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WYNNE, Arnold.

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A thesis entitled

AN ASSESSMENT OF THE PERFORMANCE OF SEMICONDUCTOR GAS SENSORS AS GAS CHROMATOGRAPHIC DETECTORS

presented by

ARNOLD WYNNE B.Sc., C.Eng., M.I.Min.E.,

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Department of Chemistry,	Collaborating Establishment
Sheffield City Polytechnic,	National Coal Board East Midlands Regional Scientific Department,
Pond Street,	Mansfield Woodhouse,
SHEFFIELD SI IWB	Nottinghamshire NG19 8AB

DECLARATION

I declare (i) that while registered as a candidate for the degree of Master of Philosophy that I have not been a registered candidate for another award of the CNAA or of a University during the research programme, and

(ii) no material contained in this Thesis has been used in any other submission for an academic award

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Abstract of a thesis by Arnold Wynne, entitled:

"An assessment of the performance of semiconductor gas sensors as gas chromatographic detectors"

Four types of commercially available n-type semiconductor gas sensors (three tin oxide types: T.G.S.711, T.G.S.812 and International Sensor Technology methane sensor, and one ferric oxide type: Matsushita L.P.G. sensor) were evaluated as gas chromatographic detectors in the G.C. analysis of mine air samples. A 1.5 meter x 4 millimeter stainless steel column packed with active carbon type 208C (60-72 B.S.mesh) at 40°C was used to separate hydrogen, carbon monoxide and methane using purified air as carrier gas. Optimum operating conditions for the T.G.S.711 sensor: heater voltage 6.5 volts DC, purified air carrier gas at 20 cm^{3}minute^{-1} and operational amplifer circuitry (LM 741), provided good sensitivity and acceptable peak symmetry, although some skewness of peaks was still evident.

A preliminary assessment of the performance of these sensors was made for the analysis of some lower hydrocarbon gases (C_1-C_3) using a 1.5 meter x 4 millimeter stainless steel column packed with activated alumina (60-80 B.S.mesh) at 60°C.

Lower limits of detection achieved were 0.002 ppm for hydrogen and 0.01 ppm for other gases, with a useful working range up to 100 ppm. An interesting finding was that carrier gases containing lower levels of oxygen gave an enhanced response in terms of peak height. It was concluded that the use of semiconductor gas sensors as G.C. detectors provided a simple and convenient method of assessing the characteristics of this type of sensor and might be employed to elucidate the mechanism of response, which is still in question.

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1 INTRODUCTION

1.1 Background to the present work.

Gas sensitive semiconductor devices form part of a relatively small but significant group of substances within the important field of semiconductor technology which has developed within the last thirty years or so. The work reported here was begun in the East Midlands Regional Laboratory of the National Coal Board and originated in an investigation into the possible usefulness of Taguchi semiconductor gas sensors in the coal mining industry.(1) The gases of main interest to Safety Engineers in coal mines are carbon monoxide and methane. Carbon monoxide provides an index of spontaneous combustion and methane is the main constituent of firedamp which can create a major explosion hazard in some underground coal mines. There was an additional interest in hydrogen during the mid-nineteen seventies and the suggestion that the hydrogen/carbon monoxide ratio might provide some indication of temperature during incidents involving spontaneous heatings.(2)

Carbon monoxide is usually present in the ventilating air in coal mines at the level of 1-10 parts per million by volume (ppm) and hydrogen is commonly present at approximately one half the concentration of carbon monoxide. Methane may be present in the mine ventilating air at almost any concentration e.g. in the event of an outburst of firedamp, but seldom exceeds 1.25% (v/v) i.e. approximately 25% of the lower explosive limit with air which is the level above which all electrical supplies to a district in an underground coal mine must be cut off.

Increased rates of coal extraction, associated with mechanised coal faces, result in increased rates of firedamp emission and require compensating increases in the flow-rates ofthe ventilating air, to ensure that the concentration levels of firedamp do not exceed the statutory limits. As a result of the increasing quantities of ventilating air required by modern techniques of mining it is often necessary to measure concentrations of carbon monoxide, in the range 1-10 ppm, with standard deviations as low as 10%.

Some of the lower hydrocarbon gases, ethane, propane, butanes and pentanes are also normally present in coal mines as minor constituents, totalling approximately five per cent of the methane, as firedamp. Ethene and ethyne are not normally present but may appear, with increasing concentrations of carbon monoxide and hydrogen, as products of spontaneous combustion.

Routine mine air analyses are required to determine the concentrations of carbon monoxide and methane, which are usually present together in the same sample. A considerable effort was therefore made in the original investigation(1), by varying the operating conditions of the semiconductor gas sensors, to see if they could be made to respond selectively to either of these gases in the presence of the other.

The five types of Taguchi gas sensors (T.G.S.) which were tested as part of a joint inter-laboratory exercise(3) were models T.G.S.102, T.G.S.105, T.G.S.109, T.G.S.202 and T.G.S.308. It had been claimed by the manufacturer that the T.G.S.102 and T.G.S.202 gave an enhanced response to carbon monoxide and, for that reason, the East Midlands Regional Laboratory of the National Coal Board(1) elected to examine these two types of sensor.

It was found that, at higher operating temperatures, the sensors gave an enhanced response to methane, whilst an increase in response to carbon monoxide was obtained at lower operating temperatures. The response to hydrogen was less affected by the temperature of the sensor. The response time of the sensor also increased markedly at lower operating temperatures and it was not found possible to obtain a completely selective response to any of these gases using the T.G.S.102 or T.G.S.202.

One of the recommendations made in August 1976, arising from this work, was that the possible usefulness of semiconductor gas sensors as gas chromatographic detectors should be examined.

1.2 The application of semiconductor gas sensors as gas chromatographic detectors by other workers.

Prior to this time, so far as is known, no reports had been published in which the Taguchi gas sensors had been used as a gas chromatographic detector, although Seiyama et.al.(4,5) had described the use of a thin film of zinc oxide as a gas chromatographic detector as long ago as 1962 and Guglia et.al.(6,7,8) described similar work extending over the period 1969-1978.

In 1977 Mallard et.al.(9) described the construction and operation of a portable gas chromatograph for assessing the conversion rate of ethyne to ethene, as a measure of nitrogenase activity in field peas. A Taguchi gas sensor type 812, with its cover removed, was used as the gas chromatographic detector. This was mounted at the outlet end of a chromatographic column 44 centimeters long and packed with Porapak R. and Porapak N. Air was used as the carrier gas at a flow rate of about 20 cm^3 min.$^{-1}$ The heater which was powered from a 12-volt car battery was operated at 5 volts. Changes in the conductance of the T.G.S. sensor were monitored on a 0-100 microampere meter but, for laboratory use, outputs to a potentiometric recorder were provided. Injecting a 1 cm.^{3} sample volume, from a graduated syringe, it was possible to detect as little as 10 ppm of ethene, with a relative standard deviation of about 3%. The sensitivity of the T.G.S.812 detector towards ethene was sufficient to detect and measure nitrogenase activity. The effect of varying the heater voltage on the response to ethene was apparently not investigated. A non-linear calibration graph of meter readings (microamperes) versus ethene concentration (1-10.10^{-9}moles) was reproduced.

A comprehensive report was issued by the Institute of Organic Chemistry in Shanghai,(10) dated 1977. This was noted in Chemical Abstracts, 1978, 89 : 173016 a and a translation was obtained some months later. In this case the gas chromatographic detector was made from an n-type semiconductor material with tin oxide as its major constituent. Small amounts of tin trioxide, aluminium trioxide, palladium chloride and a bonding agent were ground together to a slurry, with water, in a mortar. The slurry was applied to pre-fabricated platinum-gold electrodes and, after sintering at 700-800°C, small granular sensors were obtained. One of these semiconductor sensors was used as the detector in a chromatograph and its response was compared with that of a flame-ionisation chromatograph. Its sensitivity to a wide variety of organic and inorganic compounds was generally similar to that of the flame-ionisation detector. A linear relationship was shown when response to hydrogen (millivolts) was plotted against $\log_{10}$ hydrogen concentration over the range 0.01 - 100%. The lower limit of detection for hydrogen was 0.4 ppm. Methane, ethane, propane, iso- and normal-butanes had linear calibration graphs (millivolts versus concentration) over the range 0.01-0.1 per cent. The unique advantage of this type of semiconductor gas chromatographic detector was stated to be that air or nitrogen could be used as carrier gas (but not the rare gases). Examples of applications of this chromatograph included the following:

1. The determination of hydrogen impurity in the rare gases argon, krypton, xenon, neon and helium;
2. the determination of a range of lower hydrocarbon gases produced as a result of breakdown in transformer oils;
3. the determination of low (ppm) concentrations of methane, ethane, ethene and propene in air samples taken in the vicinity of an ethene plant;
4. the analysis of gas and oil samples at oil drilling sites.

It was noted that the sensitivity of the semiconductor chromatograph to the $C_2 - C_5$ hydrocarbons was higher than that of the flame-ionisation chromatograph. In this case also the effect on sensor response of varying the operating temperature of the sensor and of varying the carrier gas flow rate was not reported.

All these workers, with the exception of Mallard <u>et.al.</u>(9) manufactured their own semiconductor gas sensing devices.

At about the same time as the proposal was made to assess the Taguchi gas sensors as gas chromatographic detectors, all the original Taguchi models, except the T.G.S.109, began to be replaced by newer models, the T.G.S.711, T.G.S.812 and, later the T.G.S.813. In the meantime the range of Taguchi gas sensors has been further increased and details of the ten models stated to be currently available(11) are given in Table 1.

TABLE 1 FIGARO SEMICONDUCTOR GAS SENSORS

Sensor Type	Recommended circuit voltage (V_c - volts)	Recommended heater voltage (V_h - volts)	Applications and features
TGS.109	100	1.0	Combustible gases C_1-C_4 etc. Large output signal to drive a buzzer directly.
TGS 109M	100	1.0	City gas; suited for Japanese regulation.
TGS.711	24(Max)	5.0	Carbon monoxide.
TGS.712D	24(Max)	2.5	Carbon monoxide; low sensitivity to hydrogen.
TGS.812	24(Max)	5.0	Organic solvent vapours e.g. alcohol, benzene, etc. Toxic gases(CO, NH_3, SO_2, etc.)
TGS.813	24(Max)	5.0	General combustible gases like C_1 - C_4 etc.
TGS.813C	24(Max)	5.0	General combustible gases; prepared for an easier process of making a domestic gas detector.
TGS.814D	24(Max)	5.0	Ammonia gas.
TGS.816	24(Max)	5.0	TGS 813 suited for high temperature circumstances with ceramic body.
TGS.911	24(Max)	1.2	TGS 813 suited for corrosive atmosphere with noble metal heater.

Other types of semiconductor gas sensors which are commercially available in the U.K. are listed in Table 2.

TABLE 2

DETAILS OF SOME OTHER SEMICONDUCTOR GAS SENSORS AVAILABLE IN THE U.K.

Manufacturer	Applications and features	Recommended operating voltages:		Address of retailers
		circuit voltage (V_C) volts	heater voltage (V_H) volts	
Sema Electronics Limited, Unit 32, Dundonald Camp, Irvine, Ayrshire, KA11 5BJ	Detection and measurement of a wide range of specified gases; ppm or % L.E.L.	Not stated	3.5	Direct from the manufacturer.
International Sensor Technology, 3201 South Halladay Street, Sant Ana, California 92705 U.S.A.	Detection and measurement of specified gases ppm or % L.E.L.	6	2.25-2.5 (for % L.E.L. methane)	MDA(UK) Limited, Ferndown Industrial Estate, 86 Cobham Road, Wimborne, Dorset, BH21 7PQ
Matsushita Electrical Industries Co.Ltd., Kadoma, Osaka 571, Japan	Propane (LPG sensor), Natural gas (LNG sensor); Gas leak alarm; γ Fe_2O_3 semiconductor.	6	4.15-4.2 (for LPG sensor)	National Panasonic (U.K.) Ltd., 107 Whitby Road, Slough, Berkshire SL1 3DR

1.3 Review of U.S. Patents relating to metal oxide Semiconductor gas sensors

A review of the United States Patents relating to metal oxide semiconductor gas sensors does not give a clear picture of the actual composition of the sensors which are commercially available. Numerous alternative formulations are given whilst many of the specific claims appear to be repeated, both within a given Patent and also between different Patents granted to the same inventor.

Of the seven U.S. Patents granted to N.Taguchi(12 - 18) the first application was submitted in January 1969 and granted in December 1971, four more applications were submitted during 1970, a single application was submitted in 1972 and another in 1973; grant of these Patents being spread over the years 1971-75.

The comprehensive Patent in the names of Bott, Firth, Jones and Jones(19) was originally submitted in August 1971, re-submitted in October 1973 and granted in February 1975.

Two more recent Patents in the names of Chou and Chou(20,21) were filed in September 1974 and June 1976; they were granted in May 1976 and March 1977.

The seven Patents in the name of N.Taguchi are considered first.

In referring to the prior art, Taguchi(13) refers to n-type metal oxides such as tin, zinc, iron, titanium, vanadium, manganese, tungsten, thorium, molybdenum, cadmium and lead,whose conductivity increases in the presence of reducing gases such as hydrogen, carbon monoxide, alcohols and hydrocarbon gases, but whose conductivity decreases in the presence of oxidising gases such oxygen, chlorine and sulphur dioxide. The conductivity of p-type semiconductor metal oxides such as those of nickel or chromium increases in the presence of oxidising gases and is reduced in the presence of reducing gases. In two of the Patents(12,14) it is stated that sensors in the form of thin films, and those manufactured by heating powdered semiconductor particles to produce sintering, respond too slowly and with insufficient sensitivity to be useful. Two methods are suggested to increase the porosity of the sensors. Four Patents(12,15,16,17) recommend incorporating a volatile organic compound such as stearic acid, wax, sugar, polyvinyl alcohol or acrylic resin with the semiconductor metal oxide powder which, after forming under pressure, may be heated to a temperature at which the organic compound volatilises but at which sintering does not occur. Another Patent(14) recommends incorporation of a substance such as ethyl silicate or a silicate hydrosol which will yield silica gel on heating.

Other recommendations are intended to improve the mechanical strength of the sensors. Three Patents(13,16,17) describe various forms of metallic support for the sensor and four Patents(14,15,16,17) recommend incorporation of alumina or quartz to strengthen the body of the sensor and to prevent the formation of cracks. An alternative method of reinforcing the strength of the sensor is proposed(15) in which a porous outer coating of asbestos, glass fibre or cement is provided, using alumina as a binder. It is claimed that the addition of 0.3% (w/w) of palladium(14) or 0.1% of gold(15) gives an improved response rate and sensitivity to butane.

Some time is required for the sensor to become stable at the pre-set operating temperature (usually between 170° and 230°C) and an impedance circuit is proposed(13) which can be matched to the alarm circuit, where one is used, and for which it may be substituted until the sensor has become stable.

The U.S.Patent in the names of Bott, Firth, Jones and Jones(19) is concerned with activated semiconducting elements in which the addition of a second metallic species causes the gas which it is required to detect to react more strongly than in the absence of the activator. Numerous examples of primary and secondary activators are given and methods of increasing the sensitivity of response toward various basic or acidic and oxidising gases. The recommended method of preparing the gas sensitive elements utilises a salt, such as ammonium nitrate, as solvent for the metal ammine, both of which are subsequently decomposedby heating to a temperature in the region 200°-400°C, with deposition of the activated metal oxide into particles of uniform size and high surface area. Gas detecting instruments for field use must have a low power requirement, so that they can be operated satisfactorily from batteries. Both forms of transducer proposed under this Patent(19) are physically small and designed for low current requirement.

Two Patents in the names of Chou and Chou(20,21) give specific details of the composition of their sensor, which they describe as a solid state electrolytic cell gas sensor. The particular example, which is quoted in both Patents(20,21), stipulates six parts of stannic oxide mixed with one part of silica gel and this mixture activated at a temperature between 200° and 300°C. The activated powder is formed into a paste with two per cent platinum oxide (Pt_2O) using two parts of alcohol to one part of water as solvent. The paste is applied to the heating element and electrodes and dried out and re-activated by the controlled application of heat.

This formulation is similar to one in the name of Taguchi. Nevertheless the second Chou Patent(21) states that "... a sensor prepared according to the applicants invention differs from the prior art in that the prior art comprises a semiconductor whose electrical conductivity is dependent upon the concentration of the gas in the atmosphere. A sensor prepared according to the present invention causes a dissociation of the gases or gas to be measured into charged species such as ions and complex ions and does not operate by changing its electroconductivity in response to the adsorption of a particular impurity or combination of impurities. The difference between a sensor according to the present invention and a sensor which changes its electro-conductivity is somewhat similar to the difference between causing a given number of charged particles to pass between selected points by reducing the resistance of the electrical conductivity (sic) between the two points and (as illustrative of the present invention) dissociating impurities so that there are more ions and complex ions which can begin to make the trip."

It would be interesting to be able to assess the evidence upon which this claim is based.

1.4 Theories of the mode of operation of semiconductor gas sensing devices

The most widely used solids in this type of sensor are the oxides of the transition metals and heavy metals such as tin. As noted by Firth *et.al.*(22,23) these oxides are semiconductors because of the ability of the metal to exist in different oxidation states. These oxides are non-stoichiometric; n-type semiconductors containing a slight excess, and p-type semiconductors a slight deficiency, of metal within the lattice.(61) In order to preserve electrostatic neutrality of the oxide the excess metal in n-type semiconductors is present as a species with a charge lower than that of the parent metal ion in the oxide lattice e.g.Sn^{2+} in SnO_2, or Zn^o in ZnO. Such ions can be represented as localised impurity centres, with valence electron energies only slightly below those of the conduction band of the oxide. Valence electrons can thus be thermally excited into the conduction band and cause it to have electrical conductivity. In the process, of course, Sn^{2+} is converted to Sn^{4+} and, unlike metallic conductors, the conductance of a semiconductor increases with temperature, because thermal energy enables increasing numbers of valence electrons to make the transition into the conductance band.(61,62)

Chemisorption of a gas can produce a change in the conductivity of an oxide by changing the concentration of those metal ions in the oxide lattice which have a charge different from that of the main metal ion in the lattice. Thus, in clean air, n-type semiconductors exhibit reduced conductivity. This is now generally accepted as being due to the adsorption of oxygen molecules on the surface of the semiconductor in the form of negative ions. Adsorption of a neutral oxygen molecule may, for example, result in the formation of 2 O^{2-} ions. This process is seen to involve the transfer of four valence electrons from the semiconductor and their localisation, on the surface, in the form of oxygen ions, resulting in reduced conductivity of the n-type semiconductor.(63)

Adsorption of a reducing gas, such as carbon monoxide or methane, on the surface of an n-type semiconductor, results in an increase in conductivity. Two mechanisms have been proposed to account for this. In the first, if the reducing gas is adsorbed as positive ions, e.g.CO , this is seen to involve the direct transfer of electrons to the solid with a resultant increase in conductivity. The second mechanism involves the chemical reaction between the reducing gas and oxide ions, which may be present on the surface, to form, ultimately, carbon dioxide and water. The overall reaction is the removal of oxygen ions from the surface of the semiconductor in a neutral form, and the reversion of those electrons, previously localised in these ions, back to the oxide lattice.

In the case of a mixture of a reducing gas, such as carbon monoxide, in air oxygen will re-adsorb on the surface so that, at any concentration of carbon monoxide, an equilibrium concentration of adsorbed oxide ions and carbon monoxide is present on the surface of the oxide and hence the conductivity will be determined by the partial pressure of each gas. However since, in general, oxygen is strongly adsorbed on most oxides, large changes in the gas phase oxygen concentrations (1 - 50% v/v) above a certain minimum concentration produce only small changes in the conductivity of the oxide. Carbon monoxide, however, is generally weakly adsorbed so that relatively large changes in the conductivity are produced by changing the gas phase concentration of carbon monoxide.

In a recent paper Ihokura(11) of Figaro Engineering Inc. presented further data concerning the performance of Taguchi gas sensors. He suggested that adsorption of oxygen on the surface of a semiconductor is influenced by the palladium catalyst which is present and which helps to decrease the activation energy for the chemisorption of oxygen. It is further stated that chemisorption of oxygen produces a potential barrier on the surface of the sensor, which plays an important role in relation to the conductance of the sensor. Comparing two sensors, both operated at 350°C, one containing 1.5% palladium and the other 0.2% palladium, it is shown that the former gives a smaller response to carbon monoxide relative to methane, whereas the latter gives a relatively larger response to carbon monoxide. A graph showing the relationship between sensor resistance and partial pressure of oxygen in the atmosphere is shown to give a good linear relationship on a log/log scale over a wide range of pressure. At a very low partial pressure of oxygen (i.e.less than 10^{-2}mm.Hg.) an irreversible change in resistance was noted, presumably due to removal of oxygen from within the semiconductor crystal lattice.

Ihokura(11) interpreted the changes in conductance of the sensor, after switching on the heater current, in terms of the foregoing. The almost immediate steep rise in conductivity after switch-on he attributed to the promotion of electrons from lower energy levels, the so called donor levels, into the conductance band. This is a fast reaction. Thermal energy bridges the 3.7 electron-volt gap between the donor levels and the conductance band. When the sensor is in clean air this rapid increase in conductance is followed by a relatively slow fall in conductance which he suggests is due to the adsorption of oxygen on the surface of the semiconductor and localisation of electrons, formerly in the conduction band, in the oxygen ions at the surface. The time required for the semiconductor to reach its full resistance (minimum conductance) he termed the "initial action" time, which varied according to the amount of palladium incorporated within the sensor. A highly activated sensor, containing 1.5% palladium had an initial action time of only a minute or two, whereas a moderately activated sensor, containing 0.2% palladium required five to ten minutes, or more.

relatively fast for the highly activated sensor, but was considerably slower for the moderately activated sensor.

Semiconductor gas sensors are generally used to detect the presence of reducing gases in the air and very little information seems to have been published concerning the effect on their response of working in atmospheres deficient in oxygen or in which oxygen is virtually absent. Recent work at the Health and Safety Executive Research Laboratories(24) concerning the response of various forms of zinc oxide sensors to methane, carbon monoxide and water vapour, however, shows that the response to carbon monoxide in nitrogen containing less than 1 ppm oxygen, expressed as % change in conductance i.e. $\frac{\Delta C.100}{C}$ is less than its response to an equivalent carbon monoxide/ air mixture by a factor of four or five times.

In summary, knowledge concerning semiconductor gas sensors is growing but the precise mechanism of response is not yet clear and factual knowledge concerning the detailed composition of the sensors is not generally available. This state of affairs was commented upon by two Japanese workers(25) who, in a recent paper which listed almost one hundred literature references, wrote :

> ". . . . although many views have been offered on the mechanism of the sensor operation, these have not yet been brought together to provide a unified view . . . "

1.5 Characteristics of gas chromatographic detectors with particular reference to their sensitivities towards hydrogen and carbon monoxide

Gough and Walker(26) listed what they considered to be the most important attributes of a gas chromatographic detector.

They suggested that it should be a simple piece of equipment, being easily constructed or readily available commercially and requiring the minimum of maintenance in use. It should be insensitive to small random fluctuations in carrier gas flow rate or pressure, and to changes in temperature. It should have high sensitivity combined with an extensive linear dynamic range. They suggested that it should have a predictable response which, ideally, would be the same for all compounds.

Adlard,(27) in a more recent review of gas chromatographic detectors, suggested that a more significant way of classifying detectors was between "universal" and "selective" types. In the former category he put the flame ionisation and katharometer detectors and referred to the flame photometric, flame thermionic, electron capture and microwave plasma detectors as examples of "selective" detectors.

In practice it must be admitted that an ideal gas chromatographic detector does not yet exist. The approach of Adlard is more realistic in suggesting that the choice of detector must be governed by the nature of the analysis which is required, selective detectors being particularly useful in analysing for trace components in complex matrices.

The flame ionisation detector(28,29) is probably the most widely used gas chromatographic detector. It responds with high sensitivity to almost all organic compounds, with the exception of formaldehyde, formic acid and such compounds as carbon disulphide and carbonyl sulphide. It is capable of providing an exceptionally wide linear dynamic range and having, in addition, a small dead volume it is suitable for use with capillary columns. However it has the disadvantage that the substances passing through it are destroyed and the column effluent stream must be split, if it is to be operated in conjunction with another type of detector or analyser. The actual ionisation mechanism is not fully understood and, for the highest accuracy, individual calibration is required for each component. It does not normally respond to the permanent gases and, only under abnormal conditions of operation does it give any response to hydrogen or to carbon monoxide (28,30)

A more sensitive response to carbon monoxide may be achieved by placing a small nickel reduction furnace at the outlet end of the chromatographic column (32,33) which, in the presence of hydrogen, will quantitatively reduce carbon monoxide to methane before it enters the detector. This method has been used in the routine determination of carbon monoxide in mine air samples (34). Similarly, if a trace quantity of carbon monoxide is included in the carrier gas, the nickel reductor will provide a sensitive response from the flame ionisation detector to low levels of hydrogen. Unfortunately this technique cannot be used for the simultaneous analysis of trace quantities of carbon monoxide and hydrogen in the same sample.

For the analysis of permanent gases the katharometer is normally used but its sensitivity is at least two orders of magnitude less than that of the flame ionisation detector and, except for the specially designed micro-versions, manufactured by Taylor Servomex Limited and Gow-Mac Limited, it may have a relatively large dead volume. In this case, also, calibration is usually necessary. Earlier versions of the katharometer were operated with a constant voltage applied to the bridge network which incorporates the reference and sensing elements. Particularly when major components were passing through the detector, and those whose thermal conductivity was very different from the carrier gas, the temperature of the sensing element changed sufficiently to produce an appreciable change in its electrical resistance and, hence, in the electrical current flowing it. When operated in this way there was thus a significant degree of non-linearity built into its mode of operation. A katharometer with the sensing elements operated at a constant temperature is advantageous in this respect.(35,36) For most types of analyses involving a katharometer detector helium is the preferred carrier gas since, having a very high thermal conductivity, it gives a high response to most substances. For the analysis of mixtures containing hydrogen, however, distorted peaks and an anomalous response may be obtained(37,38). In neither case is the sensitivity toward hydrogen and carbon monoxide sufficient for the analysis of mine air samples containing low ppm levels of hydrogen and carbon monoxide.

In its normal mode of operation the electron capture detector will respond neither to carbon monoxide nor to methane, although Phillips <u>et.al</u>.(39) showed that an enhanced response to non electron-attaching compounds could be obtained by including a few parts per million of nitrous oxide in the nitrogen carrier gas. In this way a lower limit of detection of approximately 0.01 ppm was claimed for hydrogen and 0.02 ppm for methane. The sensitivity toward carbon monoxide was not quoted.

The ultrasonic detector(40) responds with good sensitivity to all gases and may be adapted for use with a variety of carrier gases. A phase monitor responds to changes in phase of the ultrasonic waves between the sensing and reference cells; it requires sophisticated electronic circuitry and is a costly item of equipment. To achieve the lowest limits of detection the temperature of the detector must be controlled to between 10^{-3} and 10^{-4} °C. It is extremely sensitive to the presence of oxygen and nitrogen, so that the performance will suffer as the result of even the smallest gas leak in the system.

