin oxide semiconductor sensor in chromatographic detection and , as described above , there is excellent potential for the sensor to be developed for use in portable GC systems .

The work of this study has gone some way towards more fully understanding the nature and factors affecting the response of tin oxide sensors to reducing gases . However as discussed in chapter 5 it is still not possible to formulate a complete description of the response mechanism . It appears from this work that there could be a number of different interactions of gases with tin oxide surfaces . This work does however seem to suggest that the principal mode of interaction is via chemisorbed oxygen species . This theory is not new , but the work carried out here adds to the considerable weight of evidence supporting the theory . Also this work has presented evidence suggesting that compounds such as alkanes , alcohols , aldehydes and ketones may bind to tin oxide surfaces in very similar ways on the basis of the response and recovery characteristics . Differences in the response of tin oxide to compounds such as these could be explained in terms of the ease with which the proposed carboxylate-type link is formed . Further work with compounds such as ethers , esters and carboxylic acids might support this

hypothesis .

The results from the XRF analyses of the three "different" sensors , the TGS 813 , 831 and 822 were quite surprising . It had been expected that these sensors would have had different types of activators added because they were supposedly sensitive to different types of compounds . It is probable that all of the activators present were found in the analysis due to the relatively high concentrations (1-3%) required in order that they are effective . In fact the only conclusion to be drawn from this work regarding the affect of surface activators is that they appear to adversely affect sensor recovery . This conclusion , drawn from comparison of the TGS 831 , 813 and 822 , is enlightening since it suggests that the activators cause stronger interaction between analyte and sensor surface . Furthermore there is a suggestion that reducing the concentration of the activators may improve the recovery of the sensors . The affect of such an action on the sensitivity of the sensor is not easily predicted since the results from the TGS 822 , which showed an increase of approximately a factor of 10 over the TGS 813 and TGS 831 , suggested that activators did affect sensitivity , whilst the results from the TGS 831 and TGS 813 , which showed very little difference in sensitivity for similar differences in impurity concentrations , suggested that the activators did not markedly affect sensitivity . The main problem in this is that the extent to which the surface roughness (and hence surface area) can affect sensitivity . It may be that the latter is more significant and that the suggested move to the higher surface area to volume ratio thin film sensors would improve the

"intrinsic" sensitivity of the tin oxide . The omission of the activators may then be less important and possibly facilitate better peak shapes . There is certainly more work to be done in this area . Comparison of the sensitivities and recovery rates between sensors with different surface types and additives would yield useful information about the optimal design of a tin oxide based gas chromatographic detector .

One of the few observed disadvantages of the tin oxide detectors used in this work was the linear calibration range . Typically for the hydrocarbons this was between three and four orders of magnitude . This does not compare very favourably with the standard FID detector which normally is linear over at least seven orders of magnitude , although it is similar to other detectors such as the electron capture detector which is linear over approximately 4 orders of magnitude [74] . This is another point which could be addressed in a further study of tin oxide detectors . The linear range of the sensor ultimately depends upon the number of active sites available for sensing and there would therefore be an upper limit which could be reached when the concentration of the analyte in the detector housing caused all of the available active sites to be occupied . One possible way of overcoming this problem could be the use of a variable make-up gas flow at the detector , which , as shown in this work , reduces the response of the sensor . The advantage of this is that it is considerably more simple than attempting to dilute gaseous samples prior to injection . Another suggestion would be to increase the non-stoichiometry of the tin oxide as this is the factor controlling the number of active sites . A possible way to

achieve this would depend upon the method for manufacture of the sensors . For example , a thin film device can be made using the technique of reactive radio frequency (RF) sputtering in which tin is sputtered into an oxygen atmosphere and the resultant oxide deposited on a suitable substrate [75] . Altering the oxygen concentration in the atmosphere could change the stoichiometry of the oxide produced . By this method Chang [75] was able to prepare a device with a tin:oxygen ratio of approximately 1:1.85 this is lower than the 1:1.95 usually obtained by hydrolysis of tin chloride [68] .

In summary this work , has demonstrated the excellent potential of a gas chromatographic detector based on a tin oxide semiconductor . It is envisaged that the major application of such a detector would lie in a portable chromatograph where the low power consumption , light weight , simplicity , sensitivity and ruggedness could be fully exploited . Also some information has been gained about the mechanism of action of tin oxide sensors . The phenomena observed could all be explained in terms of interactions of the analyte gas with surface oxygen species . Two potential problems with the application of the sensor as a GC detector have been identified namely poor recovery and relatively short linear calibration . However there is reason to suggest that these potential problems could be alleviated by the optimisation of the sensor design with respect to chromatographic detection .

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CONFIGURATION AND OPTIMIZATION OF SEMICONDUCTOR GAS SENSORS AS GAS CHROMATOGRAPHIC DETECTORS

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SUMMARY

A tin oxide, gas-sensitive semiconductor sensor was configured as a gas chromatographic detector and its performance was optimized. Two sensor housings were compared but little difference was found in performance. The flow rate and temperature of the column and the internal heater voltage of the sensor affected both the sensitivity and peak shape. The temperature of the sensor surface was the most critical parameter. Optimal conditions for the gas chromatographic detection of a mixture of alkanes (C_1 - C_6) and hydrogen were identified by using the simplex technique. The detection limit for hydrogen was improved by a factor of five to 20 ppb (v/v), illustrating the value of optimization and the excellent sensitivity of the detector. It is concluded that semiconductor gas sensors offer significant advantages as gas chromatographic detectors for the determination of reducing gases.

The sensitivity of some semiconductors to gases has been known since the early 1950s [1]. The term gas-sensitive semiconductor generally refers to a semiconductor which exhibits a change in surface conductivity according to the gaseous composition of its surrounding atmosphere. It was not until the early 1960s [2], however, that the phenomenon began to be applied to the sensing of gases. Since that time, considerable development has taken place and currently a range of possible sensors is being studied.

Metal oxide semiconductors have been shown to have many desirable sensor properties including low cost, chemical stability, fast reproducible response and sensitivity. Many metal oxides have been studied including zinc [2], titanium [3], zirconium [4] and tin [5] oxides. Of these, zinc and tin oxides are perhaps the best characterized and the latter is the most promising. The use of tin oxide as a gas-sensitive semiconductor was noted as early as 1966 by Seiyama and Kagawa [6]. Following this work, Taguchi [5,7,8], amongst others, filed a series of patents covering the development of tin oxide sensors from

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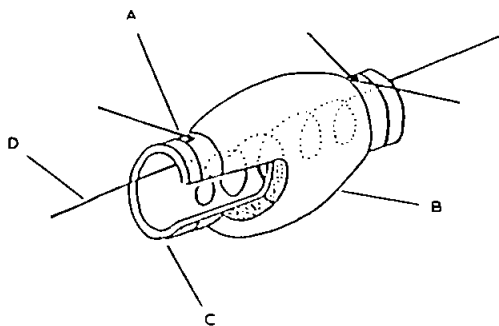


Fig. 1. Design of the gas sensor used: A, electrode; B, sintered tin oxide; C, alumina tube; D, heater filament.

the early thin-film intrinsic devices to what is essentially the current sensor conformation. The configuration of the current commercial sensors is shown in Fig. 1. A layer of tin oxide is sintered around a cylindrical ceramic former containing a resistive heater filament, and electrodes interleaved between the ceramic former and the oxide layer allow the measurement of sensor conductivity. A certain degree of selectivity can be imparted to the sensor by the inclusion of precious metal catalysts such as platinum and palladium [9]. Despite these additions, semiconductor gas sensors remain disappointingly unselective and this limits their analytical application.

Gas chromatography (GC) is one of the most widely applied analytical techniques. The availability of various detectors with differing capabilities considerably enhances its versatility. In general, unselective detectors are preferred, as the selectivity is imparted by the separation process on the column. Given the poor selectivity but excellent sensitivity of semiconductor gas sensors, it would seem logical to use such a sensor as a detector for GC, thus combining the selectivity of GC with the sensitivity of semiconductor gas sensors. Several reports of semiconductor sensors as detectors for GC have appeared, e.g., the work of the gas sensor semiconductor group in Shanghai [10], Mallard et al. [11], Spencer [12], Christman and Hamilton [13], Wynne [14], Rowley et al. [15] and Rowley [16].

Their low cost, excellent sensitivity, low power consumption, simple electronic requirements, poison resistance, compactness and suitability for intrinsically safe devices make semiconductor gas sensors extremely attractive candidates as gas chromatographic detectors, especially in isolated or hazardous environments. The aims of this work were to optimize the configuration and operating conditions for using a semiconductor gas sensor as a detector for GC.

EXPERIMENTAL

Tin oxide semiconductor sensors, manufactured by Figaro Engineering (Senbanishi, Minoo City, Osaka 562, Japan), were obtained from Envin (En-

TABLE 1

Range of Taguchi gas sensors

Type	Features
TGS 109	High sensitivity to hydrocarbon gases
TGS 812	High sensitivity to toxic gases and organic solvent vapours
TGS 813	High sensitivity to hydrogen and hydrocarbon gases; low sensitivity to alcohol and carbon monoxide
TGS 711	High sensitivity to carbon monoxide
TGS 712d	High sensitivity to carbon monoxide; low sensitivity to hydrogen
TGS 814d	High sensitivity to ammonia; low sensitivity to hydrogen
TGS 816	High sensitivity to hydrocarbon gases; low sensitivity to carbon monoxide and alcohols; special ceramic housing
TGS 817	High sensitivity to organic solvent vapours; low sensitivity to toxic gases (e.g., CO)
TGS 911	High sensitivity to hydrocarbon gases

vironmental; Wantage, Oxon). Table 1 shows the range of these gas sensors available together with their suggested applications in fixed gas alarm systems. One of these, TGS 813, was selected for study as a potential CG detector.

Two electrical circuits had to be designed for the sensor. The first circuit was a stable voltage supply for the internal resistive heating element. The manufacturer suggested that a supply voltage of 5.00 ± 0.2 V should be used for the sensor in a static gas environment. Initial experiments showed that it was desirable to be able to vary the voltage with good precision; a high degree of stability was also required. Accordingly the heater supply was controlled with a laboratory bench power supply unit (L-30-2, Farnell; RS Components, Corby, Northants), of specification $0-15 \pm 0.02$ V, 0-3A, which was stable to within ± 1 mV at 5 V. The second circuit required was that for signal measurement. Both Wynne [14] and Rowley [16] studied a range of possible circuits. The circuit used here (Fig. 2) was similar to the d.c. load resistor/operational amplifier circuit described by Rowley [16] with only very minor improvements (e.g., the use of better quality components and the decoupling of the power supply).