Low levels of detection for the

claimed by workers using various forms of radio-frequency discharge detector. Karmen and Bowman (41) reported response to a wide range of gases, including high sensitivity to hydrogen, but their detector was not sufficiently stable for it to be used over extended periods. A commercial form of the radio-frequency detector was described by Hampton(42) in which the discharge was supported between concentric platinum electrodes which were subjected to R.F. power of about 10 watts at 27.12 megacycles. A change in the gas composition altered the D.C. potential across the detector electrodes and this change was used directly as the detector signal. A lower limit of detection of about 0.04 ppm for hydrogen was claimed, although the sensitivity toward other gases was less good(42). Hampton's detector showed long term changes in sensitivity and needed a periodic clean up of the electrodes. Helium was the preferred carrier gas in each case. Lambert(43,44) used electrodes situated externally to the detector cell. Using argon as the carrier gas it was demonstrated that different components eluting from the column affected the amount of light emitted by the discharge and these changes were monitored by means of a photo-resistor. In another form of this detector helium was used as the carrier gas and the variation in the current between the electrodes was compared with a reference current and provided the signal for the recorder. In both cases the high frequency generator required temperature regulation to 0.01°C, to eliminate base line instability arising from random thermal fluctuation. Limits of detection for all the permanent gases, except neon, were approximately 0.1 ppm.

As originally described the Lovelock argon ionisation detector(45,46) did not respond to compounds having ionisation potentials above 11.2 electron-volts and this included many of the permanent gases. However Shahin and Lipsky showed that, by modifying the detector geometry, by increasing the size of the detector anode so as to leave an annular gap of only one millimeter between the electrode and the body of the detector, which was maintained at a temperature of 150 - 200°C, and by operating at an applied voltage of only 1 - 2 volts a sensitive response to the permanent gases as well as to organic vapours could be obtained. The lower limits of detection achieved were as follows :

	Limits of detection (grams/second)
hydrogen	$4.8 . 10^{-11}$
carbon monoxide	$5 . 10^{-10}$
methane	$8.8 . 10^{-11}$
ethane	$4.8 . 10^{-10}$
ethene	$3.4 . 10^{-10}$

If helium carrier gas is used, instead of argon, with this type of detector a sensitive response is obtained from those compounds having ionisation potentials up to 20 electric-volts, which includes most of the permanent gases except neon(48). In common with the ultrasonic detector its performance will suffer from even the smallest leak of air into the system. When analysing for trace components in air, the chromatographic column must provide a wide separation between air and the components of interest, since the detector responds with high sensitivity to oxygen, argon and nitrogen and the resolution of trace substances which are eluted on the tail of the air peak can present difficulties. Limits of detection have been quoted as 0.002 ppm for carbon monoxide and nitrogen and 0.02 ppm for methane(48).

Recently it has been shown that response to the permanent gases can also be obtained with ionisation-type detectors using two other experimental techniques. Gawlowski et.al[49,50] employing a high intensity tritium radiation source (20 Curies) within the detector, assessed the performance using three different designs of detector geometry. Under the optimum operating conditions they achieved limits of detection for hydrogen, carbon monoxide, methane and ethane of about 1 ppm.

Andrawes *et.al.*(51) showed that, by using an ultra-pure (research) grade of helium as the carrier gas, in conjunction with an ionisation detector containing a 250 milliCurie tritium source, negative peaks were obtained for neon, hydrogen, argon and nitrogen, and positive peaks for oxygen, methane and carbon monoxide. Using a sample size of 0.1 cm^3 limits of detection in the region of 0.01 ppm were achieved for hydrogen and methane and about 0.1 ppm for carbon monoxide. By adding a few parts per million of hydrogen to the carrier gas positive peaks were obtained for all gases except neon, but with much reduced sensitivity.Employing the normal high purity grade of helium (minimum purity 99.995%), in place of the research grade gas as carrier gas and working in the saturation region of the detector (with an applied voltage to the detector of between 20 and 200 volts) it was shown(52) that the detector response is independant of the applied voltage and limits of detection of 3.5 ppm for hydrogen, 0.004 ppm for methane and 0.02 ppm for carbon monoxide were obtained.

A summary of the limits of detection, mainly for hydrogen and carbon monoxide, obtained by the workers referred to above is presented in Table 3.

LIMITS OF DETECTION FOR VARIOUS GAS CHROMATOGRAPHIC DETECTORS

Type of detector	Literature reference number	Gas	Limit of detection quoted	Equivalent quantity expressed as ppm in 5 cm^3 sample volume
Flame ionisation detector	29	Heptane	2.10^{-12} g.sec^{-1}	0.001
" "	31	$C_1 - C_5$	0.001 ppm	
FID + nickel reductor	32	CO	approx 0.05 ppm	
	33	CO	0.0056 μl.	10
Electron capture (N_2+N_2O carrier gas)	39	(H_2 (CH_4	0.1 ppm 0.2 ppm	
Ultra-sonic	40	H_2	2.10^{-9} gram	5
Radio frequency discharge	42	(H_2 (CH_4	4.10^{-11} mole 1.10^{-10} mole	0.2 0.4
Modified argon ionisation	47	(H_2 (CO	$4.8.10^{-11}$ g.sec^{-1} 5.10^{-10} g.sec^{-1}	1 1
" "	49	H_2	1.10^{-10} g.sec^{-1}	2
" "	50	H_2	$1.3.10^{-11}$ g.sec^{-1}	0.3
Helium ionisation	51	(H_2 (CO	0.01 ppm 0.1 ppm	
" "	52	(H_2 (CO	3.5 ppm 0.02 ppm	
" "	48	(CO (CH_4	0.002 ppm 0.02 ppm	

NOTE: In an attempt to make a valid comparison between the limits of detection achieved using the Taguchi 711 semiconductor sensor and those achieved by other workers using a variety of other detectors it has been necessary to make certain assumptions in order to express all in terms of parts per million (by volume) using a sample volume of 5 cm.^{3}, as in the present work.

Where sensitivities have been expressed as micrograms per second, it is assumed that each peak of interest is twenty seconds wide and the total mass eluted is taken to be ten times the limit of detection. That mass of substance is converted to a volume, knowing the molecular weight and the Avagadro volume, and expressed in terms of concentration, in a 5 cm.^{3} sample volume.

1.6 Aims of the present investigation

In assessing the performance of semiconductor gas sensors as gas chromatographic detectors, the main aim of the investigation was to determine the most favourable conditions for the analysis of samples containing low ppm and sub ppm levels of hydrogen and carbon monoxide. Calibration graphs would be prepared, linearity of response with concentration was to be assessed and an attempt made to identify those operating conditions which would contribute towards an improvement in the linear dynamic range of the detector, the symmetry of the gas chromatographic peaks and, hence, to the overall speed of response of this type of gas chromatographic detector. Limits of detection were to be assessed and compared with those of other workers using alternative gas chromatographic systems.

Most of the work was to be concentrated on the performance of the T.G.S. 711, since this sensor was expected to give an enhanced response to the gases of main interest. Within the time available, however, a preliminary assessment of the performance of other sensors, notably the T.G.S. 812, the International Sensor Technology semiconductor methane sensor and the Matsushita semiconductor L.P.G. sensor would be made and the sensitivity of response of all these sensors to methane, ethane, ethene, propane and ethyne would be determined.

2 EXPERIMENTAL

2.1 Mounts for semiconductor gas sensors.

2.1.1. Taguchi Gas Sensors

The methods of mounting the semiconductor gas sensors, as received from the different manufacturers, varied considerably and each required modification, as described below, to enable their use as a gas chromatographic detector.

The design of the new generation of Taguchi gas sensors, which were used in the present investigation, show several improvements over the earlier models. The tin dioxide semiconductor material is deposited on the outer surface of a ceramic tubular former, through which passes a coiled electric heating element of chrome alloy wire. The more recent design of sensor thus provides as isolated heating element and the temperature is more nearly uniform than was the case with earlier models, which exhibited a definite temperature gradient across the sensor(53)

The lead wires, carrying the circuit voltage (V_c) to the sensor electrodes, are of 80 micron diameter gold alloy. These, and the heater lead wires, are spot welded to pins arranged to fit a 7-pin miniature valve socket. The base and cover of the sensor housing are made of nylon 66 and is said to have a deformation temperature in excess of 240°C. Upper and lower openings in the sensor housing are covered by a flameproof double layer of 100-mesh stainless steel gauze. Plate 1 shows the Taguchi gas sensor type 711 as supplied by the manufacturer. Plate 2 shows the sensor with the top cover and gauze removed.

In modifying the sensor for use as a gas chromatographic detector the aim was to feed the effluent from the chromatographic column directly on to the gas sensing element. This was achieved by inserting a length of thick walled copper tubing, two millimeters internal diameter, through a hole made in the stainless steel gauze in the base. The tube was secured in position using epoxy resin cement (Araldite, Ciba-Geigy (U.K.) Limited, Plastics Division, Duxford, Cambridge) with the outlet end two millimeters from the surface of the sensor (Plate 3). The upper half of the sensor was fitted into a rigid plastic hose connector, with epoxy resin cement. A one meter length of plastic tubing, two millimeters internal diameter, was secured to the outlet, in order to minimise back-diffusion of possibly contaminated laboratory air (Plate 4).

2.1.2. Matsushita L.P.G. Sensor

Electrical leads for this sensor are soldered to four metal pins, in line, which pass through the insulating base. The two inner pins are connected to electrodes embedded within the semiconductor sensor bead which is positioned within a cylindrical heater cage (Plate 5). Electrical leads for the heater are connected to the two outer pins. A double layer of 100-mesh stainless steel gauze covers the semiconductor sensor and the heater, as shown in Plate 6.

After removing the stainless steel cover, a hole was drilled through the plastic base, to one side of the pins. A length of thick walled copper tubing, two millimeters internal diameter, was inserted through the hole and secured in position using epoxy resin cement. The upper end of the tubing was bent so that effluent from the chromatographic column flowed directly on to the semiconductor sensor bead. The upper part of this sensor was mounted in a similar manner to that of the Taguchi sensors.

2.1.3 International Sensor Technology per centage L.E.L. methane sensor

The electrical leads for this sensor are attached to four pins, arranged in the form of a square. These pass through a round insulating base. Two of the pins are connected to electrodes and two to the heating element, both of which are enclosed within the semiconductor bead, which is approximately one to one and a half millimeters in diameter.

As supplied the four pins fit into sockets within a metal flameproof enclosure, which houses the electrical leads. The sensing element is enclosed within two large sintered stainless steel covers (Plates 7, 8 and 9)

In modifying this sensor for use as a gas chromatographic detector the aim was to reduce the gas dead volume within the detector housing as much as possible and to lead the gas chromatographic column effluent directly on to the sensing element. After removing the stainless steel covers (Plates 8 and 9) the sensor was removed from its socket and placed within a cylindrical rigid plastic enclosure fitted with glass inlet and outlet tubes, one millimeter internal diameter (Plates 10 and 11).

2.2 Details of the electrical circuits and components used

Each sensor was supplied with an integral electric heating element and this was connected to a variable stabilised voltage supply. A separate stabilised voltage supply unit was used for the measuring circuit.

Table 4 contains a summary of the electrical characteristics and supply requirements for the gas sensors.

TABLE 4

SUMMARY OF THE ELECTRICAL CHARACTERISTICS AND SUPPLY REQUIREMENTS FOR THE SEMICONDUCTOR GAS SENSORS

	Taguchi			Matsushita	I.S.T.sensor
	Type 711	Type 812	Type 813	Type LPG	%LEL CH_4 type
Recommended heater voltage (V_h)/volts	5 ± 0.2	5 ± 0.2	5 ±0.2	4.2	2.4
Cold resistance of heater element(R_H) /ohms	100	38 ± 3	30 ± 3	13.5 ±0.5	7
Heater current requirement (I_H) /amps.	0.05	0.13	0.17	0.31	0.34
Heater power dissipation (P_H) /watts	0.25	0.65	0.85	1.3	0.82
Recommended circuit voltage (V_c)/volts	up to 24	up to 24	up to 24	up to 6	up to 6
Recommended value of load resistor (R_L) /ohms	2K	4K	4K	n.r.	n.r.
Maximum current through sensor (TGS 711) or sensor power dissipation (P_s)/milliwatts	0.5 mA.	15 milli-watts.	15 milli-watts.	n.r.	n.r.

Note: n.r. indicates that no recommendation was given.

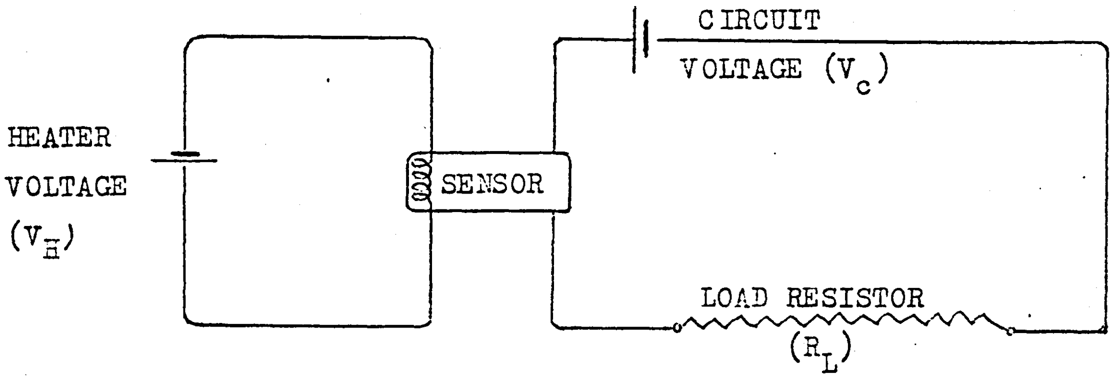
Two stabilised variable voltage supplies (Maxireg model 761, Weir Instrumentation Limited, Durban Road, Bognor Regis, Sussex) were used, one to supply the heater voltage requirement and one to supply the circuit voltages noted in Table 4.

Each was capable of supplying either up to 15 volts at 4 amperes or up to 30 volts at 2 amperes. The ten centimeter scale on these instruments was graduated in 0.05 volt divisions and readings could be estimated to the nearest 0.01 volt.

2.3 Electrical characteristics of the measuring circuit

In early exploratory studies the measuring circuit shown in Figure 1 was used, as recommended by the manufacturer of the Taguchi gas sensors.

FIGURE 1 SIMPLE LOAD RESISTOR CIRCUIT



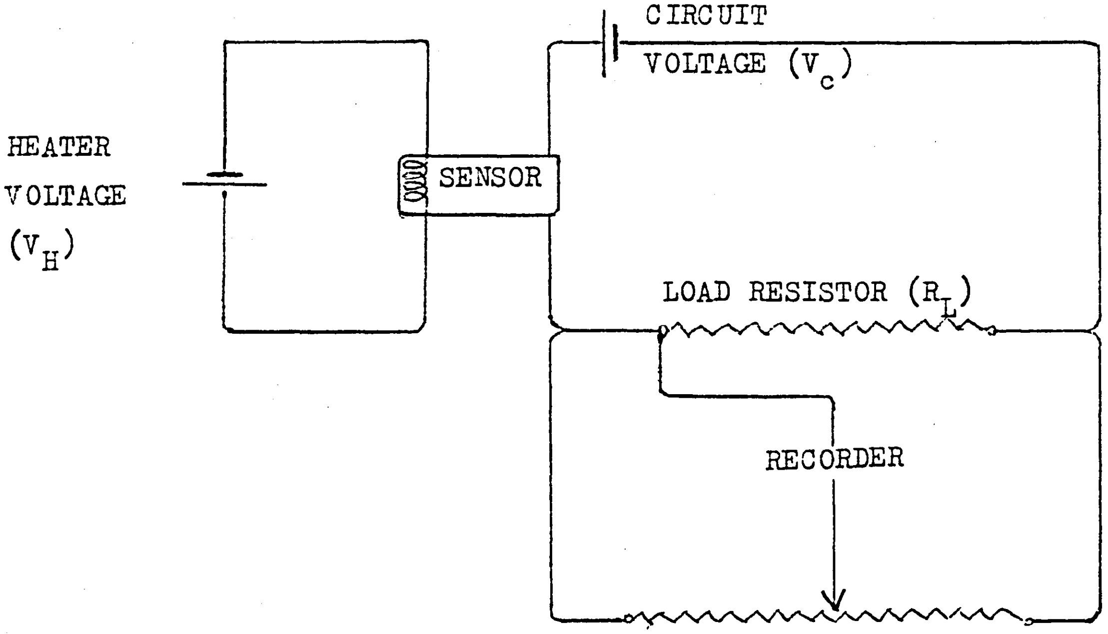
The voltage drop across the semiconductor sensor is $V_c \cdot \frac{R_s}{R_s + R_L}$ volts, where R_s denotes the sensor resistance, and the voltage drop across the load resistor is $V_c \cdot \frac{R_L}{R_s + R_L}$ volts.

When responding to the presence of a reducing gas the conductance of the n-type sensor increases, i.e. its electrical resistance decreases. This produces a decrease in the voltage across the sensor and, provided the circuit voltage is maintained constant, a corresponding increase in the voltage across the load resistor. As will be seen later, this change in voltage across the sensor as it responds to a reducing gas, is an important contributory factor to non-linearity of calibration graphs when using this type of circuit(54)

Provided a suitable value of load resistor is chosen it will also fulfil a secondary role, as a current limiter ensuring that, as stipulated by the manufacturer, no more than 0.5 milliamperes can flow through the T.G.S. 711 sensor or more than 15 milliwatts be supplied to the other types of Taguchi sensor.

The signal from the detector, i.e. the change in voltage across the load resistor, was measured using a potentiometric recorder (Servoscribe, multi-range, Model RE 511.20; Smith's Industries Limited, 50 Oxgate Lane, Cricklewood, London, NW2 7JB) In practice it was found that, under certain conditions of operation a greater range of zero control was required than was provided on the recorder. The load resistor circuit was therefore modified by incorporating the load resistor and recorder into a bridge circuit, as shown in Figure 2

FIGURE 2 MODIFIED LOAD RESISTOR CIRCUIT

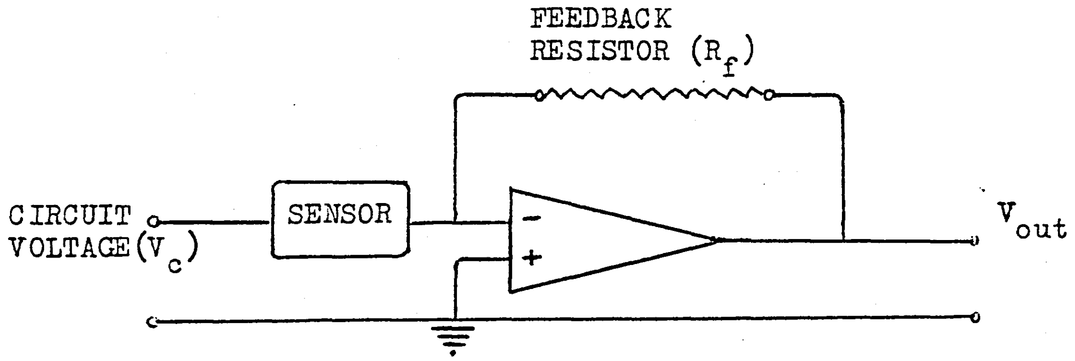


50K ohm, 10-turn
POTENTIOMETER.

The multi-turn potentiometer provided a sensitive and wide range control of the base-line position on the potentiometric recorder.

One method of maintaining the voltage across the sensor constant, even whilst it is responding to a reducing gas, is to use an operational amplifier circuit, of the type shown in Figure 3.

FIGURE 3 SIMPLE OPERATIONAL AMPLIFIER CIRCUIT



Operational amplifiers are a class of differential amplifier. The individual characteristics of different types of operational amplifier can vary widely but their performance characteristics have a number of features in common(55). These include :-

1. Large gain (10^4 to 10^6);
2. high input impedance;
3. low output impedance;
4. zero output for zero input.

It may be noted that the sensor is connected, in Figure 3, to the inverting terminal of the operational amplifier.

The circuit gain, which is independent of the amplifier gain, is :

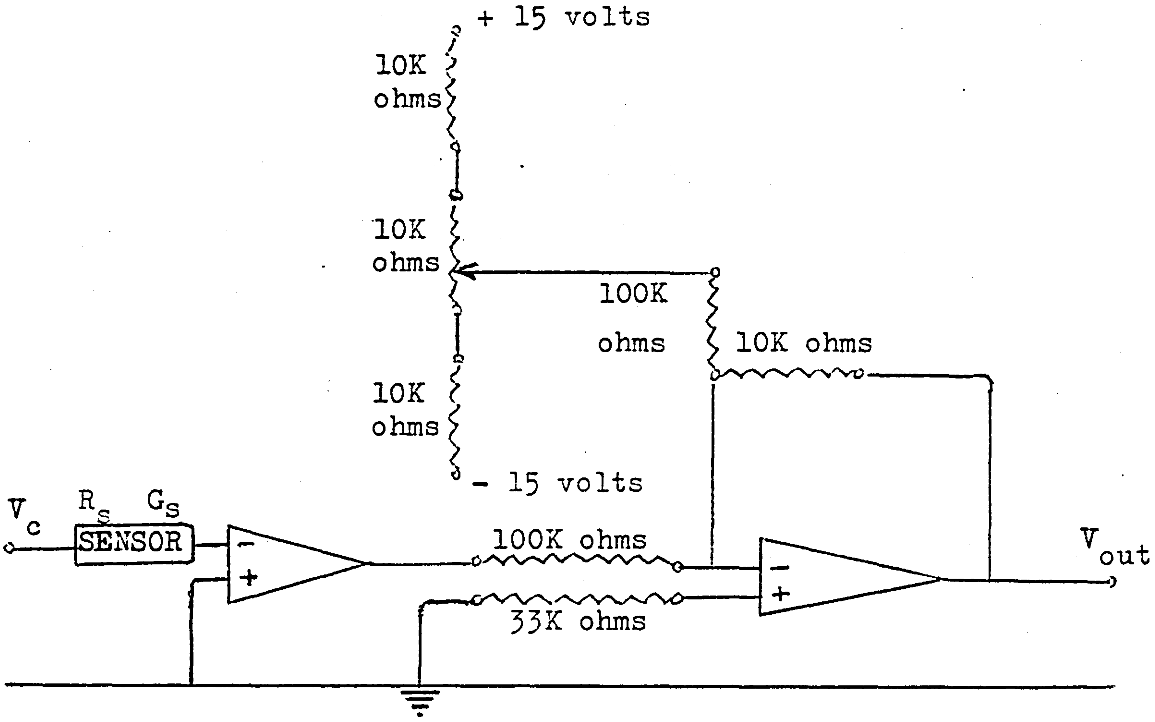
$$\frac{\text{resistance of feedback resistor}}{\text{resistance of sensor}} = \frac{R_f}{R_s} \quad \text{.. .. Equation 1.}$$

The particular characteristics of the operational amplifier (National Semiconductor Corporation, LM 741, supplied by Farnell Electronic Components Limited, Canal Road, Leeds) which was used in this work, are as follows (typical values) :-

Input impedance	2.10^6 ohms;
Output short-circuit current	25 millamperes;
Signal voltage gain	200 volts/mV.

It was found again, particularly when operating on more sensitive, i.e.narrower voltage, ranges on the recorder, that the backing-off facilities provided were sometimes inadequate. A wider range of zero control was therefore provided by using the modified operational amplifier circuit shown in Figure 4 :-

FIGURE 4 MODIFIED OPERATIONAL AMPLIFIER CIRCUIT



By applying ± 15 volts across the two 10K ohm fixed resistances in series with the 10-turn, 10K ohm potentiometer, which was fitted with a turns-counting dial numbered 1 to 999, it was possible to vary the base-line position on the recorder by up to ± 5 volts. It was also possible, by reading the dial, to measure the off-set voltage, each small division corresponding to 10 millivolts.

Using G_s to denote sensor conductance, $G_s = R_s$

and from equation 1 : $V_{out} = - V_c R_f G_s$ .. .. Equation 2

hence

$$G_s = - \frac{V_{out}}{V_c R_f} \quad \text{.. .. .. Equation 3}$$

V_{out} must allow for any off-set in the base-line (zero) position.

Use of the modified operational amplifier circuit thus enables sensor conductance values to be calculated, using the relationship in equation 3. When using the earlier circuits the amount of bias applied to the base-line was not known and actual conductance values could not, therefore be calculated.

2.4 Conditions employed for gas chromatographic analyses

As noted in Chapter 1, the main interest in this study has been in the measurement of low concentrations of carbon monoxide and hydrogen, but some time was later devoted to assessing the response of these sensors to methane, ethane, ethene, propane and ethyne.

2.4.1 Details of gas chromatographic columns used

Chromatographic columns used to assess the response of semiconductor gas sensors to these two groups of gases are described below.

Chromatographic column for hydrogen, carbon monoxide and methane

1500 x 4 millimeter internal diameter stainless steel column, packed with active carbon (Grade 208 C, 60/72 B.S. mesh particle size, supplied by Sutcliffe and Speakman Limited, Leigh, Lancashire). The adsorbent was heated in an open dish in a muffle-furnace at 200°C. for two hours immediately prior to packing the column.

Chromatographic column for methane, ethane, ethene, propane and ethyne

1500 x 4 millimeter internal diameter stainless steel column packed with active alumina (60/80 B.S. mesh particle size, supplied by Pye-Unicam, Cambridge). The adsorbent was heated in an open dish in a muffle-furnace at 250°C for two hours immediately prior to packing the column.

During the earlier stages of this work both of the chromatographic columns were operated at ambient laboratory temperature. Later a gas chromatographic oven (Series 104, Pye-Unicam, Cambridge) became available. In more recent work, the active carbon column was thermostatted at about 40°C and the active alumina column at about 60°C, using this chromatographic column oven.

2.4.2 Carrier gases used

When using cylinders of compressed air as carrier gas, in conjunction with the active carbon column, for the analysis of low concentrations of hydrogen and carbon monoxide, it was found necessary, in order to remove traces of hydrogen and carbon monoxide, to pass the carrier gas through a bed of a proprietory brand of mixed metal-oxide catalyst (Hopcalite(56), in a 150 x 5 millimeter tube, packed with plus 30 B.S. mesh particle size) electrically heated to approximately 100°C. These two gases were generally assessed to be present at sub parts per million level, but were occasionally found at the low ppm level in this commercial grade gas.

Other mixtures were used, containing various proportions of oxygen and nitrogen, including "high purity" nitrogen (Air Products Limited) as noted below.

The carrier gas flow rate was varied, as indicated in later sections but, in routine use, a carefully measured flow rate of about twenty cubic centimeters per minute was used, measured after the detector outlet at atmospheric pressure with a soap bubble flow meter.

2.4.3 Gas sample volume

Gas sample volumes, nominally half a cubic centimeter and five cubic centimeters, measured at atmospheric pressure were used, as noted below.

2.5 Preparation of standard gas mixtures

Gas mixtures required for this work were prepared on a gas-rig equipped with two pressure gauges, measuring 0 - 200 pounds per square inch and 0 - 2000 pounds per square inch, relief valve, control valves and an electrically operated air compressor.