The sensor was configured for use with a conventional gas chromatograph (PU 4550, Philips Scientific). Two possible designs for the sensor housing were studied. Figure 3A shows the housing developed by Rowley [16] and Fig. 3B shows the modified flame ionization detector (FID), compatible with the gas chromatograph, used for most of this study.

The chromatographic column used throughout was a $1 \text{ m} \times 4 \text{ mm}$ (i.d.) glass column packed with 60/80 mesh activated alumina (Philips Scientific). This provided adequate separations of low-molecular-weight gases without resort to

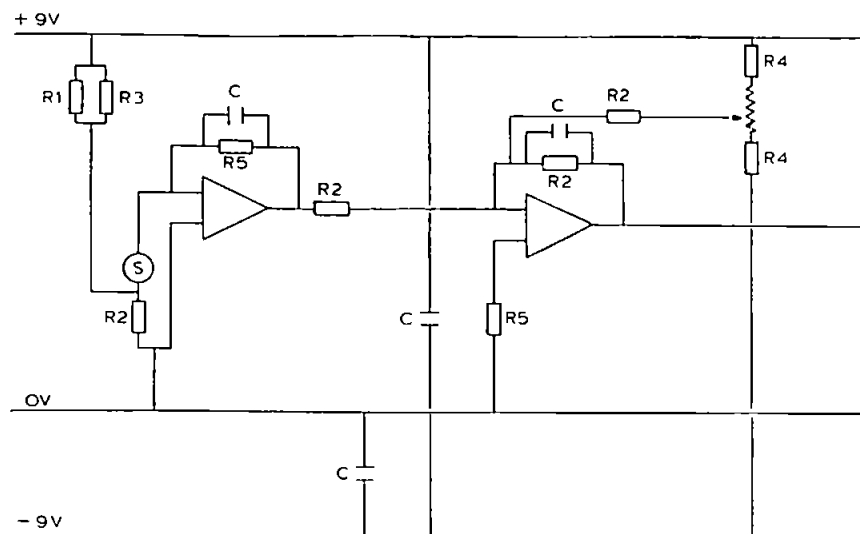


Fig. 2. Sensor signal output circuit: S, gas sensor; C, 0.15- μ F capacitors; R, resistors (R1 = 550 k Ω , R2 = 100 k Ω , R3 = 20 k Ω , R4 = 4.7 k Ω , R5 = 2.2 k Ω).

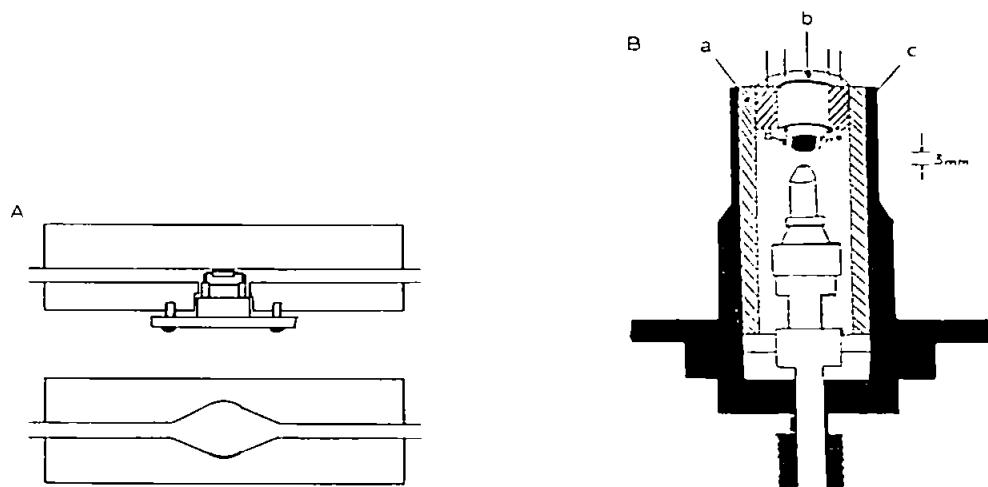


Fig. 3. (A) Initial sensor housing. (B) Modified housing based on flame-ionization detector (FID) housing: (a) PTFE insert; (b) Taguchi gas sensor; (c) FID body.

the use of sub-ambient column temperatures. In all cases, air was used as the carrier gas because this oxidizes the surface of the tin oxide after reduction by the analyte gases [8]. The alumina column chosen was compatible with the use of air as carrier gas. Samples (1 cm³ in all cases) were introduced from a conventional 6-port gas-sampling valve (Philips Scientific).

Gas samples were prepared from standard gas mixtures (P.K. Morgan,

Chatham, Kent). Mixtures of the standards were prepared by using a gas blender (Type 852-V5S; Signal Instrument Corp., Camberley, Surrey); mixing was done volumetrically in a temperature-controlled microporous block in a continuously variable ratio of 0.01–100%. In all cases, air was used as the diluent gas. The three gas standards used were 1% (v/v) hydrogen in air, 5% (v/v) methane in air, and 1000 ppm (v/v) methane, ethane, propane, isobutane, n-butane and n-pentane in air.

RESULTS AND DISCUSSION

Preliminary experiments

Reproducibility is a fundamental requirement of any analytical detection system. The reproducibility of the system with the housing shown in Fig. 3B was therefore tested. The following chromatographic conditions were used: detector flow $40 \text{ cm}^3 \text{ min}^{-1}$, column temperature 70°C , and heater voltage 5.0 V. The reproducibility was measured by calculating the percentage relative standard deviation (RSD) of the response to ten separate injections of a 50 ppm (v/v) hydrogen sample. The response was the peak area as determined by a computing integrator (Hewlett-Packard 3390A). The reproducibility of the system was found to be 3.5%, which lies within the generally accepted limit of 5% for useable instrument reproducibility.

The sensor manufacturers state that up to 24 V can be applied across the circuit for measuring the conductivity, although no lower limit was suggested. A voltage of 24 V across the electrodes in the sensor would cause a large electric field to be set up, which could affect the response characteristics of the sensor. For this reason, it was decided that a low voltage be used. To investigate the effect on response of the circuit at low voltages, the circuit voltage was varied between 0 and 6 V in 1-V steps, and responses to injections of 500 ppm (v/v) methane were measured. The peak height increased linearly with increasing sensor voltage; the equation of the line was $y = 20x$ over the range 0–6 V, which demonstrates that the sensor voltage did not affect the response of the sensor to reducing gases. The slope depended on the gain of the circuit; increasing the circuit voltage gave a higher response but increased the noise proportionally.

It has been well established [14,16] that the heater voltage, or more specifically the surface temperature of the sensor, has a great effect on the response. The surface temperature affects two important response parameters, the peak height and the peak shape. The peaks from initial evaluations showed considerable tailing associated with the detector response and it was therefore necessary to study closely the effect of the heater voltage on both peak height and skewness (tailing). In this experiment, a chromatographic column temperature of 70°C and a detector flow rate of $40 \text{ cm}^3 \text{ min}^{-1}$ were used. The heater voltage was raised from 4.0 V to 7.0 V and then decreased to 4.0 V. After each

change in voltage, the system was left to equilibrate for 30 min. The responses to ten injections of 50 ppm (v/v) hydrogen were measured at each point. Peak shapes were recorded on a chart recorder; peak height was measured by constructing the baseline under the peak and measuring the perpendicular distance to the peak maximum. The parameter used to define peak shape was the 90% skew factor, defined as the distance from the peak centre line to 90% baseline recovery divided by the distance from the peak centre line to 10% rise from baseline.

Figure 4 shows the results of the study of heater voltage. No hysteresis in response or skew factor was observed. Figure 4A clearly shows the existence of an optimum value for the response to hydrogen. This can be explained in terms of the response mechanism proposed by Taguchi [8]. The non-stoichiometry of tin oxide, which is predominantly SnO_2 but includes some SnO , means that electrons from SnO could be promoted to the conduction band and so there are lightly held electrons in the semiconductor bulk. Electronegative species such as oxygen are attracted to the surface of the tin oxide and become chemisorbed as active species (e.g., O^- , O_2^- and O_2^-). The effect of altering the temperature could be as follows. Increasing the temperature of the tin oxide increases the number of electrons in the conduction band. Hence, there will be proportionally more active sites on the semiconductor surface until saturation is achieved,

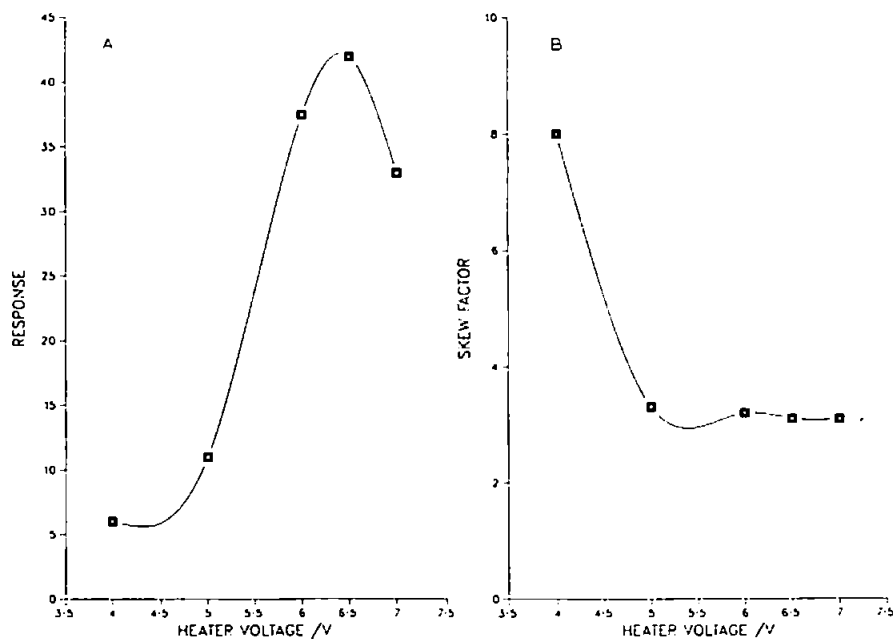


Fig. 4. Variations in response to 50 ppm (v/v) hydrogen with heater voltage: (A) peak height; (B) skew factor.

at which stage the number of active sites is equal to the number of SnO molecules when the semiconductor is at absolute zero temperature. Also with increasing temperature the reactivity of the chemisorbed oxygen species increases; but further increases in temperature beyond saturation point weaken the chemisorption bonds, leading to probable loss of the active species from the surface. Obviously, the response maximum would occur at a point where there is a balance between the reactivity and number of chemisorbed oxygen species.