Most of the cylinders used to contain the gas mixtures had a volume of approximately ten litres at atmospheric pressure, or one million cubic centimeters when pressurised to one hundred atmospheres (1500 pounds per square inch) ignoring any deviation from ideal gas behaviour. Others contained volumes of approximately five or twenty five litres at atmospheric pressure. The concentration levels of interest were in volumes per million of hydrogen and of carbon monoxide and in the low percentage levels, by volume, for methane. A range of glass gas pipettes, having double oblique-bore taps at each end, were available and these had previously been calibrated, by filling with mercury and weighing.

In order to prepare a mixture containing a nominal hundred parts per million of hydrogen, for example, in air the cylinder was flushed out a number of times with air and then evacuated.

A gas pipette was selected, having a volume as near as possible to one hundred cubic centimeters, and this was flushed out with cylinder hydrogen and then carefully filled with hydrogen at atmospheric pressure. This volume of hydrogen was transferred to the previously evacuated cylinder by allowing air to sweep it in to the cylinder. The cylinder was then pressurised to approximately 1500 pounds per square inch, making allowance for the exact volume of the pre-calibrated gas pipette.

To prepare mixtures containing percentage levels of gas, the volume of cylinder used need not be known. The cylinder was carefully flushed out, with nitrogen, and left filled with nitrogen at atmospheric pressure. To prepare a mixture containing one per cent by volume of methane in air, for example, the cylinder was pressurised with methane (approximately 99 per cent purity) to 15 pounds per square inch above atmospheric pressure, measured on the 0 - 200 p.s.i. gauge. To eliminate any possibility of an explosion, the cylinder was first pressurised to 1200 p.s.i. with nitrogen, in order to reduce the percentage of methane below the explosive limit. It was finally pressurised to 1500 p.s.i., using oxygen.

The estimated precision of these procedures was approximately ± 10 per cent (relative) at the ppm level and ± 3 per cent (relative) at the one per cent level.

On the basis of experience it was found that, when using the electrical compressor to pressurise cylinders, the air from this source contained several parts per million of hydrogen and of carbon monoxide. This created a problem in the preparation of gas mixtures which were to be used without prior gas chromatographic separation.

Hydrogen gives a considerably bigger response, with all sensors so far tested, than either carbon monoxide or methane and no great difficulty was experienced in making up mixtures containing a few parts per million of hydrogen, with less than one part per million of carbon monoxide and less than ten parts per million of methane as impurities, provided the cylinder was pressurised using cylinders of "oxygen-free" grade nitrogen and commercial grade oxygen instead of using the electrical compressor. However, since the response to hydrogen is approximately ten times that of carbon monoxide it was thought that the carbon monoxide mixture, for use without a gas chromatographic column should contain no more than one tenth of a part per million of hydrogen. It was not found possible tomake up mixtures containing such a low level of hydrogen and, for this reason, the response time to carbon monoxide, without a chromatographic column was not determined.

In determining the response time to methane, without prior chromatographic separation, the gas mixture was passed through a bed of Hopcalite(56) heated to approximately 100°C which removed trace concentrations of hydrogen and carbon monoxide without affecting the methane concentration.

The various stock gas mixtures, contained under pressure in cylinders were quantitatively diluted using a gas mixing pump (H.Wösthoff oHG, Bochum, German Federal Republic, Model 1M300/a F, supplied by E.D.Gilbert Limited, 2 Burton Road, Southampton) and cylinder compressed air, which could be purified by passing it over a heated catalyst (platinised honeycomb catalyst, supplied by Johnson Matthey Chemicals Limited, Orchard Road, Royston, Hertfordshire, SG8 5HE) operated at about 150°C, to remove traces of hydrogen and carbon monoxide from the diluent gas. The pump has two electrically operated and carefully matched piston pumps, the action of each being controlled by two sets of manually selected gears. It provides dilutions of one gas in another, ranging in steps of one per cent, from one per cent to ten per cent and, in steps of ten per cent from ten per cent to one hundred per cent by volume. Using water pressure gauges to ensure that gases were fed into the mixing pump under equal pressures, the accuracy and precision of the resultant mixtures has been estimated to be within ± 0.01 per cent by volume.

Dilutions of the stock gas mixtures, at levels below one per cent, were prepared by an initial dilution to one per cent in a second cylinder, using the gas rig, followed by further dilutions using the gas mixing pump.

3. INVESTIGATION OF THE PROPERTIES OF SEMICONDUCTOR GAS SENSORS

3.1 Effect on sensor response of varying the carrier gas flow rate at a number of different values of heater voltage

The variation in sensor response with carrier gas flow rate was investigated using a number of different heater voltages since preliminary experiments had indicated some degree of interaction between these variables.

In one series of experiments, variation in the response of the T.G.S.711 to hydrogen, carbon monoxide and methane was measured, using the active carbon chromatographic column.

Over a period of five consecutive days the above effects were investigated, as follows :-

	Day 1	Day 2	Day 3	Day 4	Day 5
Heater voltage(V_H)	6.5	6.0	5.5	7.0	7.5 volts DC.

Each day the carrier gas flow rate was increased step-wise, from a low value, generally between five and ten cubic centimeters per minute, to higher values and then reduced, in stages, back to lower flow rates again. Time was allowed for the carrier gas flow rate to become stabilised, at each level, and a chromatogram was then produced from a gas mixture containing 6 ppm hydrogen, 9 ppm carbon monoxide and 0.5 %(v/v) methane stored, under pressure, in a gas cylinder.

Graphs were prepared to show the variation in peak heights of hydrogen, carbon monoxide and methane with carrier gas flow rate, for each value of heater voltage, and these are reproduced in graphs one to five. The chromatographic peaks for day three, using the lowest heater voltage, exhibited pronounced "tailing". As a result, the apparent separation between hydrogen and carbon monoxide deteriorated to such an extent that carbon monoxide peak heights could no longer be measured with confidence, due to uncertainty in assessing the base line position. This is illustrated in Plate 12. The plot of peak heights for carbon monoxide against carrier gas flow rate also showed pronounced hysteresis, at this low heater voltage, and the carbon monoxide results for this day have therefore been excluded from the general assessment of results. The results for hydrogen at this low heater voltage also need to be assessed with some caution.

In a second series of experiments variation in the response of the T.G.S.812 to methane, ethane, ethene and ethyne was examined in relation to variation in the carrier gas flow rate, at three different heater voltages, as follows :-

	Day 1	Day 2	Day 3
Heater voltage (V_H)	6.0	5.5	6.5 volts DC.

As before, the carrier gas flow rate was increased, in stages, during each day and a chromatogram of a mixture containing a nominal fifteen parts per million each of methane, ethane, ethene and ethyne was produced using the active alumina chromatographic column.

Graphs showing the variation in peak heights with carrier gas flow rate, for each value of heater voltage, are reproduced in graphs 6, 7 and 8.

Assessment of results for carrier gas flow rate:

3.1.1 T.G.S. 711 response to hydrogen, carbon monoxide and methane

At the lower values of heater voltage hydrogen generally gives a maximum peak height at intermediate values of carrier gas flow rate. However, when a heater voltage of 7.5 volts is employed peak heights for hydrogen increase with increasing flow rates over the range five to thirty cubic centimeters per minute whilst further increases in carrier gas flow rate produce only minor changes in peak height (see graph 5)

The effect of changes in carrier gas flow rate on the peak heights of carbon monoxide is very small for each value of heater voltage tested.

Peak heights for methane show a progressive decrease as the carrier gas flow rate is increased. However methane and carbon monoxide both show a slight reduction in peak height at carrier gas flow rates below about ten cubic centimeters per minute.

3.1.2 T.G.S. 812 response to methane, ethane, ethene and ethyne

Methane and ethane show a progressive increase in peak heights as the carrier gas flow rate is reduced from fifty to ten cubic centimeters per minute using heater voltages of 5.5 and 6 volts DC, whereas at 6.5 volts, ethane shows a slight decrease in peak height for flow rates below twenty cubic centimeters per minute, and for methane for flow rates below twelve cubic centimeters per minute.

The flow rate at which the maximum peak height for ethene is obtained appears to increase with the value of the heater voltage, as follows :-

Heater Voltage (V_H)	Carrier gas flow rate at which T.G.S. 812 gives maximum response to ethene
5.5 volts DC	12 to 18 cm^3 $minute^{-1}$
6.0 " "	18 to 24 cm^3 $minute^{-1}$
6.5 " "	20 to 30 cm^3 $minute^{-1}$

Peak heights for ethyne are less susceptible to variation in carrier gas flow rate but show a progressive slight reduction at lower carrier gas flow rates.

From the general shape of these curves, relating the response of the T.G.S. 711 sensor to one group of gases and the T.G.S. 812 to another group of gases, it is clear that both of these semiconductor gas sensors must be classified as concentration sensitive rather than mass-flow dependent. The latter would be expected to show an almost proportionate increase in peak height response with carrier gas flow rate as is found, for example, with the flame ionisation detector.

3.2 Variation in peak height with heater voltage

In order to assess the effect of varying the heater voltage on the peak heights of hydrogen, carbon monoxide and methane, using the T:G.S. 711 sensor, the peak heights for each gas were read off from graphs 1 to 5 corresponding to heater voltages of 5.5, 6.0, 6.5, 7.0 and 7.5 volts DC for five values of carrier gas flow rate, viz. 10, 20, 30, 40 and 50 cubic centimeters per minute. These values have been plotted for each gas, to show the variation in peak height with heater voltage, for each of the flow rates selected, and are reproduced in graph 9 for hydrogen, graph 10 for carbon monoxide and graph 11 for methane.

The effect of varying the heater voltage of the T.G.S. 812 on its response to methane, ethane, ethene and ethyne was investigated in s similar manner using the data from graphs 6, 7 and 8. The response for each gas, at each value of heater voltage, was plotted for the same range of carrier gas flow rates and these are reproduced in graph 12 for methane, graph 13 for ethane, graph 14 for ethene and graph 15 for ethyne.

Variation in the response of the T.G.S. 812 to hydrogen, carbon monoxide and methane with changes in the value of the heater voltage were determined, during one day, using a constant carrier gas flow rate of twenty cubic centimeters per minute. Chromatograms of a mixture containing 100 ppm of hydrogen, 1200 ppm of carbon monoxide and 4% (v/v) methane were obtained at five different values of heater voltage and the peak heights have been plotted in graph 16.

The effect of varying the heater voltage on the response of the Matsushita sensor was determined for the two groups of gases: hydrogen, carbon monoxide and methane and for methane, ethane, ethene, propane and ethyne. In this case the heater voltage was varied between 3.5 and 5 volts DC and the results have been plotted in graphs 17 and 18.

The effect of varying the heater voltage on the response of the I.S.T. sensor was investigated using the active carbon chromatographic column and a mixture containing 6 ppm hydrogen, 9 ppm carbon monoxide and 0.5% (v/v) methane with an air carrier gas flow rate of twenty cubic centimeters per minute. At this time, due to a temporary increase in the requirement for potentiometric recorders within the laboratory, it was necessary to use a 0 to 250 microampere moving-coil recorder, having an internal resistance of 1.4K ohms.

The I.S.T. sensor was intended for measuring the percentage of the lower explosive limit of methane and the suppliers recommended that the heater voltage be operated between 2.3 and 2.45 volts DC. The heater voltage was, in fact, varied over a wider range, extending from 2.0 to 3.0 volts DC. The variation in response to hydrogen and methane within this range of heater voltage was noted and the results have been plotted in graph 19.

In order to facilitate comparison of response between different types of sensor to the same range of gases under the same operating conditions the current drawn by each sensor was measured using a milliammeter in series with each sensor, over a range of heater voltages, and the energy dissipated by each sensor, at each heater voltage, was calculated. These values are given in Tables 5, 6 and 7 and are reproduced in graph 20.

Since the physical form of the three Taguchi gas sensors appear to be identical it may be expected that the same wattage dissipation for each sensor will produce equal temperatures. This consideration will not apply to the Matsushita nor to the I.S.T. sensors, however, since their physical forms are quite different from the Taguchi models.

An attempt was also made to measure the temperature of each of the Taguchi gas sensors over a range of heater voltages. Two methods of temperature measurement were attempted.

The first method involved the use of a differential infra-red scanner (Probeye, manufactured by Hughes Aircraft Corporation, Industrial Products Division, Image Devices, Carlsbad, California, supplied by Mine Safety Appliances Limited, East Shawhead, Coatsbridge, Scotland, ML5 1HA). The advantage of this method was that the need for physical contact with the semiconductor sensor, with consequent thermal loss, was eliminated and that, according to the claims of the manufacturer, temperature differences of only a few degrees Celsius could be distinguished. The instrument was not calibrated and, in order to measure a temperature, it was necessary to match the intensity of the image produced by infra-red radiation, as seen through the instrument, with that produced by another heat source whose temperature could be varied and measured. For this purpose a brass cylinder was used

TABLE 5 CALCULATED WATTAGES OF THREE TAGUCHI 711 SENSORS OVER A RANGE OF HEATER VOLTAGES.

Sensor 711(1)			Sensor 711(2)			Sensor 711(3)		
Heater voltage (V_H) volts	Current mA.	Calculated wattage watts	Heater voltage (V_H) volts	Current mA.	Calculated wattage watts	Heater voltage (V_H) volts	Current mA.	Calculated wattage watts
0.5	4.9	0.0024	0.5	4.8	0.0024	0.5	4.6	0.0023
1.0	9.6	0.0096	1.0	9.55	0.0095	1.0	9.2	0.0092
1.5	15.1	0.023	1.5	14.9	0.022	1.5	14.45	0.022
2.0	20.2	0.04	2.0	20.05	0.04	2.0	19.5	0.039
2.5	25.5	0.064	2.5	25.4	0.063	2.5	24.5	0.061
3.0	30.55	0.092	3.0	30.35	0.091	3.0	29.45	0.088
3.5	35.8	0.125	3.5	35.55	0.124	3.5	34.3	0.12
4.0	40.95	0.164	4.0	40.7	0.163	4.0	39.2	0.157
4.5	46.2	0.21	4.5	46.15	0.207	4.5	44.45	0.2
5.0	51.2	0.26	5.0	50.95	0.255	5.0	49.15	0.245
5.5	56.7	0.31	5.5	56.45	0.31	5.5	54.5	0.3
6.0	61.8	0.37	6.0	61.65	0.37	6.0	59.6	0.356
6.5	67.1	0.44	6.5	66.85	0.43	6.5	64.6	0.42
7.0	72.05	0.51	7.0	72.0	0.50	7.0	69.55	0.49
7.5	77.0	0.58	7.5	76.95	0.58	7.5	74.55	0.56
8.0	81.8	0.65	8.0	81.75	0.65	8.0	79.25	0.63
8.5	86.9	0.74	8.5	86.65	0.74	8.5	84.35	0.72
9.0	91.45	0.82	9.0	91.35	0.82	9.0	89	0.80
9.5	96	0.91	9.5	95.9	0.91	9.5	93.6	0.89
10.0	100.3	1.00	10.0	100.5	1.00	10.0	98	0.98

TABLE 6 CALCULATED WATTAGES OF THREE TAGUCHI 812 SENSORS OVER A RANGE OF VOLTAGES

Sensor 812(1)			Sensor 812(2)			Sensor 812(3)		
Heater voltage (V_H)volts	Current mA.	Calculated wattage watts	Heater voltage (V_H)volts	Current mA.	Calculated wattage watts	Heater voltage (V_H)volts	Current mA.	Calculated wattage watts
0.5	11	0.0055	0.5	10	0.005	0.5	10	0.005
1.0	22	0.022	1.0	22	0.022	1.0	22	0.022
1.5	33	0.05	1.5	35	0.053	1.5	36	0.054
2.0	45	0.09	2.0	48	0.096	2.0	48	0.096
2.5	58	0.145	2.5	60	0.15	2.5	62	0.155
3.0	72	0.22	3.0	75	0.225	3.0	76	0.23
3.5	83	0.29	3.5	87	0.3	3.5	88	0.31
4.0	95	0.38	4.0	98	0.38	4.0	101	0.4
4.5	106	0.48	4.5	111	0.5	4.5	112	0.5
5.0	117	0.58	5.0	122	0.61	5.0	124	0.62
5.5	128	0.7	5.5	133	0.73	5.5	137	0.75
6.0	139	0.83	6.0	145	0.87	6.0	148	0.89
6.5	151	0.98	6.5	158	1.03	6.5	160	1.04
7.0	162	1.13	7.0	170	1.19	7.0	173	1.21
7.5	173	1.3	7.5	180	1.35	7.5	183	1.37
8.0	184	1.47	8.0	191	1.53	8.0	194	1.55

TABLE 7 CALCULATED WATTAGES OF THREE DIFFERENT TYPES OF SEMICONDUCTOR GAS SENSORS OVER A RANGE OF HEATER VOLTAGES

T.G.S.813			Matsushita L.N.G. sensor			I.S.T. sensor		
Heater voltage (V_H)volts	Current mA.	Calculated wattage watts	Heater voltage (V_H)volts	Current mA.	Calculated wattage watts	Heater voltage (V_H)volts	Current mA.	Calculated wattage watts
2	62	0.124	1.0	72	0.072	0.5	100	0.055
3	95	0.285	1.5	108	0.125	1.0	113	0.11
4	128	0.51	2.0	140	0.28	1.5	174	0.26
5	158	0.79	2.5	175	0.44	2.0	222	0.44
6	185	1.11	3.0	203	0.61	2.5	280	0.7
7	215	1.51	3.5	247	0.87	3.0	326	0.98
			4.0	272	1.09	3.5	368	1.29
			4.5	307	1.39	4.0	412	1.65
			5.0	340	1.70			

approximately fifty millimeters in length and twenty millimeters in diameter. An electric heating element of nichrome wire was wound around the brass cylinder over an asbestos paper covering, and thick asbestos tape provided thermal insulation. A thermometer socket, approximately five millimeters in diameter and forty millimeters in depth was drilled into one end.A variable voltage supply for the heating element was provided from a variable voltage source (Cressall Torovolt Model 66 ZP; The Cressall Manufacturing Company Limited, Birmingham)

In order to measure the temperature of the semiconductor sensors the top covers were removed. The heater voltage to the sensor was supplied, as in normal operation, from the variable stabilised voltage supply unit.

The other method of measuring the temperature involved holding a small chrome/alumel thermocouple bead in close contact with the small cylindrical shaped gas sensing element. The thermocouple cold junction was immersed in iced water and the millivoltage output was measured using a multi-range potentiometric recorder (Servoscribe, Model RE 511.20)

In this case it must be assumed that the thermocouple bead and leads act, to some extent, as a heat sink. The recorded temperature would thus be expected to be somewhat lower than under normal operating conditions and lower than the temperature assessed when using the infra-red scanner.

The recorded temperatures for the T.G.S. 711 at heater voltages varying from 5 to 10 volts DC, for the T.G.S.812 from 3to 8 volts DC and for the T.G.S. 813 from 3 to 7 volts DC are reproduced in graph 21.

In the first series of experiments one sample each of a heater voltage of 6.5 volts DC. An attempt was made to assess the temperature of each sensor in turn, varying the heater voltage to the brass cylinder until the intensities of infra-red radiation from the semiconductor sensor and the end of the brass cylinder, when viewed with the thermal scanner appeared to be exactly matched. The temperature of the brass cylinder as indicated by a thermometer in the socket was then noted.

In a second series of experiments an attempt was made to determine what values of heater voltage for the T.G.S. 812 and T.G.S. 813 would give the same operating temperature as the T.G.S. 711 when operated at 6.5 volts DC. In this case, with the T.G.S. 711 operated at 6.5 volts, the heater voltage supplied to the T.G.S. 812 and T.G.S. 813 were varied, in turn, until the intensity of infra-red radiation from each sensor, when viewed through the thermal scanning instrument appeared to be equal.

(i) Results of temperature measurements of the gas sensors types 711, 812 and 813 when all are operated at a heater voltage of 6.5 volts DC.

	T.G.S.711	T.G.S.812	T.G.S.813
Temperature of brass cylinder when its infra-red radiation appeared to equal that of each gas sensor /°C.	150	250	315
Temperature assessment using the thermocouple method /°C.	145	250	285

As expected the temperature assessment of the T.G.S. 711, when using the thermocouple method of measurement , is lower than when using the infra-red scanner method. A corresponding the temperature difference in the case of the T.G.S. 813 is, perhaps, larger than would have been expected.

(ii) Assessment of the heater voltage requirements of the T.G.S.812 and T.G.S. 813 to match the temperature of the T.G.S. 711 when the latter is operated at 6.5 volts DC.

	T.G.S.711	T.G.S.812	T.G.S.813
Assessment using the infra-red scanning instrument /volts DC.	6.5	4.15	3.15
Temperature of each sensor, assessed by thermocouple measurement when operated at this voltage /°C.	145	141	108

In order to test the hypothesis, that equal wattage dissipation by each type of Taguchi sensor could be expected to produce equal sensor temperatures, a plot of wattage dissipation against sensor temperature, as determined by thermocouple measurement, for the three types of Taguchi sensor is reproduced in graph 22.

Good correlation is found for the T.G.S. 711 and T.G.S. 812 but a bias, equivalent to a mean temperature difference of 10 - 15°C or 0.05 to 0.07 watts is noted in the case of the T.G.S. 813.

Assessment of results for heater voltage

3.2.1. T.G.S. 711 response to hydrogen, carbon monoxide and methane

The conclusions to be drawn concerning the variation in response of the T.G.S. 711 sensor to hydrogen, carbon monoxide and methane with heater voltage, illustrated in graphs 9, 10 and 11 are as follows :-

For hydrogen, the heater voltage (wattage) giving maximum response increased with the carrier gas flow rate, as illustrated in graph 9 :

Carrier gas flow rates:	Heater voltage (V_H) at which the T.G.S. 711 gives maximum response to hydrogen (volts DC)
10 $cm^3 min^{-1}$	5.5
20-30 $cm^3 min^{-1}$	6.0
40-50 $cm^3 min^{-1}$	6.5

For all flow rates tested, carbon monoxide showed a progressive decrease in response as the heater voltage is increased from 6.0 volts to 7.5 volts DC (graph 10), whereas methane response increased with heater voltage (graph 11).

3.2.2 T.G.S. 812 response to methane, ethane, ethene and ethyne.

The variation in response of the T.G.S. 812 sensor to methane, ethane, ethene and ethyne with heater voltage is illustrated in graphs 12 to 15 inclusive. It is noted that methane and ethane show increasing peak heights with increasing heater voltage for all carrier gas flow rates except that, at the lowest carrier gas flow rate (10 cm^3 $minute^{-1}$) ethane shows a maximum response at a heater voltage of 6 volts (0.86 watts).

The two unsaturated compounds, ethene and ethyne, exhibit the opposite trend i.e. both show increasing peak heights at lower values of the heater voltage, over the range 6.5 to 5.5 volts DC (1.01 to 0.73 watts).

3.2.3 T.G.S. 812 response to hydrogen, carbon monoxide and methane

The variation in the response of the T.G.S. 812 to hydrogen, carbon monoxide and methane resulting from changes in heater voltage over the range 5.0 to 6.0 volts (0.6 to 0.86 watts) is illustrated in graph 16.

a continuous increase with heater voltage over the range tested. Hydrogen and carbon monoxide show much less variation in response with heater voltage. In this case, at a flow rate of 20 $cm^3 minute^{-1}$, hydrogen response is greatest at a heater voltage of about 5.5 volts (0.73 watts). Carbon monoxide shows a slight increase in response at lower heater voltages, down to 5 volts DC (0.6 watts).

3.2.4 Response of the Matsushita sensor to hydrogen, carbon monoxide and methane.

The change in response of the Matsushita sensor to the same three gases was determined by varying the heater voltage over the range 3.5 to 5 volts DC. Over this range, methane showed a continuous increase in response with heater voltage, the gradient of the response curve increasing markedly for heater voltages in excess of 4.2 volts.Carbon monoxide shows a maximum peak height response in the region of 4.2 volts and hydrogen response increases with heater voltage at least up to 5 volts but the slope of the curve decreases in the region 4.5 to 5 volts.

It should be noted, particularly at higher heater voltages, that the actual peak heights for methane are considerably more than ten times those of hydrogen and carbon monoxide, which have been plotted on a more sensitive scale to show up the relatively minor changes in response to these two gases.

3.2.5 Response of the Matsushita sensor to methane, ethane, ethene, propane and ethyne.

The change in response of the Matsushita sensor to methane, ethane, ethene, propane and ethyne when the heater voltage is varied over the range 3.6 to 5.2 volts DC is illustrated in graph 18. The increase in methane response with increasing heater voltage response at least up to 4.5 volts DC. Propane peak height appears to reach a maximum at a heater voltage of about 4.6 volts and the slopes of the ethane and ethene response curves are less steep above heater voltages of 4.8 and 4.6 respectively. Ethyne peak heights increase very slightly as the heater voltage is increased from 3.6 to about 4.5 volts; the slope of the response curve is noticeably steeper at values of V_H in excess of 4.8 volts.

3.2.6 Response of the I.S.T. sensor to hydrogen, carbon monoxide and methane.

The variation in the response of the I.S.T. sensor to hydrogen, carbon monoxide and methane resulting from changes in the heater voltage over the range 2.0 to 3.0 volts DC is illustrated in graph 19. No response to carbon monoxide (at the parts per million level) could be detected over this range of heater voltage.

In contrast to the other sensors examined, methane response is more critically dependent upon heater voltage and exhibits a maximum response in the region of 2.4 volts i.e. within the heater voltage range of 2.3 to 2.45 volts recommended by the suppliers. The methane response falls off sharply at heater voltages above and below these values.

Compared with Taguchi sensors, the response of the I.S.T. sensor to hydrogen is relatively small and varies rather more with the heater voltage. Maximum response to hydrogen is obtained at a heater voltage in the region of 2.2 volts DC.

3.2.7 Review of results relating variation in response with heater voltage, for all sensors.

Attempting an overall review of the results relating peak height response of the various sensors with heater voltage, a comparison may be made, firstly, between the variation in response of the T.G.S. 711, the T.G.S. 812, the Matsushita and I.S.T. sensors to hydrogen, carbon monoxide and methane and, secondly, between the variation in response of the T.G.S. 812 and the Matsushita sensors to the lower hydrocarbon gases.

The T.G.S. 711 was tested using heater voltages which were varied between 5.5 and 7.5 volts (0.3 to 0.57 watts) and exhibited a maximum response to hydrogen, for most carrier gas flow rates, within the range 6.0 to 6.5 volts (0.36 to 0.43 watts). The T.G.S. 812 was tested by varying the heater voltage between 5 and 6 volts (0.6 to 0.86 watts) and, at a carrier gas flow rate of 20 $cm^3 minute^{-1}$, a maximum response to hydrogen was obtained with heater voltages between 5.4 and 5.7 volts (0.7 to 0.78 watts).