Figure 4B shows the effect of heater voltage on the skew factor. The graph shows two distinct regions: at low heater voltages, baseline recovery improves rapidly with increasing temperature, after a certain point (5 V with the gas flows used in this experiment) little further improvement is observed. This phenomenon may also be discussed in terms of the above response mechanism. The recovery of baseline is thought to occur by the reaction of oxygen from the carrier gas with the tin oxide to replace the reactive oxygen species removed by the action of the reducing gas. If so, the rapid improvement phase could be due to an increase in the rate of the chemisorption reaction. The rate of recovery at higher temperatures could then be limited by the loss of chemisorbed oxygen species through thermal dissociation.

Selection of housing geometry for the sensor

Two types of housing for the sensor have been studied. Rowley [16] used the housing design shown in Fig. 3A, but it appeared to suffer from instability of the chromatographic baseline with variations in ambient temperature. A way to overcome this problem was to incorporate the housing into the thermally stable environment of the GC detector. This was achieved by modification of the housing for the flame ionization detector of the gas chromatograph used (Fig. 3B). In order to compare the effectiveness of these two different housing geometries, several detector parameters, namely peak-height response, skew factor, width at half height, and rise time (time taken from initial baseline disturbance to peak maximum), were measured. The chromatographic baselines were observed to be different, indicating different sensor operating temperatures caused by the differing flow characteristics of the housings. Preliminary experiments had indicated the critical dependence of the sensor response on temperature; for this reason, the heater voltage used for the new housing was adjusted so that the baseline and hence the temperature of the bead was equal to that obtained for the initial housing. Table 2 shows that there was very little difference in response between the two housings; the initial housing was slightly superior in some respects. However, because of the better thermal stability and compatibility of the modified FID housing, this was adopted for the hydrogen studies. The initial housing was used in the hydrocarbon work described.

TABLE 2

Comparison of the two housings studied^a

Housing	Initial	Modified FID
Response (cm)	20.8 ± 0.7	20.1 ± 0.5
Rise time (s)	2.3 ± 0.3	2.1 ± 0.2
Width at half height (s)	2.6 ± 0.3	2.8 ± 0.2
Skew factor	1.6 ± 0.3	2.0 ± 0.4

^aThe data are the means and three times the standard deviations for ten injections of 50 ppm (v/v) hydrogen under the chromatographic conditions given in the Experimental section.

TABLE 3

Boundary conditions for the simplex optimization of the response to the C₁-C₅ alkanes and optimum conditions located

Parameter	Boundary conditions	Optimum condition
Carrier gas flow rate ^a (cm ³ min ⁻¹)	7.5-40	21
Detector flow rate (cm ³ min ⁻¹)	10-30	122
Column temperature (°C)	50-200	27
Heater voltage (V)	4-7	5.99

^aConverted from pressures (see text).

Simplex optimization of the operating conditions

Several parameters (heater voltage, gas flow rates and column temperature) were observed to affect the performance of the detector. Because these parameters affect both chromatography and detector response, it was necessary to use a rigorous optimization technique to select the conditions for best detector performance whilst retaining adequate chromatographic separation. The variable step-size simplex algorithm [17] has proven to be successful in optimizing systems with inter-related parameters, e.g., inductively-coupled plasma optimization [18], and was selected for use in this study. Two optimizations were examined.

Optimization for the alkanes. The first optimization was that for the analysis of C₁-C₅ alkanes. A mixture containing equal concentrations of methane, ethane, propane, n-butane, isobutane and n-pentane was used. There are two important considerations in simplex optimization. The first is the choice of the boundary conditions for the search; the boundaries must allow sufficient range for the optimum to be found but must be such that sets of conditions that could cause permanent damage to instrumentation are rejected. The boundary conditions selected for this optimization are given in Table 3. The second important factor is the figure of merit which defines the optimum that

will be achieved; its importance is clearly shown in this optimization. A figure of merit which gave excellent sensitivity might not allow adequate chromatographic separation. In this case, it was decided that the figure of merit would be peak height response but sets of conditions which did not give baseline separation of isobutane and n-butane were rejected. The peak height response for ethane was selected, because preliminary experiments had indicated that it was representative of the other alkanes, and produced a very sharp peak.

It was recognised that there might be a different optimal gas flow rate for the column and the detector. A post-column splitter was therefore used; the precise flow rate through the detector was controlled by splitting the column effluent and venting to atmosphere. Because the maximum detector flow rate attainable at any time was limited by the prevailing flow of carrier gas through the column, the vernier settings of the needle valve controlling the split (rather than the actual flow rates) were used in the simplex calculation; likewise, the carrier gas pressure was used. The optimization was terminated when five (the number of variables + 1) sets of conditions gave figures of merit which did not differ by more than 5% relative from the mean average value of each variable.

To confirm the success of the optimization, univariate searches were made. The conditions were set at the centroid value of each of the variables; then each individual variable was incremented through the operating range while the other variables were held constant. The resultant detector responses are shown in Fig. 5. The centroid values of the final vertices represent the optimum determined by the simplex. These values are given in Table 3.

The final vertices for response to carrier gas pressure (Fig. 5A) did not extend over the region of maximum peak height and would therefore appear not to have located this optimum. However, when considered in conjunction with the univariate search of detector gas flow (Fig. 5B), it can be seen that there is considerable advantage in having a higher flow rate through the detector. This factor probably caused discrepancy between centroid value and apparent optimal response. Response to the univariate search of column temperature (Fig. 5C) showed that the simplex had identified a small shoulder on the general upward trend. The optimization had been prevented from moving to higher column temperatures because at such temperatures there was inadequate separation of the butane isomers. The simplex indicated an optimum value for heater voltage on the edge of a plateau of response (Fig. 5D). A feature of the simplex technique is a tendency to terminate on the edges of plateaux, rather than at the centre, because there is insufficient increase in response to be gained in moving further to the centre of the plateau. This means that while the simplex identified the optimum of 5.99 V, there are operational advantages to be gained by moving to the centre of the plateau (6.25 V). Operation in this zone reduced the effects of surface temperature fluctuations caused by minor variations in column temperature, carrier pressure or heater voltage supply.

Optimization for hydrogen. The second simplex optimization was concerned

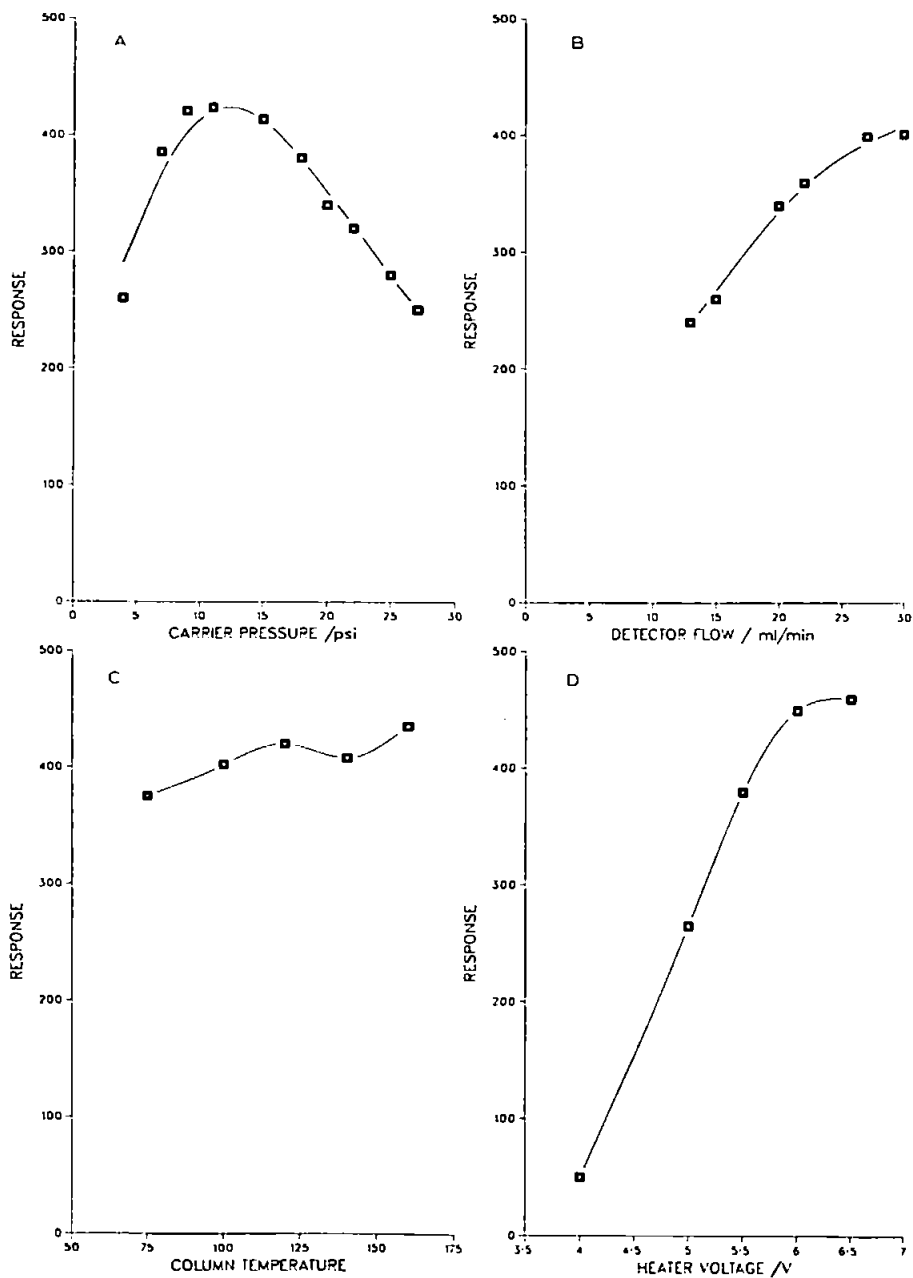


Fig. 5. Variation in ethane peak height about the simplex optimum condition for the separation and detection of the C_1 - C_5 alkanes: (A) with carrier gas pressure (13.8 psi = 21 ml min⁻¹); (B) with detector gas flow rate; (C) with column temperature (°C); (D) with heater voltage.

with maximization of the detector response to hydrogen. The FID-type housing was used. The practice of rejecting vertices used in the previous optimization was considered to be too subjective, and was replaced by incorporating the retention time of the hydrogen peak into the figure of merit. Also, more emphasis was placed on the peak shape obtained and so the skew factor was introduced. The requirement was therefore to maximize peak height and retention time whilst minimizing the skew factor. The figure of merit to be maximized was therefore defined as: (peak height \times retention time/skew factor).