The shape of the curves relating variation in hydrogen response to sensor heater voltage appear similar for the T.G.S.711 and the T.G.S. 812 sensors but the fact that the T.G.S. 711 sensor gives a maximum hydrogen response when operated at a temperature in the region of 140°C (see graph 22) and the T.G.S. 812 only achieved maximum hydrogen response at a temperature well in excess of 200°C suggests that there must be a significant difference in composition between these two sensors. The general shape of the curve relating hydrogen response to heater voltage for the Matsushita and I.S.T. sensors are not very different from those of the Taguchi sensors, but for the former sensors, temperatures of the sensor beads cannot be quoted.

The Matsushita sensor gives a maximum response to carbon monoxide within the relatively narrow range of heater voltage between 4.1 and 4.4 volts, whereas the I.S.T. sensor gives no measurable response to carbon monoxide at the parts per million level. The response of the T.G.S. 711 to carbon monoxide shows a greater variation with heater voltage than that of the T.G.S. 812.

The response to methane using the T.G.S. 711, T.G.S. 812 and the Matsushita sensor in each case increases with heater voltage over the range tested, whereas the I.S.T. sensor shows a maximum response to methane within the relatively narrow range of heater voltage of 2.3 to 2.6 volts, and a maximum response to hydrogen at the only slightly lower level of 2.1 to 2.3 volts.

The variation in response of the T.G.S. 812 and the Matsushita sensors to the lower hydrocarbon gases appear, at first sight, to be rather different. The heater voltage of the Matsushita sensor was varied over the range 3.5 to 5.2 volts. Over this range methane and ethyne exhibit increasing response with increasing heater voltage and propane gives a maximum response with heater voltages between 4.4 and 4.8 volts. The response to ethane and ethene increases fairly steeply over the range of heater voltages 3.5 to 4.5 volts but the response shows signs of levelling off at heater voltages between 4.8 and 5.2 volts

The heater voltage for the T.G.S. 812 sensor was only varied between 5.5 and 6.5 volts; within this range the saturated hydrocarbons, methane and ethane, show an increasing response with heater voltage, whereas the unsaturated hydrocarbons, ethene and ethyne, show the opposite trend. With the benefit of hindsight, it would have been interesting to test the T.G.S. 812 sensor over a wider range of heater voltage.

For the analysis of mixtures containing hydrogen, carbon monoxide and methane, using the Taguchi 711 sensor, a heater voltage of 6.0 to 6.5 volts and a carrier gas flow rate in the region of 20 to 30 cm^{3}minute^{-1} is recommended. These conditions provide :-

(i) relatively small variation in peak height with changes in carrier gas flow rate (see graph 3) and

(ii) a satisfactory compromise in terms of sensitivity to each gas, in terms of mine air analysis.

Operating with a heater voltage of 6 instead of 6.5 volts gives a slight improvement in response to hydrogen and carbon monoxide (see graphs 9 and 10), whereas increasing the heater voltage from 6 to 6.5 volts almost doubles the response to methane

3.3 The symmetry of gas chromatographic peaks using semiconductor sensors

In this section data are presented relating to the speed of response of the T.G.S. 711 to hydrogen and methane. An attempt is made to quantify peak asymmetry and to determine those operating conditions under which peak "tailing" is reduced.

To determine the true response times to individual gases it is necessary to eliminate the varying concentration profile of gas chromatographic peaks. This was done by operating with "single component" gas mixtures in air and without a chromatographic column.

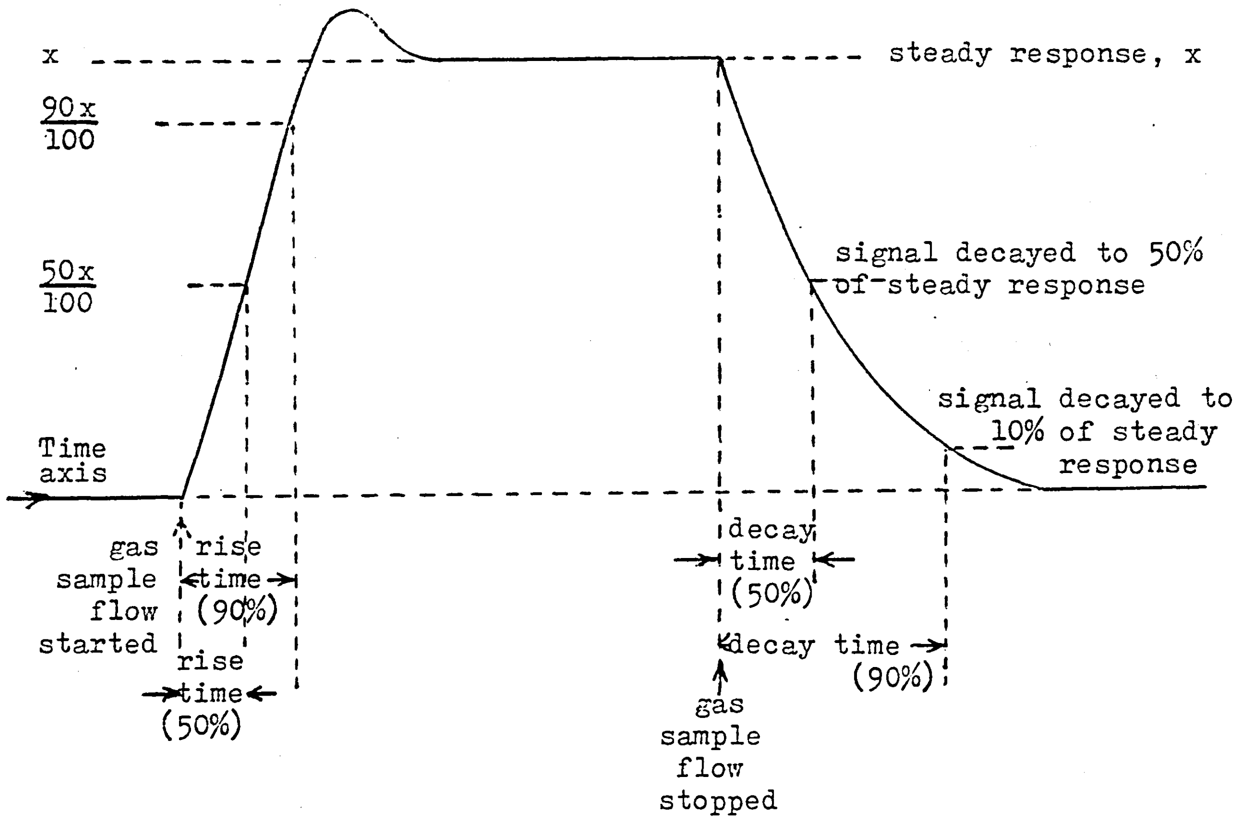
Gas was fed from a cylinder containing the hydrogen/air or methane/air mixture to one limb of a two-way oblique-bore glass tap. Compressed air from a cylinder (B.O.C. Limited), after passing through a bed of Hopcalite(53) to remove trace hydrogen and carbon monoxide impurities, was fed to the second limb of this tap. The outlet limb of the tap was connected directly to the gas inlet tube of the semiconductor gas sensor.

In the first series of experiments response times of the T.G.S. 711 sensor to a mixture containing 4 ppm hydrogen in air were measured using four different values of heater voltage (5.0, 6.0, 6.5 and 7.0 volts DC). On turning the glass tap to cut off the flow of purified air and substitute the hydrogen mixture some degree of overshoot was noted except at the lowest heater voltage. The amount of overshoot was reduced, to some extent, by inserting a short length of narrow-bore tubing between the glass tap and the inlet to the semiconductor gas sensor. The hydrogen mixture was allowed to flow for 10 to 15 minutes in order to give sufficient time for the signal to settle to a constant reading before reverting to the purified air flow. In later experiments these "exposure times" were carefully measured and varied.

The following measurements, noted in Figure 5, were made :-

Rise time (50%); Decay time (50%);
Rise time (90%); Decay time (90%).

FIGURE 5 MEASUREMENT OF THE RESPONSE TIME OF THE T.G.S. 711
ILLUSTRATION OF THE PARAMETERS WHICH WERE MEASURED.
TO 4 ppm OF HYDROGEN WITHOUT A CHROMATOGRAPHIC COLUMN;
ILLUSTRATION OF THE PARAMETERS WHICH WERE MEASURED.



of hydrogen in air mixture, without a chromatographic column.

The response and decay times of the T.G.S. 711 to a gas mixture containing 4 ppm of hydrogen in air were measured and are recorded in Table 8

TABLE 8 Response and decay times of T.G.S. 711 to a mixture containing 4 ppm hydrogen in air, without a chromatographic column.

Heater voltage (V_H) (volts)	Rise time (seconds)		Decay time (seconds)	
5.0	(50%)	40	(50%)	156
	(90%)	160	(90%)	820
6.0	(50%)	10	(50%)	41
	(90%)	25	(90%)	390
6.5	(50%)	6	(50%)	49
	(90%)	16.5	(90%)	350
7.0	(50%)	6	(50%)	22
	(90%)	12	(90%)	550

The above results have been plotted in graph 23 from which it is noted :-

(i) the response times are longer at lower heater voltages;

(ii) the reduction in response times for heater voltages above 6 volts DC are relatively small;

(iii) decay times are always considerably longer than the corresponding rise times and the large difference between the 50% and 90% decay times suggests some kind of exponential decay in the response.

Using a heater voltage of 7.0 volts the response times to 4 ppm of hydrogen were measured, using much shorter exposure times, as follows :-

TABLE 9 Variation in the response and decay times of the T.G.S. 711 to a mixture containing 4 ppm hydrogen in air, without a chromatographic column, varying the "exposure times"

	Rise time (seconds)	Decay time (seconds)
Sample flow for 60 seconds	(50%) 6 (90%) 15	(50%) 15 (90%) 90
Sample flow for 15 seconds	(50%) 7 (90%) 15	(50%) 12 (90%) 72

A shorter exposure time is clearly associated with a marked reduction in the decay times, although the rise times are hardly affected.

3.3.2 The response times and decay times of the T.G.S. 711 to a 0.38%(v/v) methane in air mixture, without a chromatographic column

In another series of experiments the rise and decay times of the T.G.S. 711 sensor to a gas mixture containing 0.38%(v/v) methane in air mixture were measured, at two different values of the heater voltage, and the results are recorded below. In this case a rotameter, calibrated for air flow rates, was connected to the outlet from the gas sensor. Flow rates of the methane/air mixture from the cylinder were varied by adjustment of the cylinder reducing valve and measured on the rotameter at the outlet. Exposure times were varied, as indicated.

TABLE 10 Rise and decay times of the T.G.S. 711 to a 0.56%(v/v) methane in air mixture, without a chromatographic column, varying the sample flow rate and exposure times.

(i) Heater voltage (V_H) = 6.5 volts DC.

Sample flow rate (cm^{3}minute^{-1})	Exposure time (minutes)	Rise times (seconds) (50%)	(90%)	Decay times (seconds) (50%)		(90%)	
20	5	9	19	48		300	
20	10	9	18	60	mean = 74	480	mean =620
20	10	9	18	90		980	
20	10	9	18	72		390	
20	5	10	19	72		342	mean =321
20	5	10	19	72		300	
35	5	6	12	90		540	
35	10	7	14	114		630	
5	10	36	63	90		440	
(ii) Heater voltage (V_H) = 7.0 volts DC							
8.8	10	14	25	84		252	
8.8	5	13	26	81		222	
20	5	6	13	30		210	
20	1	6	16	30		170	
20	1	6	17	34		180	
20	24	6	12	32		360	

Conclusions drawn from the above figures are as follows :-

(i) conclusions numbered (i) and (iii) concerning the response times of the T.G.S. 711 to hydrogen are confirmed by the above results relating to its response to methane;

(ii) small but significant reductions in response times to methane are noted as a result of increasing the heater voltage from 6.5 to 7.0 volts DC;

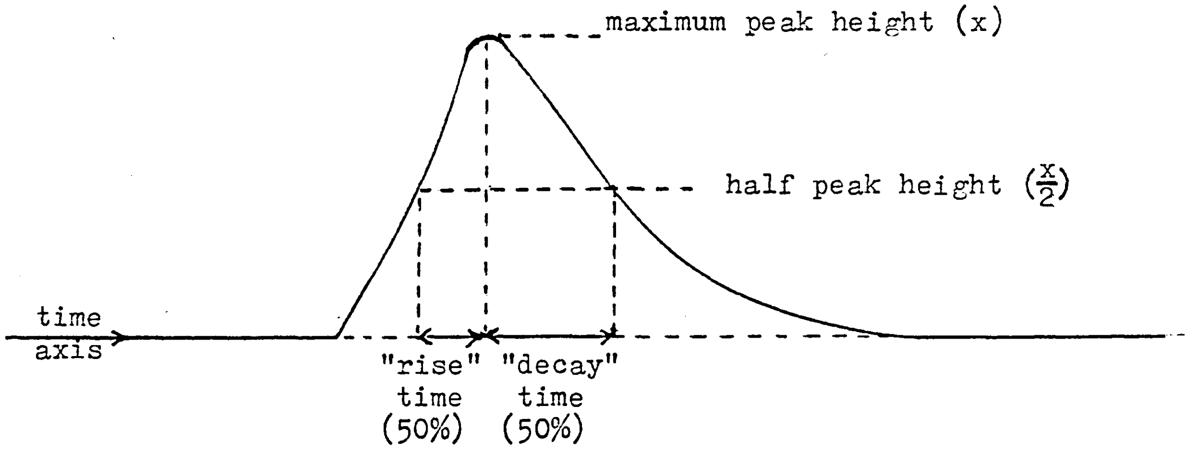
(iii) It would appear that, over the range of sample flow rates and exposure times tested, the 90% decay time is related to the total mass of methane which has passed over the sensor

It is noted that a shorter exposure time is associated with a marked reduction in the decay times, for both hydrogen and methane. The above figures consequently cannot be directly related to the degree of tailing of chromatographic peaks without some independent information concerning the time taken for each peak of interest to elute from the chromatographic column ("peak width" ≃ "exposure time"). Even then equivalence would not be exact, since the concentration profile of a chromatographic peak is approximately Gaussian shaped whereas, in the above experiments, the concentration change is almost instantaneous (square-wave).

3.3.3 Direct measurement of gas chromatographic peak asymmetry: the skew factor.

In order to obtain a direct measure of peak asymmetry chromatograms were produced using an active carbon column to separate mixtures containing 6 ppm of hydrogen, 9 ppm of carbon monoxide and 0.5%(v/v) methane in conjunction with the T.G.S. 711 sensor and the following parameters were measured :

FIGURE 6 Gas chromatographic peak parameters measured in order to determine the skew factor



In this case rather than use the 90% rise and decay times, these being particularly sensitive to changes in exposure times and heater voltage and also more difficult to measure accurately, particularly in conjunction with a slightly drifting base-line, it was decided to adopt a measure of peak asymmetry, or skewness, defined as :-

$$\text{skew factor} = \frac{\text{time from peak maximum falling to half-height(tail)}}{\text{time from half-height(front) rising to peak maximum}}$$

Perfectly symmetrical chromatographic peaks would therefore have a skew factor of 1.0.

The suggestions of some other workers for methods of measuring skewness of chromatographic peaks are given in the Appendix for purposes of comparison.

The tendency for semiconductor gas sensors to produce "tailing" of gas chromatographic peaks is probably one of their major disadvantages. It was therefore proposed to examine the variation in skew factor with carrier gas flow rate and with the sensor heater voltage, in an attempt to identify those operating conditions which would minimise peak asymmetry.

3.3.3.1 Variation of skew factor with carrier gas flow rate

A similar procedure was adopted to that used when determining the dependence of peak heights on carrier gas flow rate and sensor heater voltage. Over a period of three days chromatograms of a mixture containing 6 ppm of hydrogen, 9 ppm of carbon monoxide and 0.5%(v/v) methane were produced, using the active carbon column. A different value of sensor heater voltage was employed each day and, within each day, the carrier gas flow rate was varied. A recorder chart speed of 60 centimeters per hour was employed during these experiments to enable sufficiently accurate measurements to be taken from the charts.

Times from half peak height (front) to peak maximum and from peak maximum to half peak height (tail) were measured, for each chromatographic peak, and the skew factors calculated. The variation in skew factor with carrier gas flow rate for hydrogen, carbon monoxide and methane peaks have been plotted in graphs 24, 25 and 26 for heater voltages of 6.0, 6.5 and 7.0 volts DC respectively.

Lower skew factors i.e. more symmetrical peaks, tend to be produced at lower carrier gas flow rates. The methane skew factor is less affected by the carrier gas flowrate, however, than that of hydrogen or carbon monoxide and this dependency upon flow rate generally becomes less at higher heater voltages i.e. at higher semiconductor bead temperatures.

Methane and carbon monoxide skew factors, at heater voltages of 6.0 and 7.0 volts appear to vary in an almost linear fashion with carrier gas flow rate over the relatively narrow range of flow rates tested. At a heater voltage of 6.5 volts, however, when a wider range of carrier gas flow rates was employed, gross departure from linearity is found, particularly at the highest carrier gas flow rates.

3.3.3.2 Variation of skew factor with heater voltage

Graphs 27, 28 and 29 have been constructed for hydrogen, carbon monoxide and methane, showing the variation of skew factor with heater voltage, at four selected values of carrier gas flow rate, varying from 10 to 40 $cm^3 minute^{-1}$.

Minimum values for the hydrogen skew factor (1.40 - 1.45) occur at a heater voltage of 6.5 volts for carrier gas flow rates of 10 and 20 $cm^3 minute^{-1}$. For carrier gas flow rates of 30 and 40 $cm^3 min.^{-1}$ the minimum skew factors for hydrogen are obtained using a heater voltage of 7.0 volts (1.45 and 2.0 respectively).

For carbon monoxide, minimum values of skew factor for each carrier gas flow rate are obtained with a heater voltage of 6.5 volts.

The values increase regularly from a value of 1.6 with a carrier gas flow rate of 10 $cm^3 minute^{-1}$, up to 2.1 at a flow rate of 40 $cm^3 minute^{-1}$.

The skew factors for methane tend to reduce at higher values of heater voltage, for each of the carrier gas flow rates. The lowest skew factor for methane was 1.35 at a flow rate of 10 $cm^3 minute^{-1}$, and increase to about 1.5 for flow rates of 30 and 40 $cm^3 minute^{-1}$.

Summarising the results relating to the variation in peak symmetry with carrier gas flow rate and heater voltage (graphs 24 to 29, inclusive), it is noted that the most satisfactory conditions to employ for the analysis of mixtures containing hydrogen, carbon monoxide and methane are to use a heater voltage of 6.0 to 6.5 volts, coupled with a carrier gas flow rate in the region of 20-30$cm^3 minute^{-1}$. The main advantages of working under these conditions are :-

(i) the skew factor is low for all three gases;

(ii) the skew factor varies less with carrier gas flow rate for all three gases (see graph 25);

(iii) these conditions coincide with those already recommended in section 3.2.7 (pages 54 - 55).

3.3.4 Variation in apparent column efficiency with changes in the carrier gas flow rate and in the heater voltage (V_H)

The same series of chromatograms, as described in Section 3.3.3, were used to investigate the variation in apparent column efficiency with carrier gas flow rate and heater voltage.

3.3.4.1 Variation in apparent column efficiency with changes in carrier gas flow rate.

The apparent column efficiencies for hydrogen, carbon monoxide and methane were calculated from measurements taken from the chromatograms described in Section 3.3.3, employing heater voltages of 6.0, 6.5 and 7.0 volts DC and for each carrier gas flow rate.

The results, showing the variation in apparent column efficiency with carrier gas flow rate, are plotted in graphs 30, 31 and 32, using the relationship : number of theoretical plates, $n = 16(\frac{x^2}{y^2})$, where y denotes the peak width and x denotes the retention time to peak maximum.

Higher apparent column efficiencies tend to be obtained at lower carrier gas flow rates but, in the case of methane and, to a lesser extent for hydrogen, they tend to fall off again at the lowest carrier gas flow rates. The apparent column efficiency figures for hydrogen, being the first eluted peak, are always low, however, and show less variation with carrier gas flow rate. A summary of these results is given in Table 11.

3.3.4.2 Variation in apparent column efficiency with heater voltage

Graphs 33, 34 and 35 have been constructed, for hydrogen, carbon monoxide and methane respectively, to show the variation in apparent column efficiency with heater voltage, for each gas, at five selected carrier gas flow rates, varying from 10 $cm^3minute^{-1}$ to 50 $cm^3minute^{-1}$.

This data is summarised in Table 11 (next page).

Hydrogen shows consistently higher apparent column efficiencies, for each carrier gas flow rate, at higher values of the heater voltage.

Carbon monoxide exhibits highest apparent column efficiencies at a heater voltage of 6.5 volts, whilst the efficiency figures at a heater voltage of 7.0 volts are consistently higher than those obtained with a heater voltage of 6.0 volts, for each carrier gas flow rate.

Apparent column efficiencies for methane at lower carrier gas flow rates (10 to 30 $cm^3minute^{-1}$, inclusive) are higher at a heater voltage of 6.5 volts. At flow rates of 40 - 50 $cm^3minute^{-1}$ apparent column efficiencies are higher at a heater voltage of 7 volts.

TABLE 11 Variation in apparent column efficiency with heater voltage and over a range of carrier gas flow rates

Heater voltage (V_H) volts DC	Carrier gas flow rate $cm^3 minute^{-1}$	Apparent number of theoretical plates		
		Hydrogen	Carbon monoxide	Methane
6.0	10	40	182	278
6.0	20	31	114	218
6.0	30	22	68	145
6.0	40	13	38	92
6.0	50	6	20	50
6.5	10	54	245	285
6.5	20	52	195	327
6.5	30	35	132	284
6.5	40	29	88	214
6.5	50	24	65	157
7.0	10	60	247	278
7.0	20	55	177	284
7.0	30	49	121	263
7.0	40	43	80	240
7.0	50	37	44	171
Mean column efficiency with katharometer detector	25	290	not detected	380

The same chromatographic column as was used in the foregoing experiments was operated, using argon as carrier gas, in conjunction with a thermistor-type katharometer detector to compare the column efficiencies for this system with the one already described, using the T.G.S. 711 sensor as the gas chromatographic detector.

Column efficiencies for hydrogen were approximately five times higher when using the katharometer detector with argon carrier gas and the column efficiency for methane was almost twice as high with the katharometer system as the apparent column efficiency when using the semiconductor detector.

All of the above findings tend to confirm that the problem of peak "tailing" is an inherent characteristic of the semiconductor gas sensor when used as a gas chromatographic detector, rather than being due to some shortcoming in the performance of the gas chromatographic column.

An attempt was made to reduce the response time of one sample of T.G.S. 711 and one sample of T.G.S. 812 by reducing the gas dead-volume within the detector housing by using a proprietory brand of alumina cement, but no success was achieved in this direction.

3.4 Effect on sensor response of varying the percentage of oxygen in the carrier gas

This effect was investigated, using the T.G.S. 711 sensor, by producing chromatograms of a mixture containing 6 ppm of hydrogen, 11 ppm of carbon monoxide and 0.5% (v/v) of methane in air, with carrier gases containing five different levels of oxygen.

Graph 36 shows the variation in peak heights for each gas at each level of oxygen in the carrier gas. The gas chromatographic peak heights and the response ratios at three different levels of oxygen content are summarised in Table 12, below :-

TABLE 12 Variation in the gas chromatographic response of the T.G.S.711 to hydrogen, carbon monoxide and methane with variation in the percentage of oxygen in the carrier gas

Percentage of oxygen in the carrier gas:		100%(v/v)	50%(v/v)	1%(v/v)
Peak heights (volts) :	hydrogen	2.7	3.1	3.8
	carbon monoxide	0.6	1.0	1.8
	methane	1.8	2.4	4.3
Response ratios :	hydrogen	1	1.15	1.4
	carbon monoxide	1	1.7	3.0
	methane	1	1.3	2.4

Conditions employed :- Heater voltage (V_H) = 6.5 volts DC;
Circuit voltage (V_C) =16 volts DC;
Load resistor (R_L) = 10K ohms + 50Kohms variable in a Wheatstone bridge circuit;
Carrier gas flow rate : 28 $cm^3 minute^{-1}$ for each gas.

The response for each gas increases as the oxygen level in the carrier gas is reduced.

This result was unexpected, particularly in view of the role of oxygen in the mechanism of response of semiconductor gas sensors proposed by Firth et.al.(22,23) and referred to in section 1.4.

At the level of one per cent oxygen in the carrier gas distortion of the hydrogen peak occurs, which makes the peak height measurement for this component less certain (see Plate 13).

When high purity nitrogen was used as the carrier gas similar distortion of the hydrogen peak occurs. It is followed by a large negative peak which overlaps and distorts the carbon monoxide peak. This large negative peak is probably due to excess oxygen present in the sample over that in the carrier gas (probably less than 10 ppm) and which would be expected to elute between the hydrogen and carbon monoxide peaks.

In order to investigate this effect further it was therefore decided to change from the active carbon column to the activated alumina column, on which oxygen would have a shorter retention time, and to assess the change in response to ethene with varying percentage of oxygen in the carrier gas.

It was also decided to investigate the variation in response with heater voltage at each level of oxygen in the carrier gas. This was done over a period of three days, changing the carrier gas each day, and the results are plotted in graph 37.

The main point of interest in these results is that, by operating with a carrier gas containing an even lower level of oxygen, a still further increase in response is obtained.

The value of the heater voltage at which maximum response to ethene is obtained also appears to increase slightly, from 11 volts when using air as carrier gas, to 12 volts with a carrier gas high purity nitrogen is used as the carrier gas.

The increases in the ethene response, at the optimum heater voltage for each carrier gas, are summarised

	Maximum peak height for ethene (millivolts)		
	Air carrier gas	1% oxygen/99% nitrogen	High purity nitrogen
	5.8	25	82
Response ratio	1	4.3	14

In another series of experiments the variation in response of the I.S.T. sensor to methane, ethane and propane was determined using a Chromosorb 102 column with air, argon and high purity nitrogen carrier gases at a flow rate of 25 $cm^3 minute^{-1}$. The results, summarised in Table 13, show a significant difference in response between argon and nitrogen carrier gases, possibly due to the differences in thermal conductivity.

TABLE 13 Variation in the gas chromatographic response of the I.S.T. sensor to methane, ethane and propane with different carrier gases

Peak height response to a nominal 100 ppm each of : (millivolts)	methane	ethane	propane
Air carrier gas	0.68	0.83	0.16
Argon carrier gas	11	8.2	1.9
Nitrogen(high purity)carrier gas	28.5	18.4	5.8
Response ratios: Air	1	1	1
Argon	16	10	12
Nitrogen	42	22	36

Sample volume : 5 cm^3

Volume of $C_1 - C_3$ gases injected : 0.5 ul.

In this case the I.S.T. sensor was operated in conjunction with the power unit supplied with the sensor; the heater voltage was therefore 2.5 volts DC.

These results, obtained with the I.S.T. sensor, confirm the considerable increase in response which is obtained when using carrier gases other than air, which contain very low levels of oxygen. It should be noted, however, that the methane was immediately preceded by a large negative peak due to oxygen and the possibility that the methane peak could have been affected, in some way, should be borne in mind.