The figure of merit for each set of conditions selected by the simplex algorithm was calculated from the mean values of measurements from three injections of 50 ppm (v/v) hydrogen. The splitter was not used in this case because it was considered that the simplex algorithm would compensate for the detector flow requirement by using the interdependence of the column flow rate and column temperature. Thus, only three variables were involved in the optimization. The boundary conditions selected are shown in Table 4. As before, at least 30 min was allowed for equilibration after changes in conditions. In this optimization, the iteration was terminated when four sets of conditions gave figures of merit within 8% of the mean of the individual figures of merit. The precision of this evaluation was adversely affected by the additional terms, in particular the skew factor. The centroid was then calculated by using a weighted mean, which was considered to give a closer approximation to the true optimum. The weighted mean, \bar{x} , was calculated from:

$$\bar{x} = [(V_1^1 \times F_1) + (V_2^1 \times F_2) + (V_3^1 \times F_3) + (V_4^1 \times F_4)] / [F_1 + F_2 + F_3 + F_4]$$

where F_1, F_2, F_3 and F_4 are the four figures of merit and V_1^1, V_2^1, V_3^1 and V_4^1 are the four values of variable 1.

The optimum conditions located are given in Table 4. The importance of these conditions was then investigated by univariate searches as before. The results of the univariate searches are illustrated in Fig. 6. It is evident that in each case the simplex algorithm has selected either the maximum point for the

TABLE 4

Boundary conditions for the simplex optimization of the response to hydrogen and optimum conditions located

Parameter	Boundary conditions	Optimum condition
Carrier gas flow rate* (cm ³ min ⁻¹)	15-45	30.5
Column temperature (°C)	30-150	120
Heater voltage (V)	3.5-7.0	4.85

*Converted from pressures (see text).

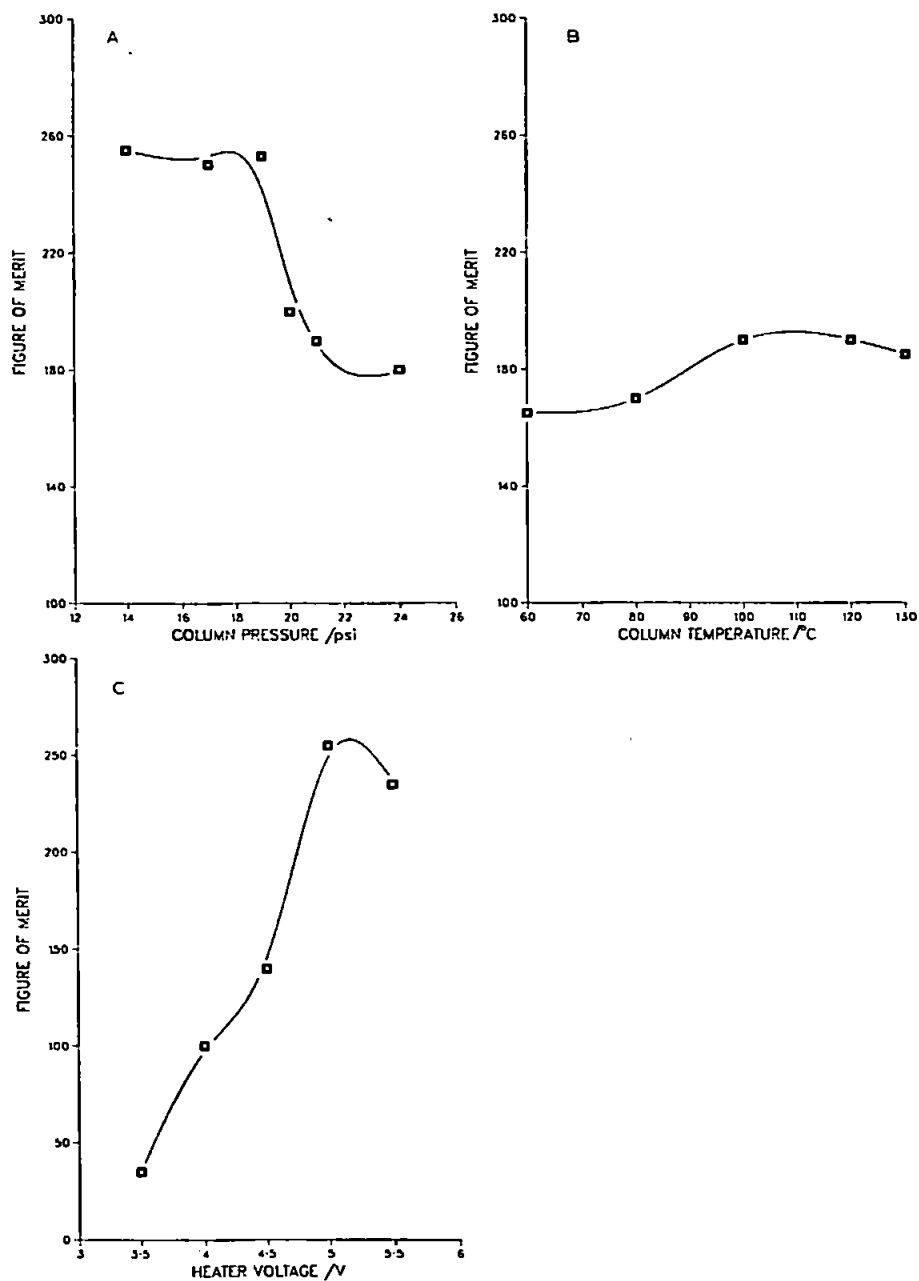


Fig. 6. Variation of simplex figure of merit about the optimum conditions for hydrogen detection: (A) with column pressure (20 psi = 30.5 ml min⁻¹); (B) with column temperature; (C) with heater voltage.

variable or the edge of a plateau of maximum response as noted previously. Evidence of the improved response was obtained by evaluating the limit of detection for hydrogen. The limits of detection quoted were calculated from measurements of the signal-to-noise ratio (3σ) for 21 ppm (v/v) hydrogen in air (the lowest concentration obtainable with the gas blender and hydrogen standard) and as such are only approximate. Before the simplex optimization, the limit of detection was 100 ppb (v/v) but this was reduced to 20 ppb (v/v).

Response to C_1 - C_5 alkanes

The study was extended to the light alkanes in order to assess the effect of chemical composition of the analyte gas on detector response. Obviously, the first parameter to be investigated was the effect of heater voltages on the responses to each of the C_1 - C_5 alkanes. Peak height measurements were used because the variations in skew factor observed in preliminary experiments would have produced unrepresentative peak area data. The chromatographic

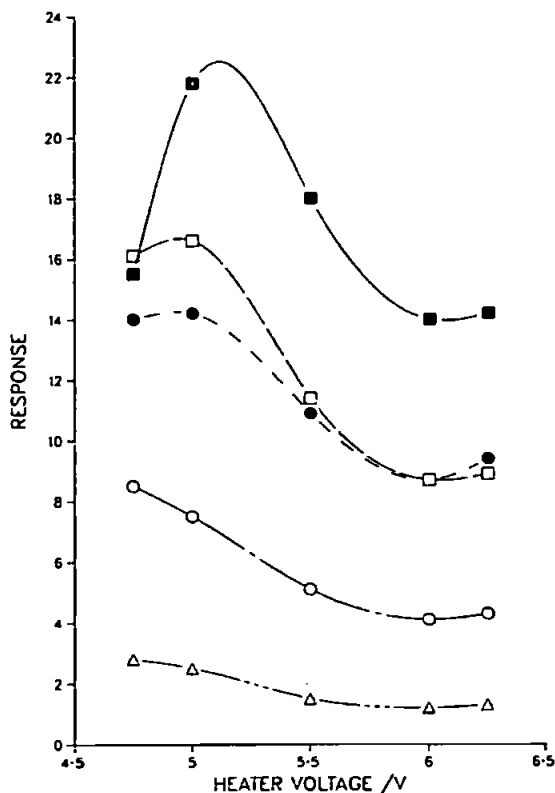


Fig. 7. Heater voltage/peak height response profiles for the C_1 - C_5 alkanes: (■) methane; (□) ethane; (●) propane; (○) butane; (△) pentane.

conditions were a carrier gas flow rate of $55 \text{ cm}^3 \text{ min}^{-1}$ and a column temperature of 100°C . The heater voltage was varied between 4.75 and 6.25 V; as before, at least 30 min was allowed for equilibration. In each case, the peak heights given are the averages from ten injections measured with the computing integrator. Figure 7 shows the response profiles for the C_1 - C_5 alkanes. It is clear that there are discrete heater voltage optima for each of the five gases. This result again supports the theory of Taguchi [8] that there is a balance between the number and activity of reactive oxygen species. The oxygen species are charged and there is thus probably a charged intermediate in the reaction between the alkane and the oxygen. The higher-molecular-weight alkanes would be better able to stabilise the charged intermediate, leading to the requirement of a lower heater voltage for maximum response. Further support for this theory comes from the fact that the heater voltage maximum tends to a limit as the molecular weight increases presumably because there will be proportionally less improvement in intermediate stabilisation. This is fortunate, as it would be impracticable to change the heater voltage for each analyte gas.

Conclusion

The results illustrate the potential of semiconductor gas sensors for gas chromatographic detection. These inexpensive, simple and compact, yet sensitive, detectors offer real advantages for the determination of reducing gases such as hydrogen, and the light alkanes, and they are readily interfaced to existing GC hardware.

This study also illustrates the real improvements in detectability that can be gained by using rigorous optimization procedures for interdependent variables. A five-fold improvement in detection limit for the determination of hydrogen by GC was obtained by using simplex optimization. The detection limit of 20 ppb (v/v) for hydrogen illustrates the excellent sensitivity of this semiconductor gas sensor.

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