In a similar series of experiments the variation in response of the Matsushita sensor to a mixture containing a nominal 100 ppm each of methane, ethane,ethene, propane and ethyne in air was determined using the activated alumina column and carrier gases containing varying proportions of oxygen. As the proportion of oxygen in the carrier gas is reduced the negative peak, due to oxygen in the sample, increases in size and produces interference with the methane peak. For this reason peak heights for methane could not be measured with certainty when using a carrier gas containing 1%(v/v) oxygen, and have been omitted. The results of these experiments are summarised in Table 14

TABLE 14 Variation in the gas chromatographic response of the Matsushita sensor to ethane, ethene, propane and ethyne with carrier gases containing different levels of oxygen

Peak height response to a nominal 100 ppm each of : (volts)	ethane	ethene	propane	ethyne
Air carrier gas	0.5	0.51	0.39	0.165
1% oxygen/99% nitrogen carrier gas	2.1	2.5	2.6	0.65
Response ratios :				
Air carrier gas	1	1	1	1
1% oxygen/99% nitrogen carrier gas	4.2	4.9	6.5	4

Carrier gas flow rate : 25 $cm^3 minute^{-1}$; heater voltage (V_H) = 5 volts DC; Circuit voltage (V_C) = 6 volts DC; operational amplifier feed-back resistor (R_f) = 200K ohms; sample volume = 5 cm^3.

In this case the conductivity of the ferric oxide Matsushita sensor increased to such an extent, when using high purity nitrogen as the carrier gas, that the backing-off facility, using the modified operational amplifier circuit (Figure5), was insufficient and a chromatogram could not be obtained. Nevertheless, it is of interest to note that the increase in response to ethane, ethene, propane and ethyne resulting from a change from air to one per cent oxygen in nitrogen, is similar in magnitude to the change in response of the tin oxide type T.G.S. 711 to ethene, under similar circumstances.

Summarising the results obtained under this section of the investigation it is noted that the T.G.S. 711, the I.S.T sensor and the Matsushita ferric oxide sensor all give an enhanced response, to a variety of gases, as the percentage of oxygen in the carrier gas is reduced.

The precise mechanism of response of semiconductor gas sensors is still not fully understood and the reason why semiconductor sensors should give an enhanced response, as gas chromatographic detectors, when used with carrier gases containing a low level of oxygen is still not certain.

When using a carrier gas containing oxygen, however, it is presumed that, due to the strong adsorption of oxygen on the semiconductor surface, a relatively small proportion of the reducing gas molecules will be able to reach the semiconductor surface to chemisorb on to it. Under these circumstances the response to reducing gases will result mainly from chemical combination between reducing gas and surface-adsorbed oxygen, with reversion of electrons, previously localised on the surface, into the body of the semiconductor sensor. This was characterised as mechanism two in section 1.4 (pages 12 - 13). It is further presumed that a relatively small proportion of these molecules actually combine with surface adsorbed oxygen ions.

When using a carrier gas containing a much reduced proportion of oxygen it must be presumed that a large proportion of the semiconductor surface will then be free of chemisorbed oxygen ions. Under these circumstances it seems likely that mechanism one will predominate, and that a higher proportion of reducing gas molecules will have an opportunity to chemisorb on to the semiconductor surface, donating an electron to the semiconductor in the process (mechanism 1).

3.5 Examination of semiconductor gas sensors using a scanning electron microscope

In an attempt to obtain information concerning the chemical composition of the semiconductor sensors they were examined on a scanning electron microscope with facility for energy dispersive analysis of the characteristic x-rays, using a silicon/lithium detector. At this time the multi-element standards had not been received and reliable quantitative analysis could not be performed. Nevertheless each of the gas sensors was examined under the same conditions and the following observations are made on the basis of the spectra of counts versus energy for each sensor, reproduced in Plates 17 - 21, inclusive.

With the exception of the Matsushita sensor a major component, in each case, appeared to be tin (presumably as tin oxide). The spectra for the T.G.S.711, Plate 17, and the T.G.S.813, Plate 18, were very similar showing, in addition to tin, smaller peaks due to silica, aluminium and nickel. The T.G.S.812, Plate 19, also exhibited a major peak due to tin and minor peaks for silicon and nickel but with a considerably larger peak for aluminium than was shown by the T.G.S.711 or T.G.S.813 sensors. A major peak for tin was again evident in the spectrum of the I.S.T. sensor, Plate 20, but with only small peaks for aluminium and silica. In this case no peak due to nickel could be seen

Iron was confirmed as a major component in the Matsushita sensor, Plate 21, but a ralatively large peak due to aluminium was also noted, together with a small peak for phosphorus.

4. SOME PRACTICAL APPLICATIONS OF THE T.G.S. 711 SEMICONDUCTOR GAS SENSOR AS A GAS CHROMATOGRAPHIC DETECTOR.

4.1 CALIBRATION GRAPHS

4.1.1. Calibration graphs for hydrogen, carbon monoxide and methane

Calibration graphs were initially prepared using the modified load resistor circuit, described in Section 2.3, Figure 2 (page 29).

A stock gas mixture was made up to contain 100 ppm of hydrogen, 1200 ppm of carbon monoxide and 4% (v/v) of methane, in air. The mixture was prepared, under pressure, in an F-type (10 litre) mild steel cylinder and was serially diluted, using a gas mixing pump as described in Section 2.5. A sample volume of 0.5 cm^3 was used in conjunction with the activated charcoal chromatographic column to separate the three component gas mixture, at ambient laboratory temperature.

Graph 38 was prepared using dilutions of this mixture and covers the concentration ranges 10 - 100 ppm hydrogen, 120 - 1200 ppm carbon monoxide and 0.4 - 4.0% (v/v) methane, in air. Graph 39 was prepared covering the concentration ranges 1 - 10 ppm hydrogen, 12 - 120 ppm carbon monoxide and 0.04 - 0.4% (v/v) methane, under the same conditions.

As noted in Section 2.5, dilutions containing less than 1% (v/v) of gas mixtures could not be prepared directly using a single gas mixing pump. In order to extend the range to lower concentrations a gas mixture was prepared in a second cylinder to contain 1% of the stock gas mixture (i.e. 1 ppm hydrogen, 12 ppm carbon monoxide and 0.04% (v/v) of methane) and serial dilutions from 90% to 10% (v/v) of this mixture were made, as above, using the gas mixing pump. Graph 40 was prepared in this way and covers the concentration range 0.1 to

1.0 ppm hydrogen and 1.2 - 12 ppm carbon monoxide. In this case the response to methane, in the concentration range 0.004 - 0.04% (v/v) (i.e. 40 - 400 ppm) was too small, particularly at the lower concentration levels, for accurate peak height measurements to be made. A calibration graph for methane over this concentration range was therefore not produced.

It will be seen from graph 40 that, over this rather limited concentration range, the response curves for hydrogen and carbon monoxide are virtually linear but that, as illustrated in graphs 39 and and 38, divergence from linearity becomes increasingly apparent at higher concentration levels.

In an attempt to improve linearity of response, and for the reasons already discussed in Section 2.3 (page 29), new calibration graphs were prepared using the modified operational amplifier circuit in Figure 4 (page 31), incorporating two operational amplifiers, type 741 C, and a 2K ohm feed-back resistor. Graph 41 was prepared in this way covering the concentration ranges 10 - 100 ppm hydrogen, 120 - 1200 ppm carbon monoxide and 0.4 - 4.0% (v/v) for methane.

In order to assess the improvement in linearity of these calibration graphs, resulting from substitution of the operational amplifier circuit for the load resistor circuit, graph 41 should be compared with graph 38 which, apart from the different measuring circuits, were prepared under the same conditions. The improvement in linearity of response is very considerable and serves to demonstrate that, provided satisfactory methods of calibration are available, the T.G.S. 711 semiconductor sensor may be used as a gas chromatographic detector up to concentration levels of at least 100 ppm for hydrogen, 1000 ppm for carbon monoxide and 4% (v/v) for methane.

Another set of calibration graphs for hydrogen, carbon monoxide and methane was prepared during this period in the investigation and under the same experimental conditions but using a different T.G.S. 711 sensor (T.G.S. 711(2)). These are reproduced in graph 42. It is noted that the degree of linearity is similar for both sensors but that the response of the second sensor is about twice that of the first for hydrogen and carbon monoxide and about 30% more for methane.

4.1.2 Calibration graphs for methane, ethane, ethene, propane and ethyne

In order to examine the possible useful applications of the semiconductor gas sensor as a gas chromatographic detector to a wider range of gases, another gas mixture was made up to contain a nominal 100 ppm each of methane, ethane, ethene, propane and ethyne. This gas mixture was serially diluted, using the Wösthoff gas mixing pump and cylinder compressed air (B.O.C. Limited). A sample volume of 0.5 cm^3 was used in conjunction with the activated alumina chromatographic column, operated at about 60°C.

The sensor was operated at a heater voltage of 11 volts DC in conjunction with the modified operational amplifier circuit (Figure 5) and a feed-back resistor of 2K ohms. Graph 43 was prepared using this gas mixture and dilutions covering the concentration range 10 - 100 ppm for each gas.

Graph 44 covers the lower concentration range 1 - 10 ppm for each gas and it is noted that, over this concentration range, the response curve for each gas is linear. Over the more extended range of concentrations, covered by graph 43, the response curves are not linear but they show that this type of detector can, nevertheless, be used satisfactorily at least up to concentration levels of 100 ppm for each gas, provided that adequate calibration procedures are available.

Another way of extending upwards the concentration levels which may be measured using the semiconductor gas chromatographic detector is to employ a smaller gas sampling loop.

4.2 Assessment of lower limits of detection

4.2.1 The lower limits of detection for hydrogen and carbon monoxide

Attempts were made to assess the lower limits of detection for hydrogen and carbon monoxide, firstly using the T.G.S. 711 (1) sensor. A cylinder of compressed air (B.O.C. Limited) was analysed, using the cylinder mixture containing 6 ppm hydrogen, 19 ppm carbon monoxide and 0.32% (v/v) methane for calibration purposes. The cylinder of compressed air was found to contain 0.85 ppm hydrogen and 1.5 ppm of carbon monoxide. The methane content in this cylinder was below the limit of detection, using the active carbon column. Attempts were then made to prepare dilutions of the air from this cylinder using the Wösthoff gas mixing pump, and passing another portion of air from the same cylinder over heated Hopcalite in order to remove the hydrogen and carbon monoxide impurities. It was found that the Hopcalite furnace did not remove all the hydrogen and carbon monoxide at the flow rates required by the Wösthoff pump (between 600 and 700 cm^3 $minute^{-1}$) and this method was therefore abandoned.

Another attempt was made to prepare low dilutions of the cylinder air by passing it more slowly through the Hopcalite furnace and collecting the purified air in plastic bags, capable of containing approximately three litres of gas. It was confirmed that the purified air, after passing over the heated Hopcalite furnace and directly to the chromatographic sample loop, contained no detectable levels of hydrogen or carbon monoxide. After collecting sufficient of the purified air in the plastic bag this was sealed off, using a screw clip, and 30 cm^3 increments of unpurified cylinder air were injected into it using a graduated 10 ml. syringe. After each addition of unpurified air a chromatogram was produced, 50 cm of the gas mixture being removed for this purpose on each occasion. Calibration graphs were prepared in this way, the actual volume of air in the plastic bag having been determined by displacement of water from a graduated cylinder. The calibration graphs covered the approximate range 0.007 to 0.043 ppm hydrogen and 0.013 to 0.08 ppm of carbon monoxide. The calibration graphs were acceptably linear but that for hydrogen showed a significant intercept. This was subsequently shown to be due to diffusion of atmospheric levels of hydrogen into the plastic bag. In a separate experiment it was found that the hydrogen concentration in the plastic bag had risen almost to 0.03 ppm after two hours and to 0.3 ppm after twenty hours.

Another attempt to produce satisfactory calibration graphs down to the limits of detection of hydrogen and carbon monoxide was considered, in which the gas mixture would be contained in 2.5 litre glass bottles. However this would seem to involve either lengthy purge times or displacement of water from the bottle, in which case the levels of dissolved gases might present a problem. Due to shortage of time this attempt was therefore abandoned.

From a comparison of the peak heights for hydrogen and carbon monoxide at the lowest levels encountered, with the peak heights produced by those gases from the unpurified cylinder air, and the short-term noise level on the recorder base-line at high sensitivity, the following estimates of the lower limits of detection for two T.G.S.711 sensors were made:-

Estimated limits of detection (ppm) for :-

	T.G.S. 711(1)	T.G.S.711(2)
hydrogen	0.002	0.002
carbon monoxide	0.015	0.006

4.2.2 The lower limits of detection for ethane, ethene, propane and ethyne

In order to assess the lower limits of detection of the T.G.S. 711(2) sensor to the lower hydrocarbon gases it was necessary, first of all, to prepare a gas mixture containing a nominal 1 ppm of each gas which could be further diluted using the gas mixing pump. The initial dilution level was prepared from the gas mixture containing 100 ppm of each gas, using the gas mixing pump with compressed cylinder air. The diluted gas mixture, containing a nominal 1 ppm of each gas was stored in a large plastic bag, having a capacity of up to 25 litres at S.T.P.

A chromatogram of this gas mixture containing a nominal 1 ppm of each gas, contained in the plastic bag, was compared the following day with a chromatogram prepared from a mixture containing 1% (v/v) of the stock cylinder gas mixture, produced directly from this gas mixture, using the gas mixing pump and compressed cylinder air. Peak height measurements were as follows :-

	ethane	ethene	propane	ethyne
Peak heights from the gas mixture contained in plastic bag (mV)	14	29.5	11.5	6.5
Peak heights: direct dilution of cylinder mixture using the gas mixing pump (mV)	15.5	32	13.3	7

It was thus confirmed that no contamination of the gas mixture in the plastic bag had occured and that losses due to adsorption did not exceed 15%. The gas mixture in the plastic bag could therefore be used to produce further dilutions. These were prepared at the 1%, 2%, and 5% level, which thus contained a nominal 0.01 ppm, 0.02 ppm and 0.05 ppm of each gas. Chromatograms were produced of the gas mixtures, at each concentration level, and the results have been plotted in graph 45. Despite the fact these response curves do not pass directly through the origin, they nevertheless show a fairly satisfactory relationship between peak height measurement and concentration. From a comparison of these chromatograms with one produced employing 100% dilution air, from the gas mixing pump, it was concluded that the approximate lower levels of detection (the concentration, for each gas, at which the peak height is no more than twice the short term "noise level" on the recorder chart, at the same sensitivity setting) in parts per million were :-

ethane	ethene	propane	ethyne
0.01	0.01	0.01	0.02

It was not possible to assess the limit of detection for methane in this way since, at the nominal 0.01, 0.02 and 0.05 ppm levels, a peak of unvarying height was present in the methane position. This was presumably due to hydrogen and/or carbon monoxide and/or methane (all of which would be expected to elute in virtually the same position from the activated alumina chromatographic column) which must be present in the cylinder diluting air. Catalytic removal of methane would require a considerably higher temperature than that for the removal of hydrogen and carbon monoxide. A suitable furnace, to operate at this elevated temperature was not available at this time.

4.3 Practical application of the T.G.S. 711 semiconductor gas chromatographic detector to mine air analysis

4.3.1 Laboratory analysis of underground mine air samples

Having achieved a considerably lower limit of detection for hydrogen and carbon monoxide than was previously available, it became possible to use the semiconductor gas chromatographic detector for the analysis of the low concentrations of these gases found in mine air samples.

For many decades the concentration of carbon monoxide in mine air samples and the Graham ratio

$$\frac{\text{Concentration of carbon monoxide (\% v/v) x 100}}{\text{oxygen deficiency}}$$

has been used as an index of spontaneous combustion in coal mines. More recently it was postulated (2) that the ratio :

$$\frac{\text{concentration of hydrogen (ppm)}}{\text{concentration of carbon monoxide (ppm)}}$$

might provide useful additional information, giving some indication of the temperature at the seat of a "heating" and also, possibly, giving an earlier indication of the onset of a spontaneous heating underground than is given by the Graham ratio (above).

In order to obtain some background information concerning the relative levels of hydrogen and carbon monoxide to be found under normal conditions in coal mines a number of samples were collected and analysed. It is customary for routine mine air samples to be collected, under pressure, in cylindrical duralumin containers. In the course of some previous work, however, some erratic results were obtained in the analysis for low levels of hydrogen, possibly due to reaction between acid mine water and the duralumin container. It was therefore decided, in the present instance, to collect samples in 250 ml. gas sampling bulbs made of glass, with double oblique-bore taps fitted at each end.

In the first two series, samples were taken in the air intake roadways leading to coal faces, at intervals across each coal face, and in the return roadways. Hydrogen and carbon monoxide concentrations were determined using the semiconductor chromatograph; carbon dioxide and methane concentrations were measured using the routine non-dispersive infra-red instruments.

The results, relating to 82's face at colliery A and K14's face at colliery B, are represented graphically in graphs 46 and 47.

It is seen that the concentrations of hydrogen, carbon monoxide and methane all tend to increase in passing from the intake to the return side of the coal face, due to oxidation of the freshly exposed coal surfaces, at ambient temperatures, and to the release of firedamp from the recently fractured coal substance. It is noted that, across both coal faces, the carbon monoxide concentration increases more rapidly than that of hydrogen, and that the methane concentration increases more rapidly across coal face A (in a typically "gassy" seam) than across coal face B. The analysis of sample 11 at colliery A does not fit into the general pattern since this sample was taken from the waste area, which is only partially ventilated, behind the coal face chocks.

Not infrequently mine ventilating air becomes contaminated during its passage through the mine roadways, by carbon monoxide originating from shot-firing and diesel exhaust fumes, giving rise to false suspicions of spontaneous "heatings". It was therefore of interest to know the relative concentrations of hydrogen and carbon monoxide in samples from these sources. A number of samples were collected and the range of these results for the hydrogen and carbon monoxide concentrations are given in Tables 15 and 16 :-

<u>TABLE 15</u> <u>Typical analysis of shot-firing fumes</u>

Hydrogen	: 300 - 650 ppm
Carbon monoxide	: 600 - 1700 ppm
Approximate H_2/CO ratio	: 0.45 (approximately)

<u>TABLE 16</u> <u>Typical analysis of diesel exhaust fumes</u>

Hydrogen	: 5 - 15 ppm
Carbon monoxide	: 330 - 350 ppm
Approximate H_2/CO ratio	: 0.03 (approximately)

In view of the high level of hydrogen in shot-firing fumes, these samples were analysed using the katharometer chromatograph, and both sets of carbon monoxide figures were determined using the Wösthoff Ultragas conductimetric carbon monoxide analyser.

4.3.2 T.G.S. 711 gas sensor used in automatically operated gas chromatographic mine air monitoring equipment

In order to provide more reliable and up to date information concerning fluctuations and trends in the concentrations of mine gases of interest in coal mines, information from the analysis of manually collected air samples is increasingly being supplemented by pumping samples continuously from strategic points underground and analysing these, on a semicontinuous basis, on the surface. In line with these developments an automatically operated gas chromatograph was constructed to analyse samples for hydrogen, carbon monoxide and methane.

Electrically operated valves (Schräder Type 457/TF to operate on 44-55 volts AC or 20-26 volts DC, supplied by Economatics Limited, 411 Petre Street, Sheffield, S4 8LL) actuated the pneumatic gas chromatographic injection valve (Pye/Unicam, Cambridge). An electronic timer and relays controlled the frequency of sample injection, at approximately twenty minute intervals. The active charcoal chromatographic column and the sample loop were thermostatted (A.E.I.Limited, cold-junction thermostat) since the instrument was required to operate at collieries, under widely varying ambient temperatures.

This instrument was commissioned within the laboratory and, operating on a synthetically preparedgas sample contained under pressure in a gas cylinder, gave the following repeatability over a twelve hour period :-

	Hydrogen	Carbon monoxide	Methane
(95% confidence limits)	2 ± 0.02 ppm	11 ± 0.3 ppm	0.4 ± 0.0044% (v/v).

This automatically operated semiconductor chromatograph was subsequently operated, on an experimental basis, over a period of several months each, at two collieries.

On one occasion a spontaneous heating developed behind a stopped off area adjacent to the return roadway from which the sample for our chromatograph was being pumped. Prior to this incident the hydrogen and carbon monoxide levels were approximately 3.4 and 14 ppm respectively (see Plate 14) During the course of the heating the hydrogen and carbon monoxide concentrations almost doubled, to mean levels of 6.1 and 20 ppm respectively (see Plate 15). Subsequently remedial action was taken to re-build the stopping and, within three hours, the hydrogen and carbon monoxide concentrations had fallen to approximately the same level as before the onset of the heating (Plate 16)

5. CONCLUSIONS AND GENERAL ASSESSMENT

5.1 Some practical advantages of using a semiconductor gas chromatographic detector.

Reviewing the results quoted in Section 4.2.1 it is claimed that the limits of detection for hydrogen and carbon monoxide using the Taguchi semiconductor gas sensor,Type 711,as a gas chromatographic detector, are similar to those achieved using the most sensitive alternative methods (see Table 3, page 22). The chief advantage of the semiconductor gas chromatographic detector lies in the fact that it can be used with air as the carrier gas. This single attribute brings with it a number of associated advantages in operation.

Since no response is given to oxygen, argon or nitrogen when using the semiconductor sensor with air as carrier gas, no problem is encountered in the gas chromatographic separation of trace components which are eluted on the tail of these major components e.g. carbon monoxide and methane which are eluted after nitrogen when using active carbon or molecular sieve chromatographic columns, or methane which is eluted immediately after the air peak when using an activated alumina chromatographic column in conjunction, for example, with the helium ionisation detector.

Again, in contrast to the helium ionisation detector, the performance of which is seriously affected by even the smallest air leak into the system, the semiconductor is not affected in this way. The semiconductor sensors are cheap to buy, easy to operate, robust, and may be used continuously over extended periods. They require no expensive ancillary equipment and operate with the cheapest carrier gas available. In theory at least, for purposes of semi-continuous monitoring of atmospheric pollutants, the semiconductor gas sensor could be operated in conjunction with an adsorption type chromatographic column operated at reduced pressure, using purified atmospheric air as the carrier gas, thus eliminating the need for periodic replacement of carrier gas cylinders.

As already noted in Section 3.3.3 (page 61) the remaining disadvantage of using the semiconductor gas sensors as gas chromatographic detectors is their slow recovery time after exposure to reducing gases and the consequent "tailing" of gas chromatographic peaks. During the course of the present investigations those operating conditions have been identified which will generally improve response to different gases and minimise the skewness of gas chromatographic peaks. Nevertheless the slow recovery times and the tendency to produce asymmetric gas chromatographic peaks are still their major disadvantages.

5.2 Suggestions for future work

It is considered that semiconductor gas sensors show sufficient promise in their response to hydrogen, carbon monoxide and the lower saturated and unsaturated hydrocarbon gases to warrant further investigation. It is suggested that the T.G.S. 812 should be tested over a wider range of heater voltage together with the T.G.S. 813, the Matsushita L.N.G. sensor and others which may become available. The performance of the T.G.S. 816, which has a ceramic body, should also be assessed and, in this case, the possibility of direct heating investigated. The long term stability of these sensors should be assessed and their usefulness in the semi-continuous analysis of atmospheric pollutants, including hydrogen sulphide, could be investigated.

In the more general field it is suggested that using semiconductor gas sensors as gas chromatographic detectors provides a simple and convenient way of assessing the characteristics of these devices to a range of gases, under conditions which may be easily standardised.

Further work to elucidate the mechanism of response of semiconductor gas sensors might well involve using sample gases made up without oxygen present and using other carrier gases, including helium, so as to compare the response obtained when using nitrogen, argon and helium as carrier gases.

LITERATURE REFERENCES

1. S.Gibson and A.Wynne, National Coal Board, East Midlands Regional Scientific Department Report No.EMRL/49/76, dated 1976.
2. A.Wynne, National Coal Board, East Midlands Regional Scientific Department Report No.EMRL/108/76, dated 1976.
3. T.A.Jones, "Final Report of the Working Party on Semiconductor Gas Detectors, set up by the Coal, Electricity and Gas (C.E.G.) Research Liason Committee" Health and Safety Executive Report, dated 1/9/1978.
4. T.Seiyama, A.Kato, K.Fujiishi and M.Nagatani, Anal.Chem.,1962, 34, (11), 1502-3.
5. T.Seiyama and S.Kagawa, Anal Chem., 1966, 38, (8), 1069-1073.
6. V.G.Guglya, A.D.Gol'den and A.A.Zhukhovitskii, Zavodskaya Laboratoriya, 1969, 35, (2), 141-143.
7. V.G.Guglya and G.S.Korobeinik, Zavodskaya Laboratoriya, 1974, 40, (5), 628-630.
8. V.G.Guglya, G.S.Korobeinik and A.A.Zhukhovitskii, Zavodskaya Laboratoriya, 1978, 44, (5), 539-540.
9. T.M.Mallard, C.S.Mallard, H.S.Holfeld and T.A.LaRue, Anal.Chem.,1977, 49, (8), 1275-1277.
10. The Gas Sensitive Semiconductor Group, Shanghai Institute of Organic Chemistry, Academia Sinica, Translation from: Huaxue Xuebo, 1977, 35, (34), 183-192.
11. K.Ihokura, "Tin Oxide Gas Sensor for Deoxidising Gas", paper presented to A.C.S./C.S.J. Chemical Congress, Hawaii, U.S.A.,1979.
12. N.Taguchi, U.S.Patent 3 625 756, 7/12/1971.
13. N.Taguchi, U.S.Patent 3 631 436, 28/12/1971.
14. N.Taguchi, U.S.Patent 3 644 795, 22/2/1972.
15. N.Taguchi, U.S.Patent 3 676 820, 11/7/1972.
16. N.Taguchi, U.S.Patent 3 732 519, 8/5/1973.
17. N.Taguchi, U.S.Patent 3 835 529, 17/9/1974.
18. N.Taguchi, U.S.Patent 3 900 815, 19/8/1975.
19. B.Bott, J.G.Firth, A.Jones and T.A.Jones, U.S.Patent 3 865 550, 11/2/1975.
20. Chou and Chou, U.S.Patent, 3 955 268, 11/5/1976.
21. Chou and Chou, U.S.Patent, 4 013 943, 22/3/1977.
22. J.G.Firth, A.Jones and T.A.Jones, I.E.R.E. Symposium on Environmental Sensors and Applications, Manchester, 1974, 57-65.
23. J.G.Firth, A.Jones and T.A.Jones, Ann.Occup.Hyg., 1975, 18, 63-68.
24. T.A.Jones, Research and Laboratory Services Division, Health and Safety Executive, Red Hill, Sheffield S3 7HQ, Private communication.

25. M.Takata and H.Yanagida,
Journal of the Ceramic Society of Japan, 1979, 87, (1), 13-27.

26. T.A.Gough and E.A.Walker,
Analyst, 1970, 95, 1-15.

27. E.R.Adlard,
Critical Reviews in Analytical Chemistry, May 1975, 1-36.

28. I.G.McWilliam,
J.Chromatogr., 1961, 6, 110.

29. D.H.Desty, C.J.Geach and A.Goldup,
"Gas Chromatography 1960" Edited by R.P.W.Scott, 46-64.

30. B.A.Schaefer and D.M.Douglas,
J.Chromatog.Science, 1971, 9, 612-619.

31. K.Jones and R.Green,
Nature., 205 (4966) 21 Jan.1965, 67-68.

32. U.Schwenk, H.Hachenberg and M.Forderreuther,
Brennstoff-Chem., 1961, 42, 295.

33. K.Porter and D.H.Volman,
Anal.Chem., 1962, 34, 748-749.

34. G.S.Vizard and A.Wynne,
Colliery Engineering, August 1965, 353-357.

35. M.Krekci and M.Dressler,
Chromatog.Rev., 1970, 13, 1-59.

36. R.T.Wittebrood,
Chromatographia, 1972, 104, 311.

37. J.J.Madison,
Anal.Chem., 1958, 30, 1859-1862.

38. L.J.Smauch and R.A.Dinnerstein,
Anal.Chem., 1960, 32, 343-352.

39. M.P.Phillips, R.E.Sievers, P.D.Goldan, W.C.Kuster and
F.C.Fehsenfeld, Anal.Chem., 1979, 51, (11), 1819-1825.

40. J.J.Sullivan and M.J.O'Brien, in "Modern Practice of Gas
Chromatography, Edited by R.L.Grob, Published by John Wiley
and Sons, New York, , 281-282.

41. A.Karmen and R.L.Bowman,
Ann.N.Y.Acad.Sci., 1959, 72, 714.

42. W.C.Hampton,
Journal of Gas Chromatography, 1965, 3, 217-225.)quoted in
)J.H.Glover,
43. C.H.Lambert, French Patent 1 062 975, 15/9/1962.)"Control and
44. C.H.Lambert, French Patent 1 407 759, 23/6/1964.)Instrumentation"
May,1976, 31-32.

45. J.E.Lovelock,
J.Chromatogr., 1958, 1, 35.

46. J.E.Lovelock, in "Gas Chromatography 1960", Edited by
R.P.W.Scott, Academic press, New York, 1961, 16.

47. M.M.Shahin and S.R.Lipsky,
Anal.Chem., 1963, 35, (4), 467-474.

48. Anon, Varian Aerograph, Manufacturers' publicity material,
A/68/550 A - 1007 S15, 1968.

49. J.Gawlowski, J.Niedzielski and A.Wieckowski, J.Chromatogr. 1978, 151, 370-373.

50. J.Gawlowski, J.Maurin and J.Niedzielski, J.Chromatogr. 1979, 168, 1-7.

51. F.F.Andrawes and E.K.Gibson Jr., Anal.Chem. 1980, 52, 846-851.

52. F.F.Andrawes, R.S.Brazell and E.K.Gibson, Anal Chem. 1980, 52, 891-896.

53. J.Watson, "Recent developments and applications of the Taguchi Gas Sensor (T.G.S.)", Paper presented to International Conference on monitoring of Toxic Gases in the Working Environment, held at City University, London, December 1977.

54. J.Watson, University of Wales, University College of Swansea, Department of Electrical and Electronic Engineering, Private communication.

55. D.A.Skoog and D.W.West, "Principles of Instrumental Analysis", 2nd.Edition, Saunders College, Philadelphia, 1980, 55.

56. H.Hachenberg, "Industrial Gas Chromatographic Analysis", Published by Heyden, 1973, 77.

57. G.S.Vizard, National Coal Board, Yorkshire Regional Laboratory, Golden Smithies Lane, Wath-on-Dearne, Nr. Rotherham, South Yorkshire, Private communication.

58. A.J.B.Cruikshank, D.H.Everett and M.T.Westaway, "Thermodynamics of Hydrocarbon Solutions from G.L.C. Measurements, Part 2, Solutions in Squalane" Trans.Farad.Soc., 1965, 61, 235-243.

59. S.M.Roberts, D.H.Wilkinson and L.R.Walker, Anal.Chem. 1970, 42, (8), 886-893.

60. J.J.Kirkland, W.W.Yau, H.J.Stocklosa and C.H.Dilks Jr., J.Chrom.Sci., 1977, 15, 303-316.

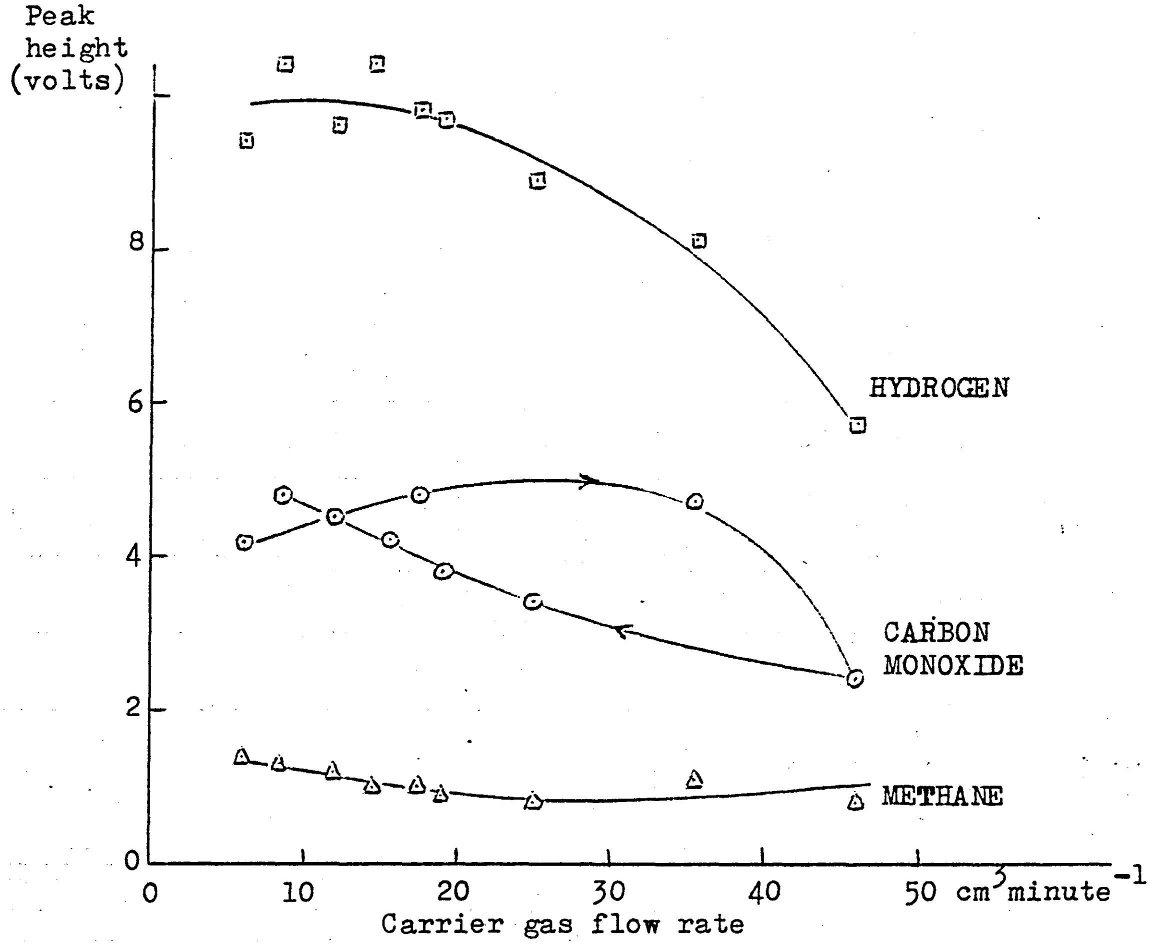
61. Per Kofstad, "Non-Stoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides", Wiley-Interscience, a Division of John Wiley and Sons, Inc., New York, 1972, 355.

62. Z.M.Jarzebski, "Oxide Semiconductors" (Translated by D.B.Grzybowska-Swierkosz) Edited by Dr.Brian R Pamplin, International Series of Monographs in the Science of the Solid State, Volume IV, Published by Pergamon Press, 1973, 252.

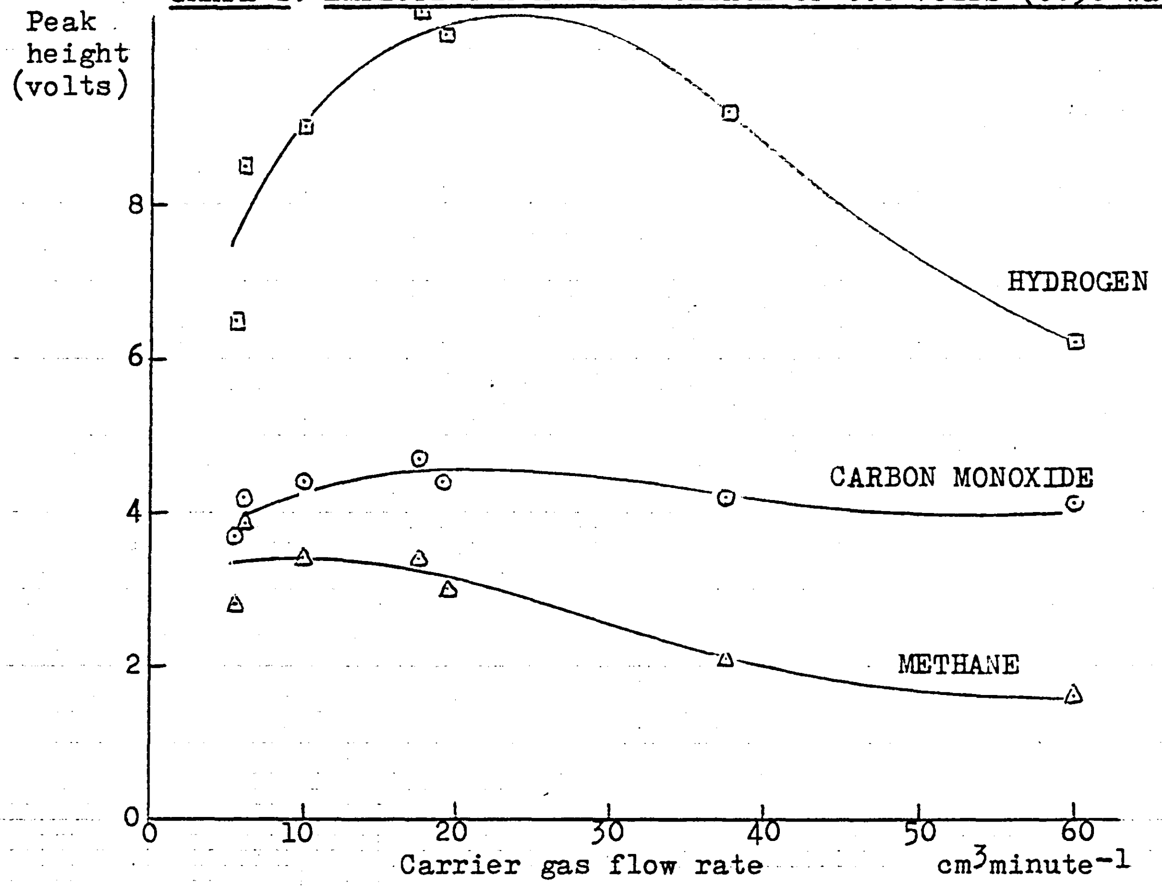
63. A.Clark, "The Chemisorptive Bond, basic concepts" Academic Press, New York and London, 1974,

CARBON MONOXIDE AND METHANE WITH CARRIER GAS
FLOW RATE, USING THE TAGUCHI 711 SENSOR

GRAPH 1: EMPLOYING A HEATER VOLTAGE OF 5.5 VOLTS (0.30 watts)

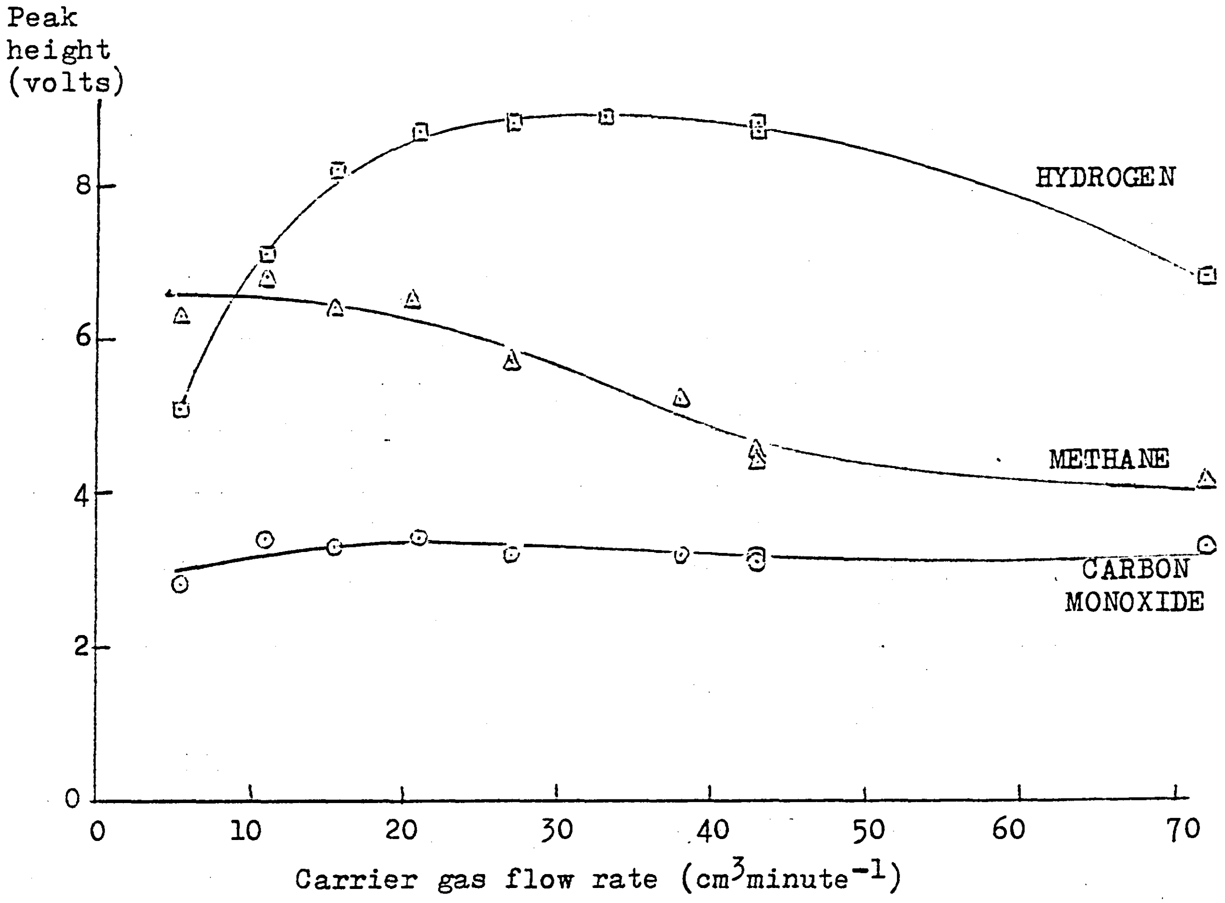


GRAPH 2: EMPLOYING A HEATER VOLTAGE OF 6.0 VOLTS (0.36 watts)

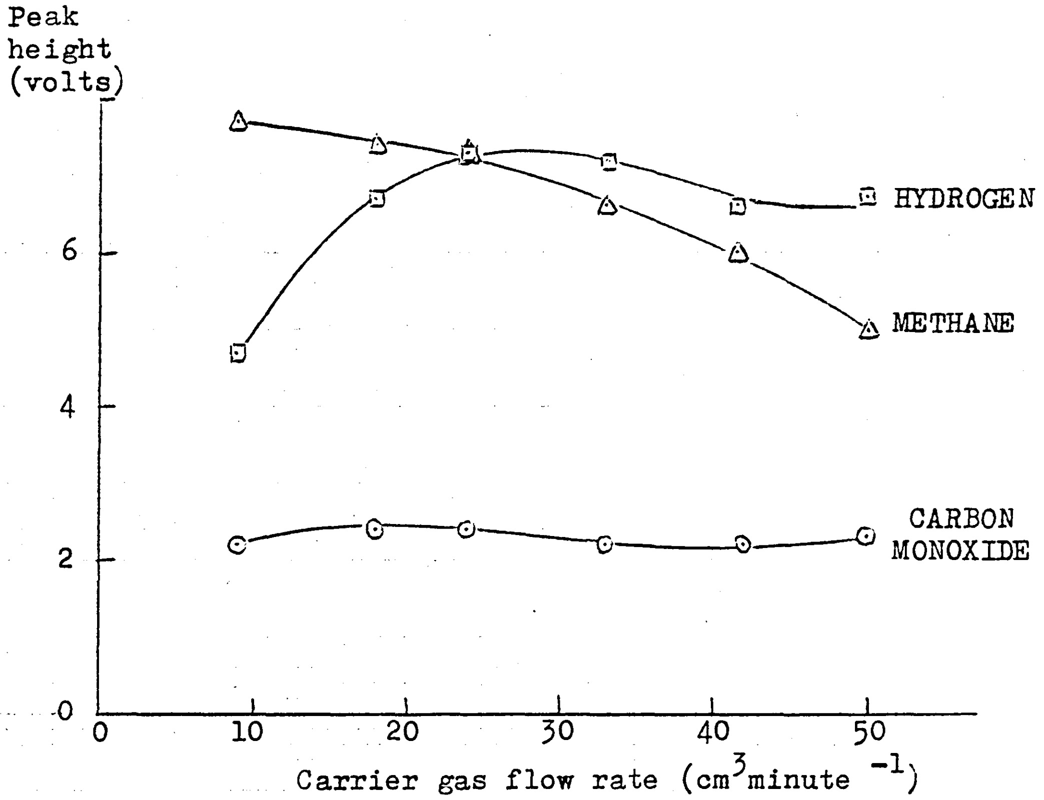


CARBON MONOXIDE AND METHANE WITH CARRIER GAS FLOW RATE, USING THE TAGUCHI SENSOR TYPE 711

GRAPH 3: EMPLOYING A HEATER VOLTAGE OF 6.5 VOLTS (0.43 WATTS)

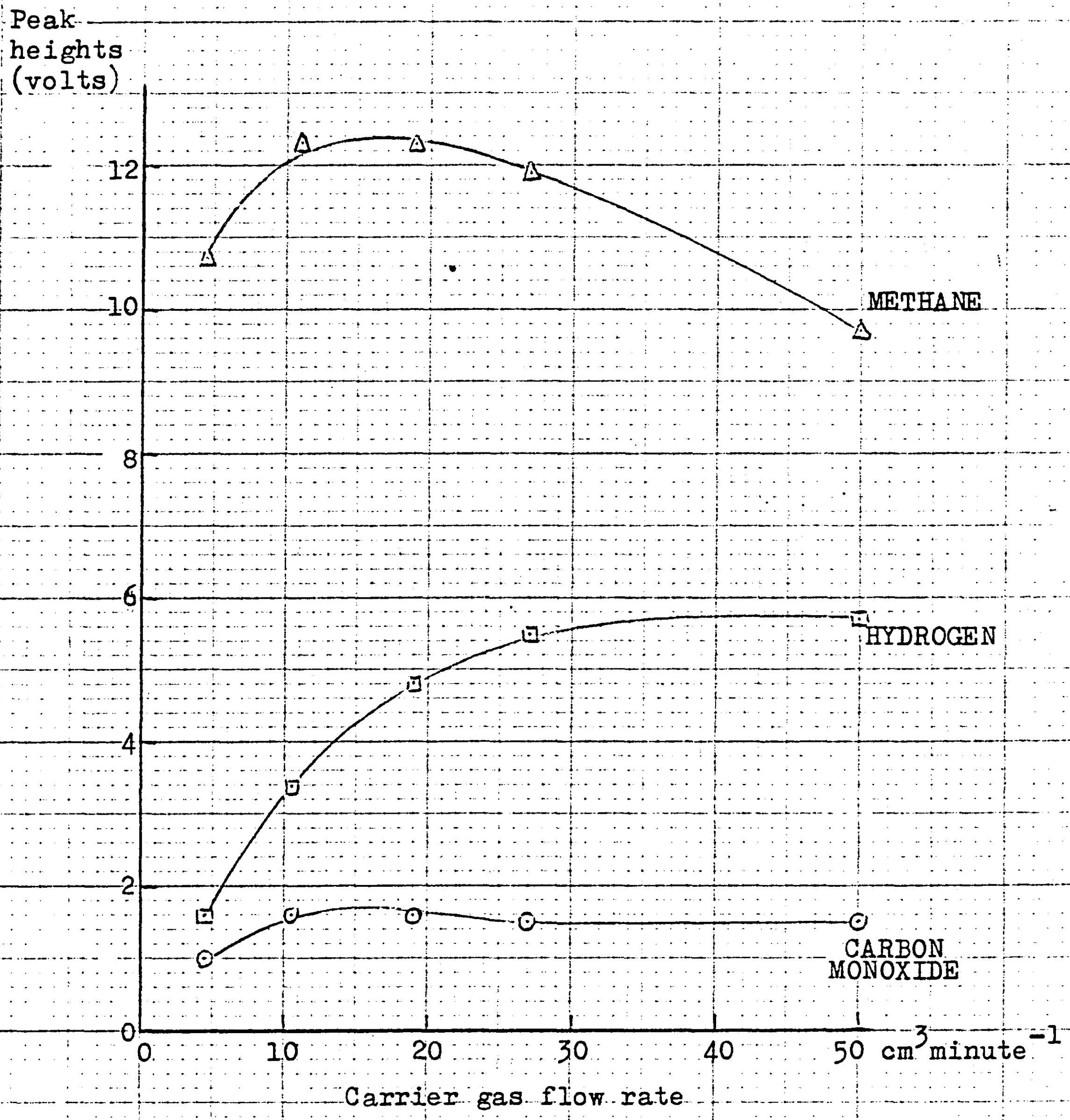


GRAPH 4: EMPLOYING A HEATER VOLTAGE OF 7.0 VOLTS (0.50watts)



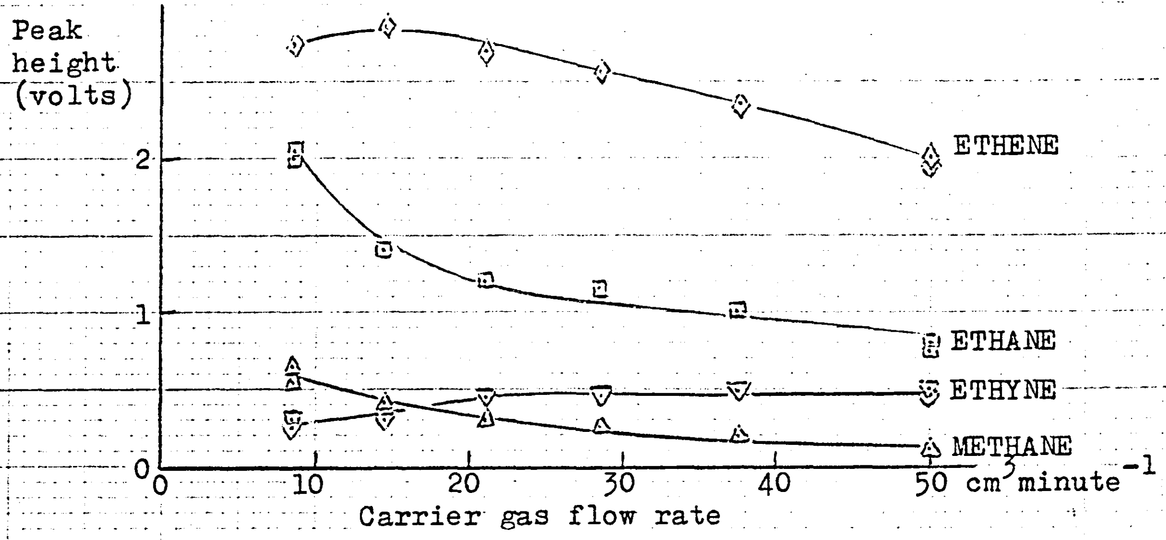
GRAPHS 1 to 5: VARIATION IN THE PEAK HEIGHTS FOR HYDROGEN, CARBON MONOXIDE AND METHANE WITH CARRIER GAS FLOW RATE, USING THE TAGUCHI SENSOR TYPE 711

GRAPH 5: EMPLOYING A HEATER VOLTAGE OF 7.5 VOLTS (0.57 watts)

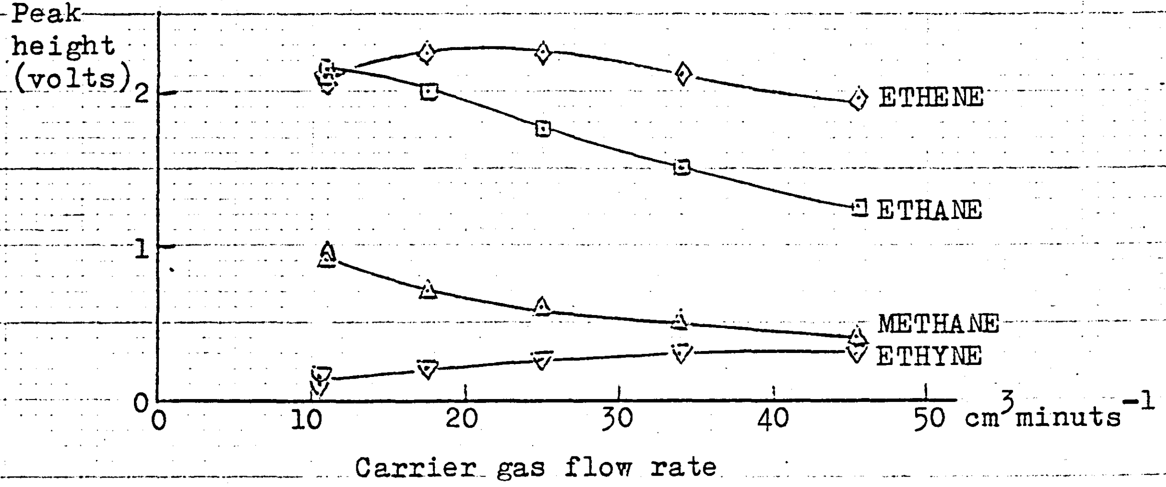


ETHENE AND ETHYNE WITH CARRIER GAS FLOW RATE,USING THE TAGUCHI SENSOR TYPE 812

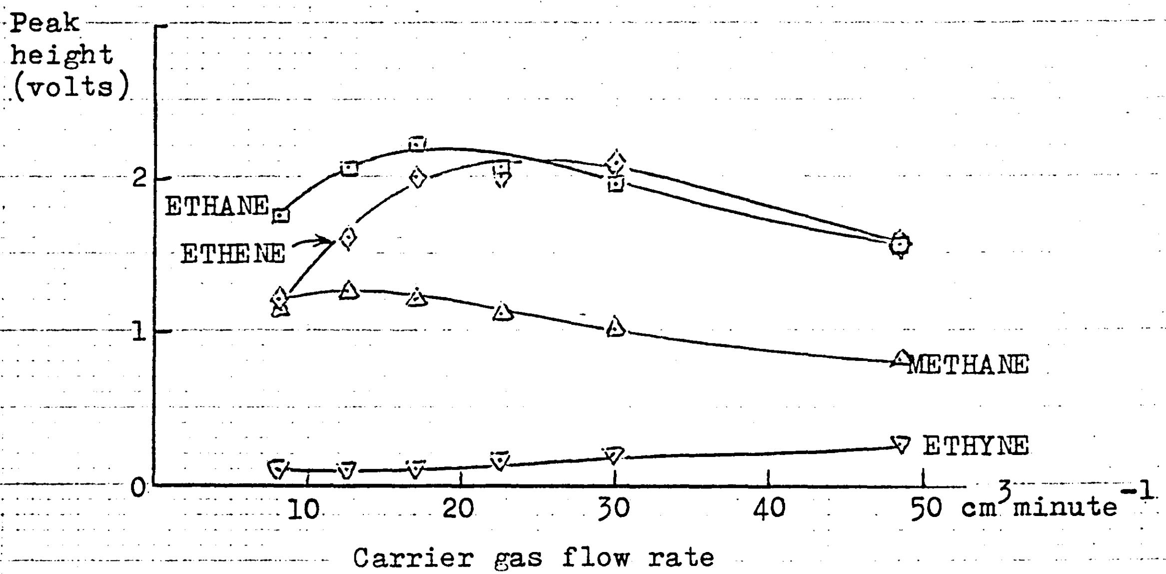
GRAPH 6: EMPLOYING A HEATER VOLTAGE OF 5.5VOLTS (0.73 watts)



GRAPH 7: EMPLOYING A HEATER VOLTAGE OF 6.0 VOLTS (0.86 watts)

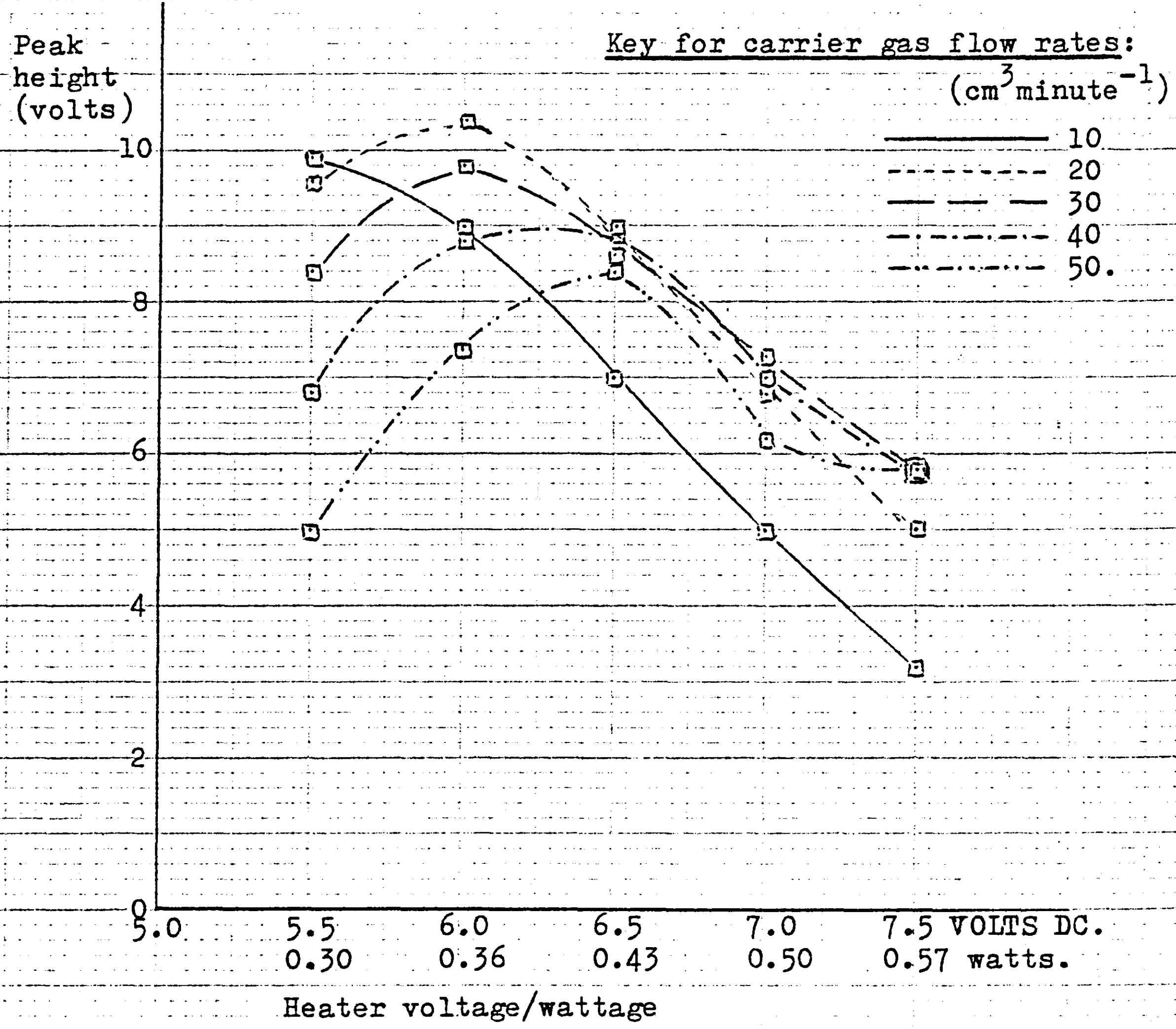


GRAPH 8: EMPLOYING A HEATER VOLTAGE OF 6.5 VOLTS (1.01 watts)

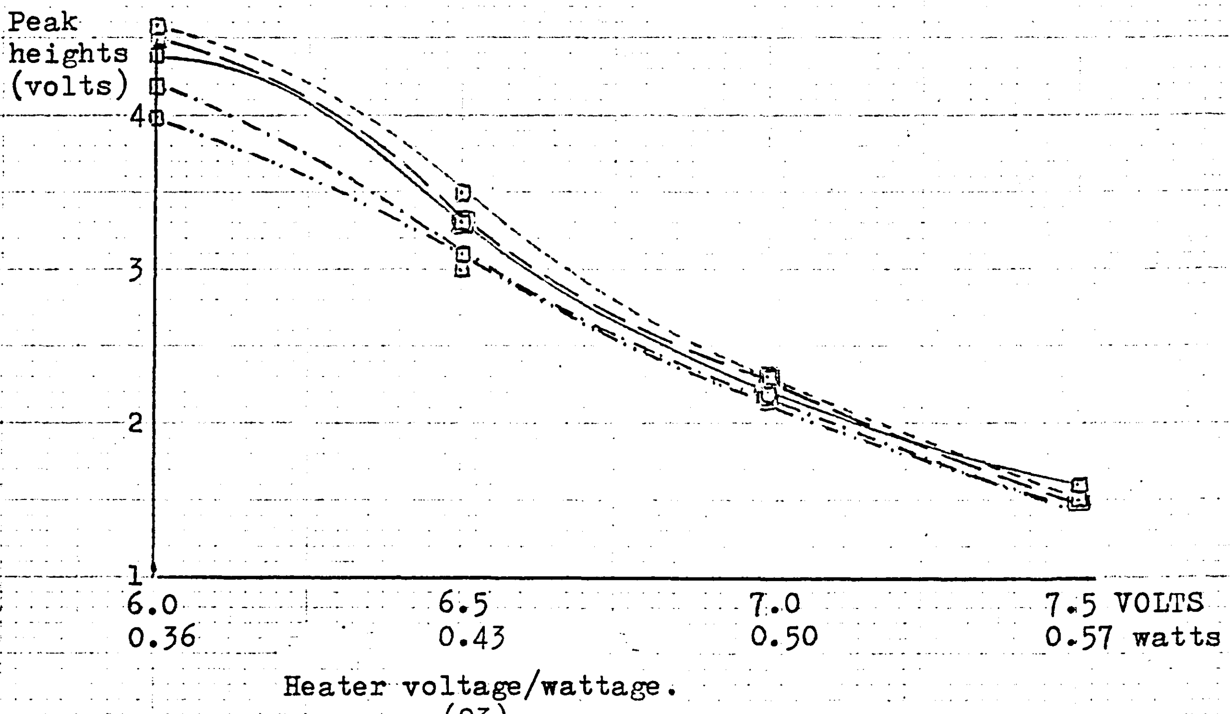


GRAPHS 9-10: VARIATION IN THE PEAK HEIGHTS FOR HYDROGEN AND CARBON MONOXIDE WITH HEATER VOLTAGE USING THE T.G.S.711 AT VARIOUS CARRIER GAS FLOW RATES.

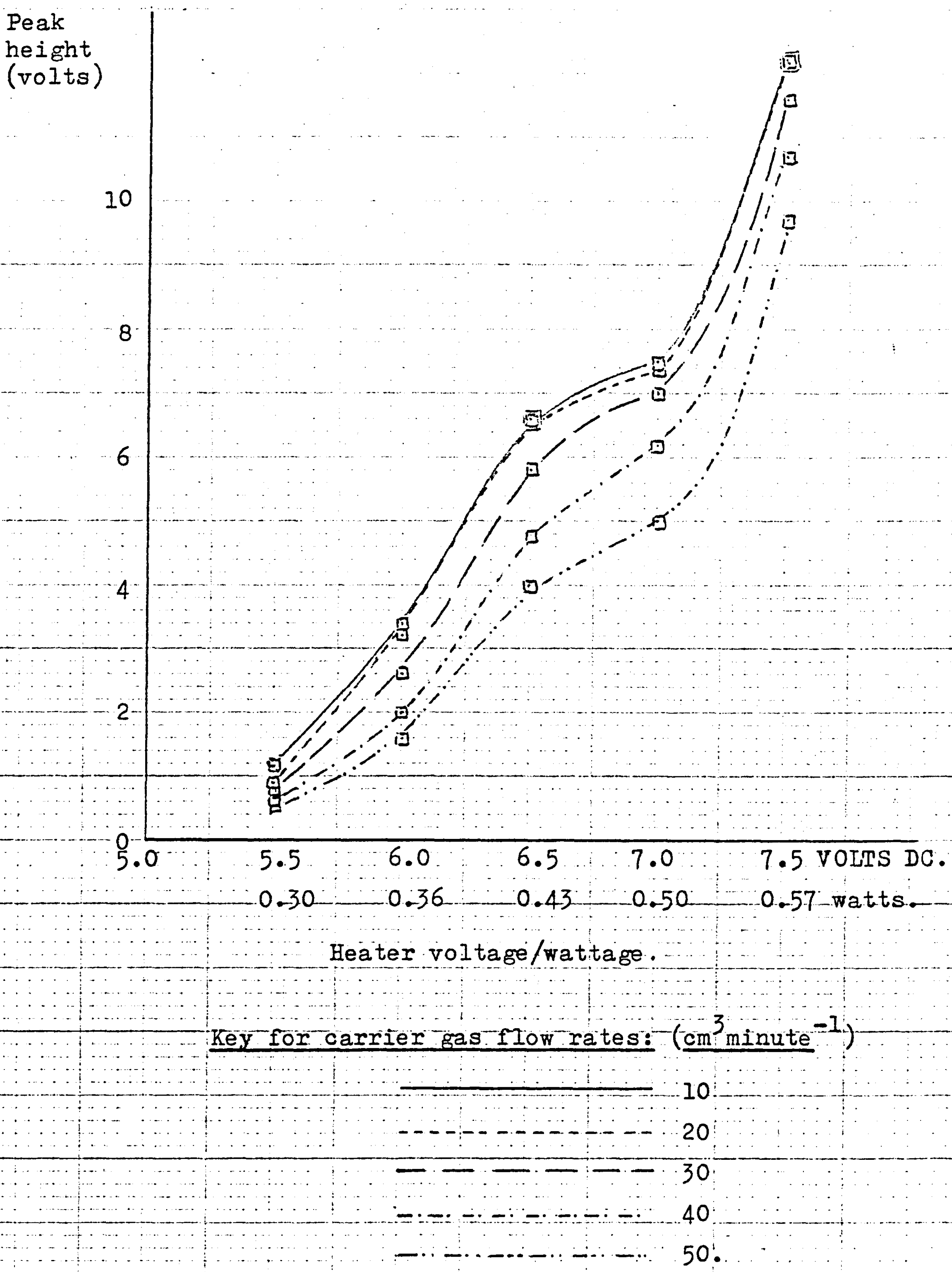
GRAPH 9: VARIATION IN PEAK HEIGHTS FOR HYDROGEN



GRAPH 10: VARIATION IN PEAK HEIGHTS FOR CARBON MONOXIDE



GRAPH 11: VARIATION IN THE PEAK HEIGHTS FOR METHANE WITH HEATER VOLTAGE USING THE T.G.S.711 AT VARIOUS CARRIER GAS FLOW RATES

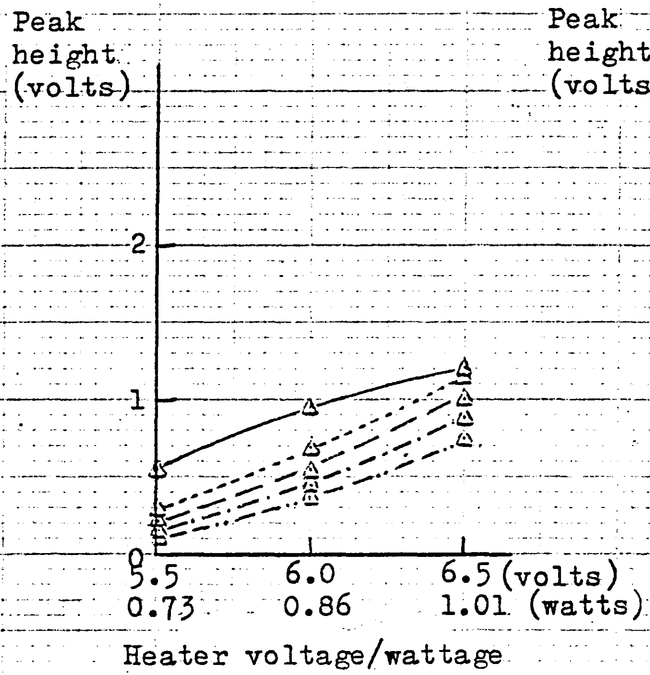


GRAPHS 12-15: VARIATION IN THE PEAK HEIGHTS FOR METHANE, ETHANE, ETHENE AND ETHYNE WITH HEATER VOLTAGE USING THE T.G.S.812 AT VARIOUS CARRIER GAS FLOW RATES

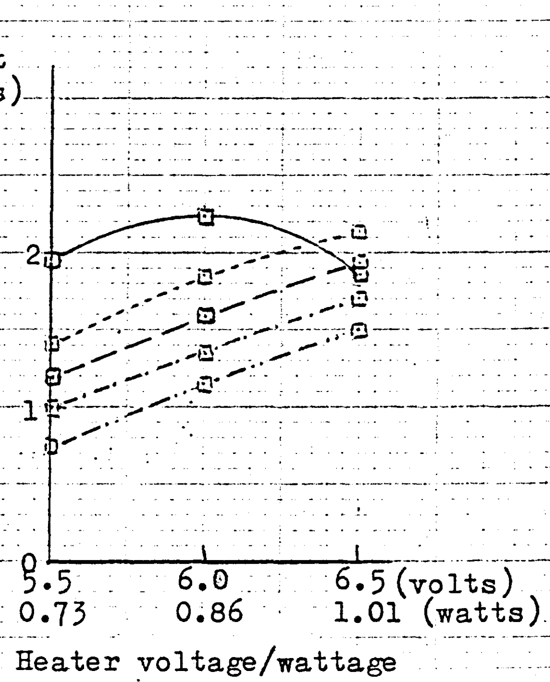
Key for carrier gas flow rates ($cm^3 minute^{-1}$)

10 ——————— 20 --------- 30 — — — —
40 —·—·—·— 50 —·—·—··

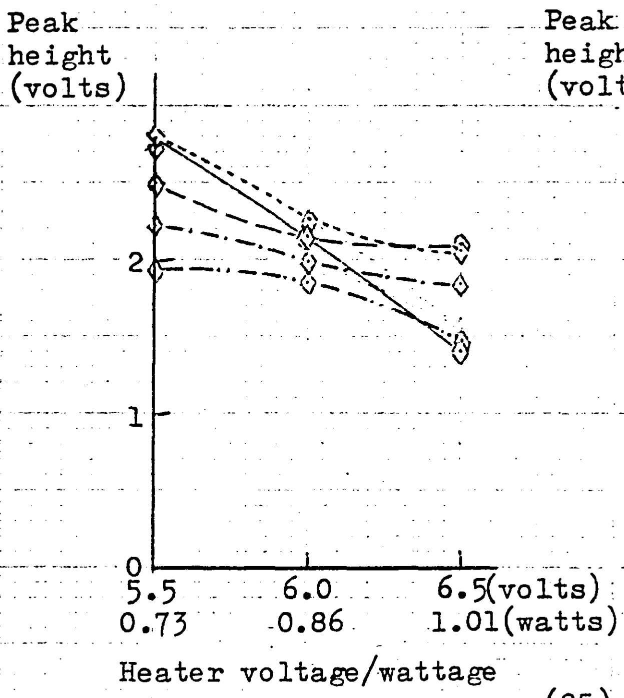
GRAPH 12: VARIATION IN PEAK HEIGHT FOR METHANE



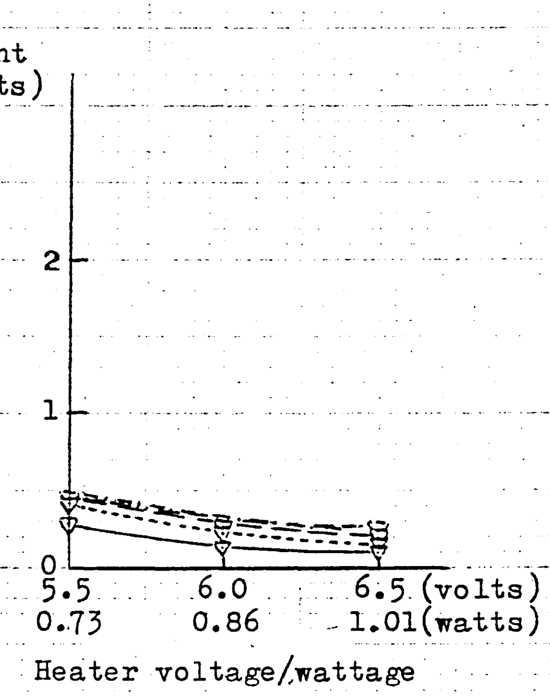
GRAPH 13: VARIATION IN PEAK HEIGHT FOR ETHANE



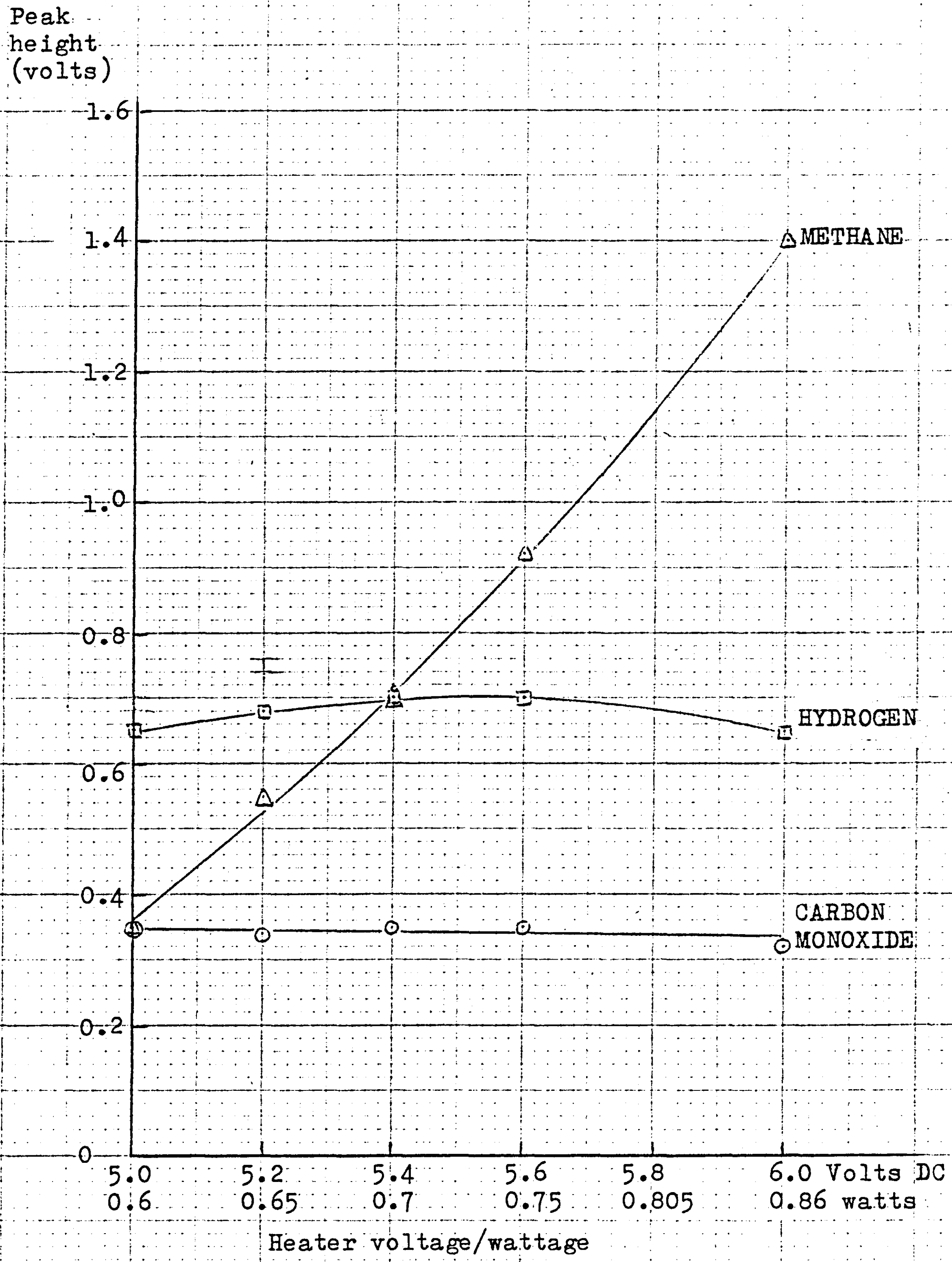
GRAPH 14: VARIATION IN PEAK HEIGHT FOR ETHENE



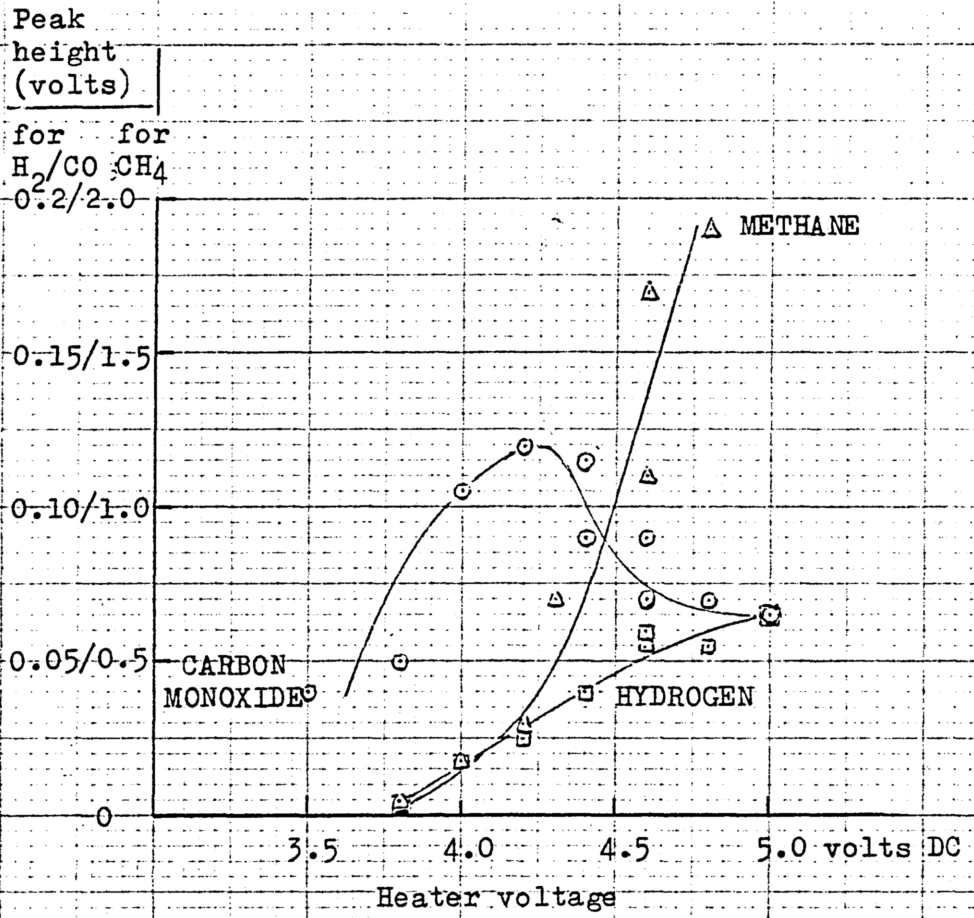
GRAPH 15: VARIATION IN PEAK HEIGHT FOR ETHYNE



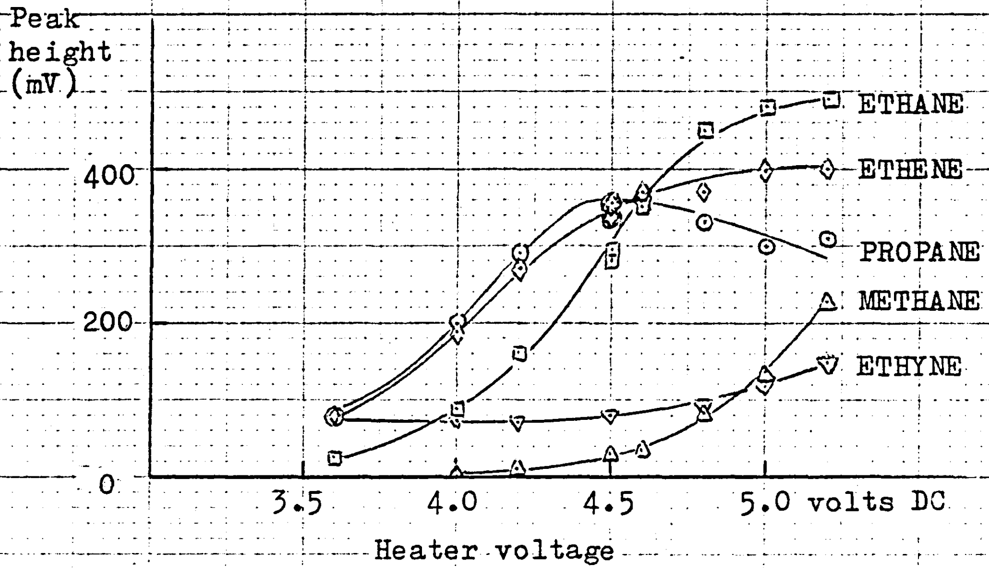
GRAPH 16: VARIATION IN THE PEAK HEIGHTS FOR HYDROGEN, CARBON MONOXIDE AND METHANE WITH HEATER VOLTAGE (WATTAGE) USING THE T.G.S.812 AND EMPLOYING A CARRIER GAS FLOW RATE OF 20 $cm^3 min^{-1}$



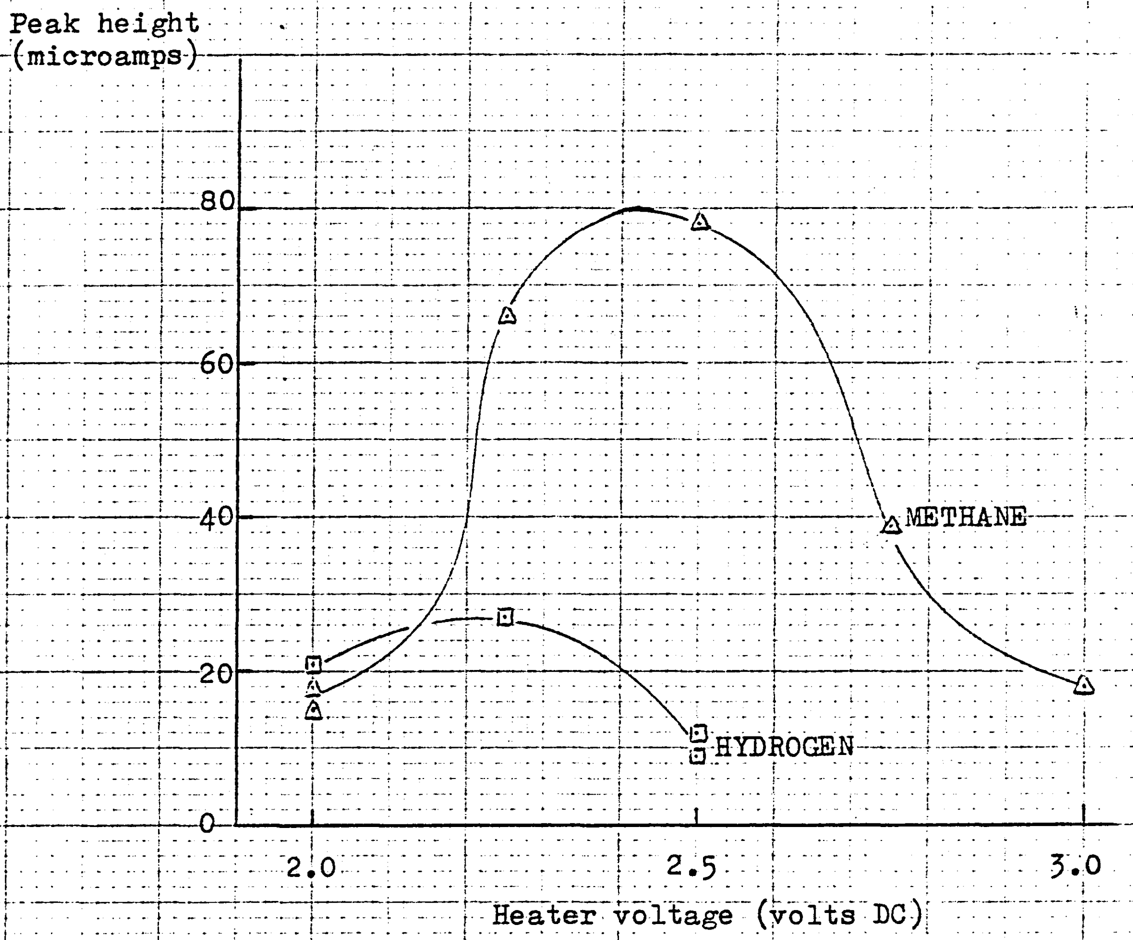
GRAPH 17: VARIATION IN THE PEAK HEIGHTS FOR HYDROGEN, CARBON MONOXIDE AND METHANE WITH HEATER VOLTAGE USING THE MATSUSHITA SENSOR AND EMPLOYING A CARRIER GAS FLOW RATE OF 20 $cm^3 minute^{-1}$



GRAPH 18: VARIATION IN THE PEAK HEIGHTS FOR METHANE, ETHANE, ETHENE, PROPANE AND ETHYNE WITH HEATER VOLTAGE USING THE MATSUSHITA SENSOR AND EMPLOYING A CARRIER GAS FLOW RATE OF 30 $cm^3 min^{-1}$

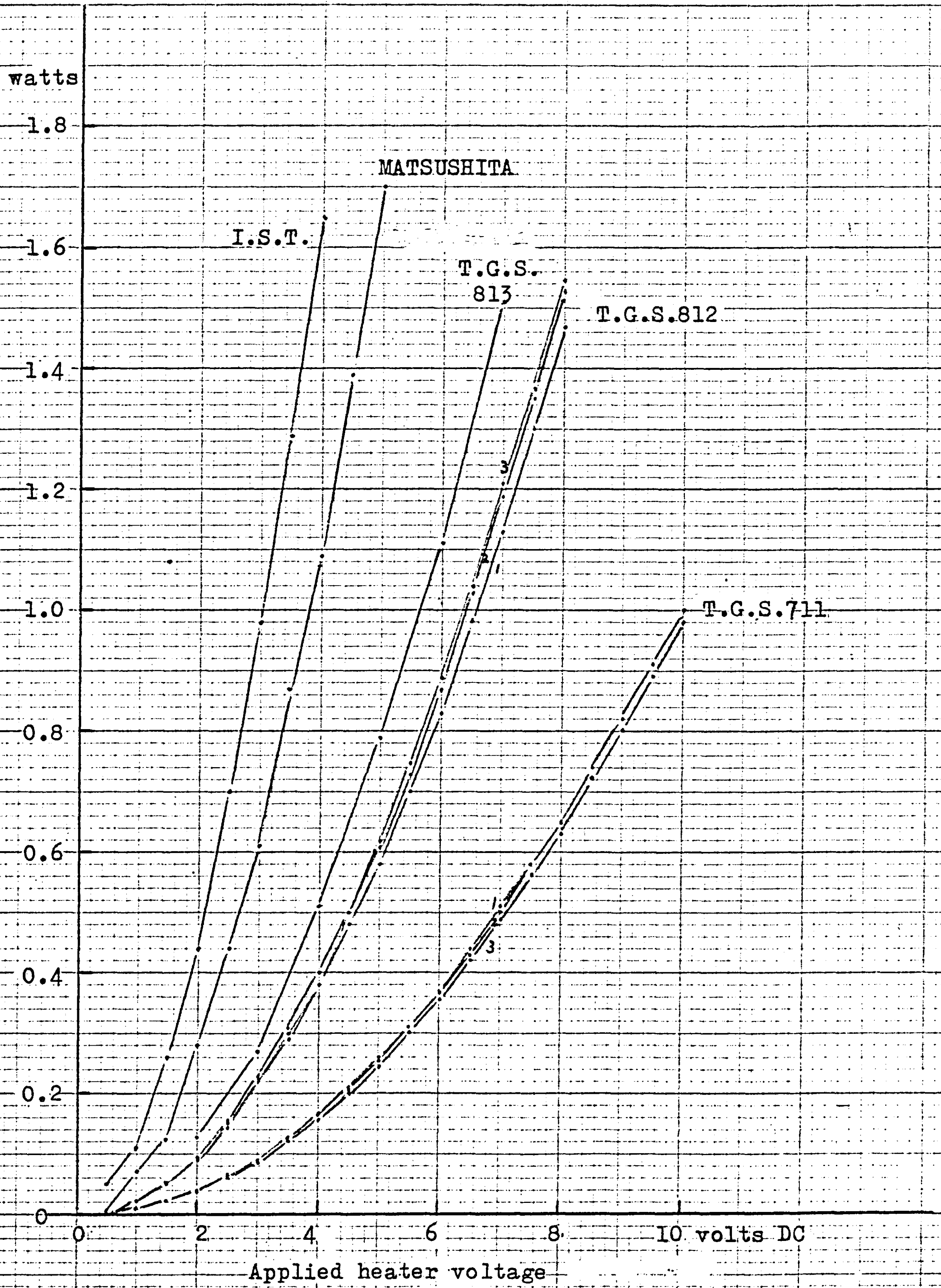


GRAPH 19: VARIATION IN THE PEAK HEIGHTS FOR HYDROGEN AND METHANE WITH HEATER VOLTAGE USING THE I.S.T. SENSOR AND EMPLOYING A CARRIER GAS FLOW RATE OF 20 $cm^3 minute^{-1}$



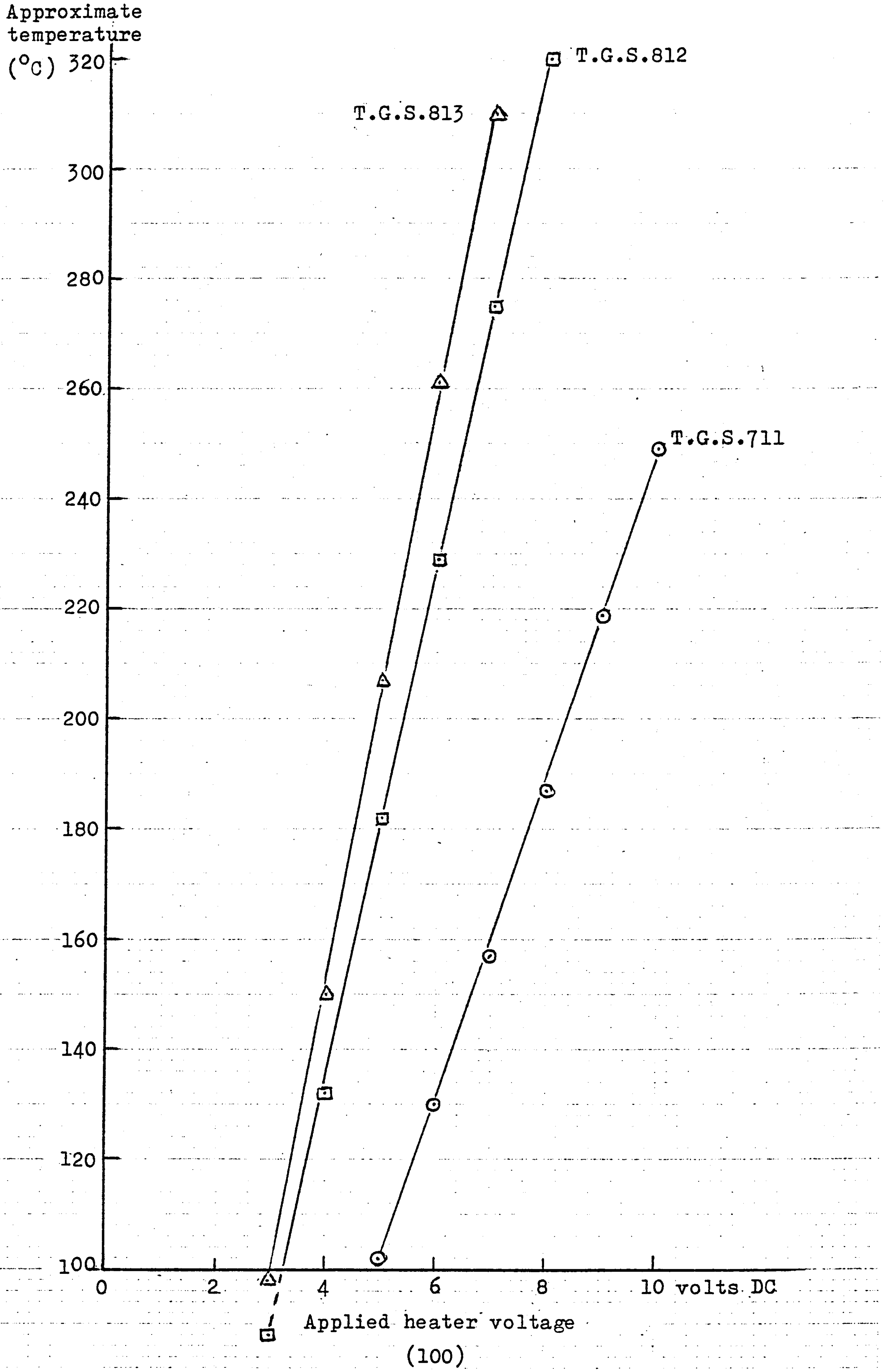
GRAPH 20

VARIATION IN THE ENERGY DISSIPATED (WATTS) BY THE T.G.S.711, T.G.S.812, T.G.S.813, MATSUSHITA AND I.S.T. GAS SENSORS OVER A RANGE OF HEATER VOLTAGES

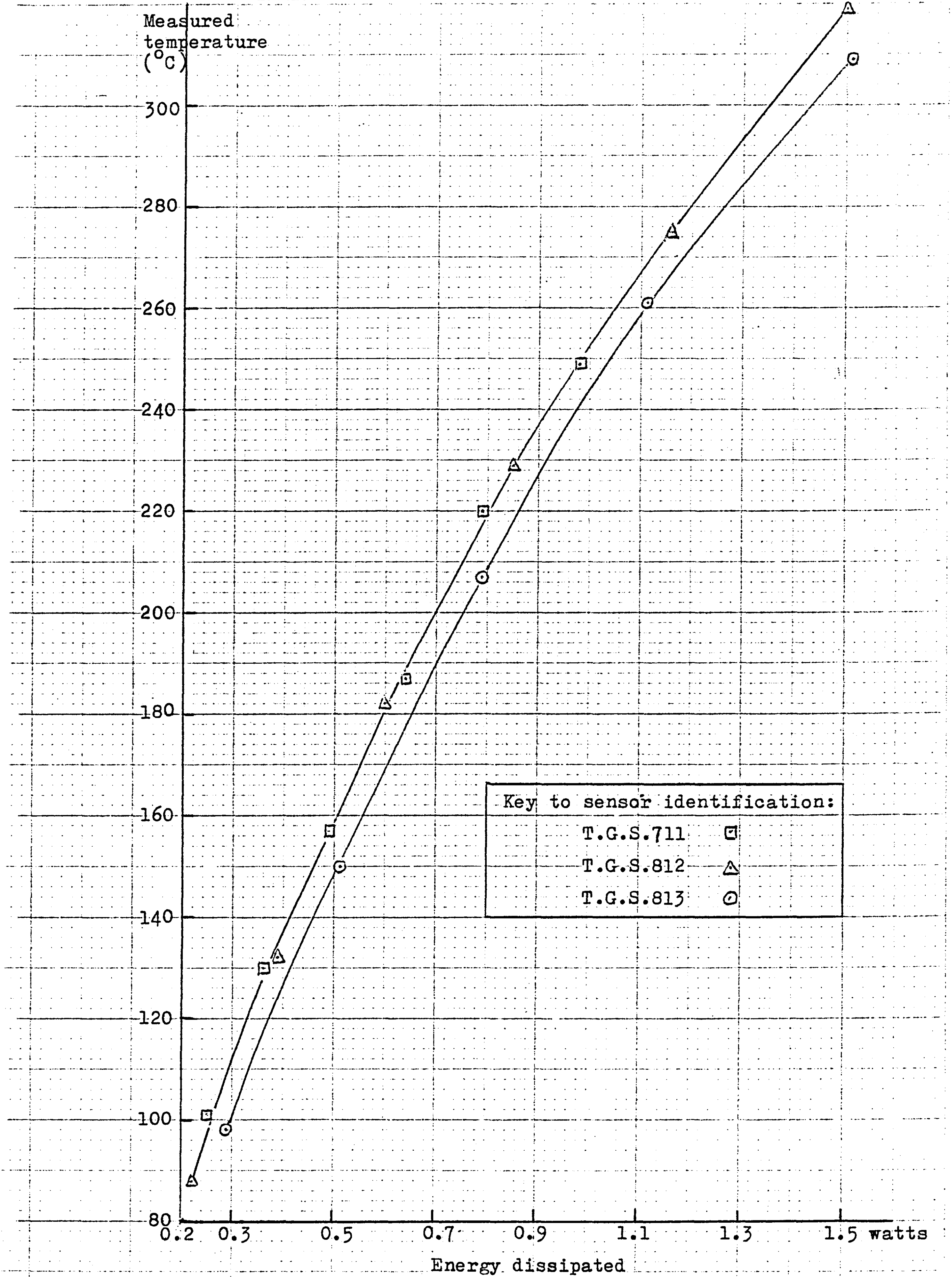


GRAPH 21

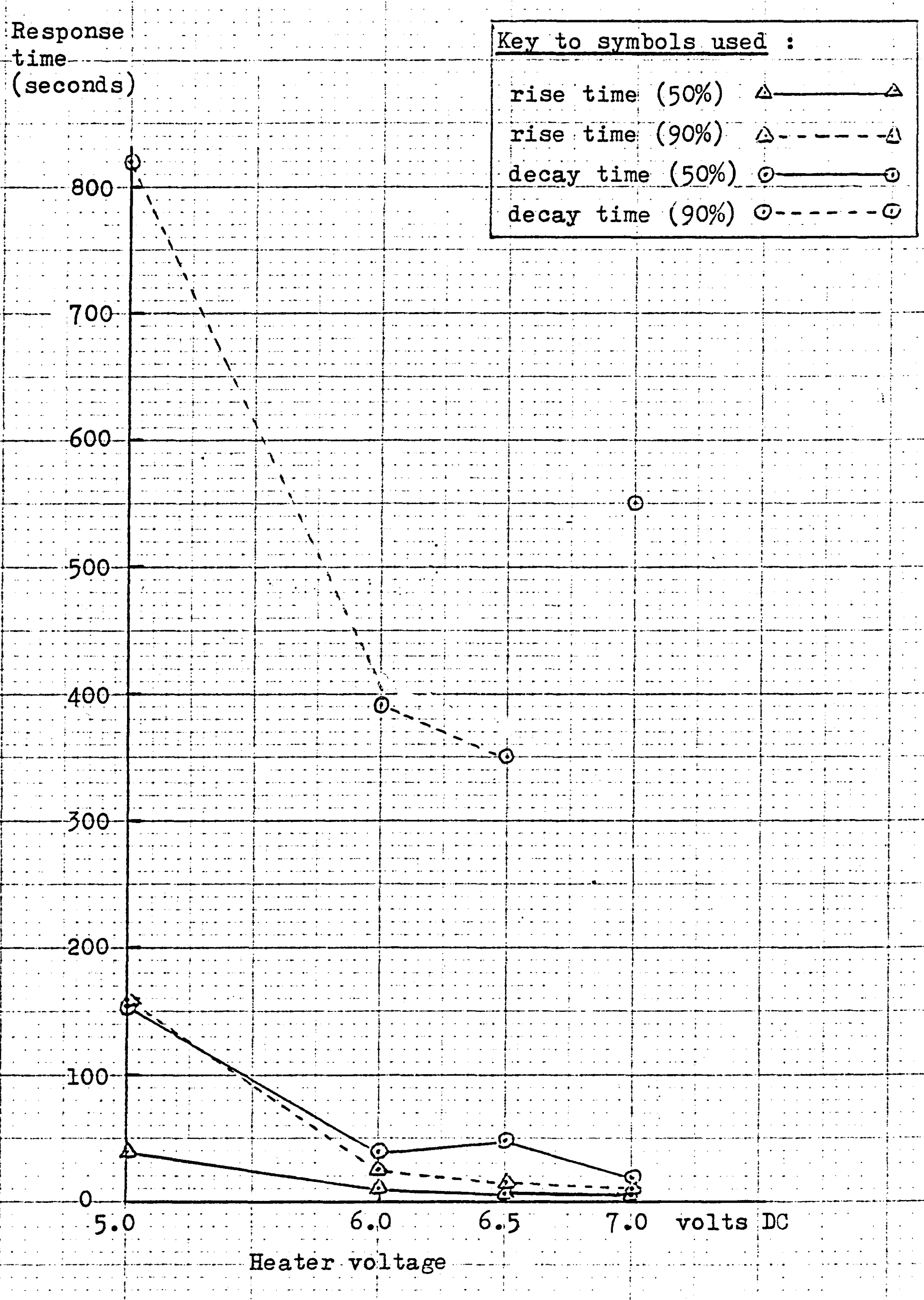
VARIATION IN TEMPERATURE OF THE T.G.S.711, T.G.S.812, AND T.G.S.813 GAS SENSING ELEMENTS WITH HEATER VOLTAGE



GRAPH 22: CORRELATION BETWEEN ENERGY DISSIPATED AND MEASURED TEMPERATURE OF THE T.G.S.711, T.G.S.812 and T.G.S.813.

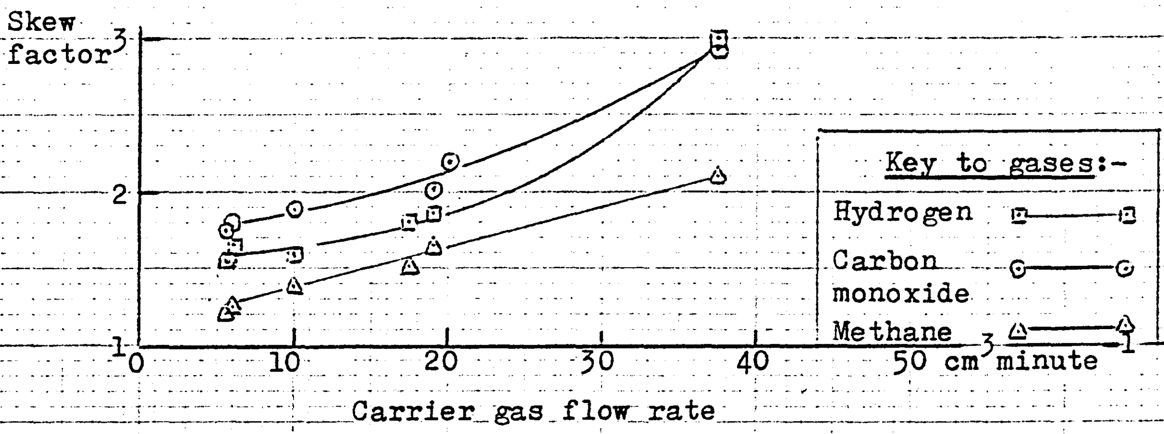


GRAPH 23: RESPONSE TIMES OF THE T.G.S.711 TO 4 ppm OF HYDROGEN IN AIR WITHOUT A CHROMATOGRAPHIC COLUMN, AT DIFFERENT VALUES OF THE HEATER VOLTAGE

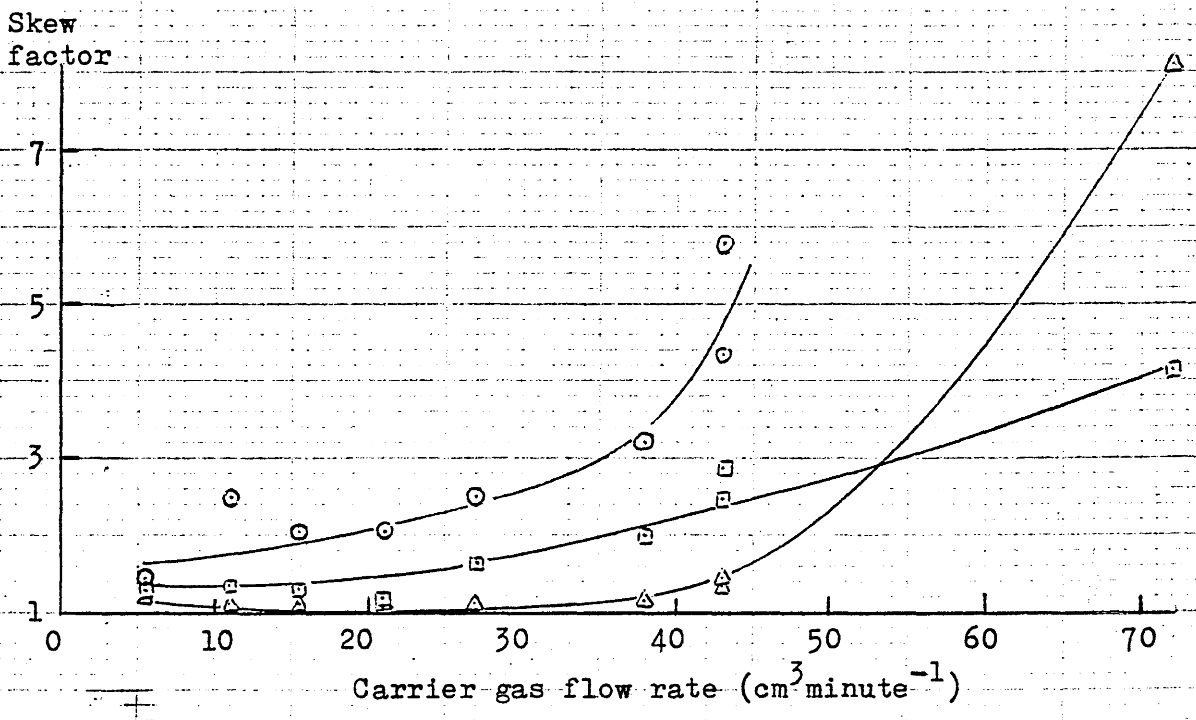


GRAPHS 24-26: VARIATION IN THE SKEW FACTOR OF FOR HYDROGEN, CARBON MONOXIDE AND METHANE WITH CARRIER GAS FLOW RATE USING THE T.G.S.711 AT THREE DIFFERENT VALUES OF HEATER VOLTAGE

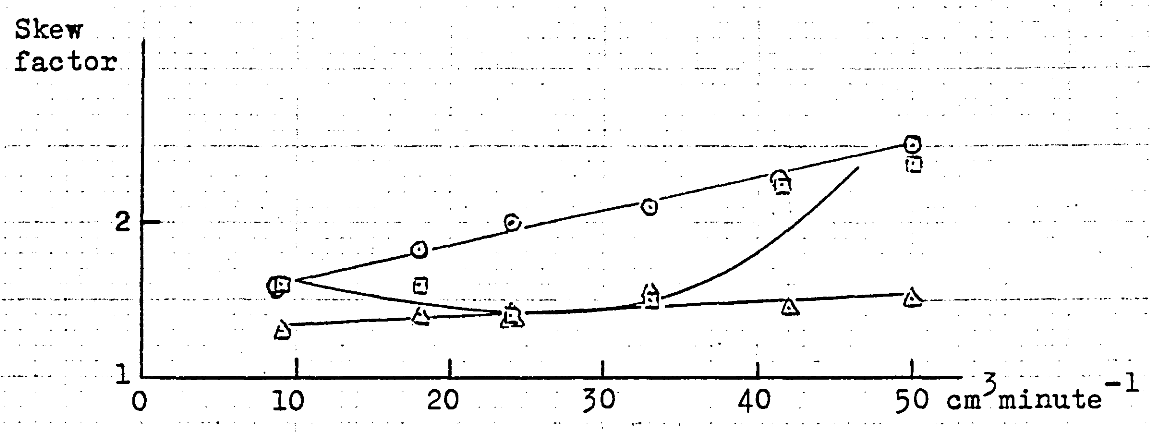
GRAPH 24: USING A HEATER VOLTAGE OF 6.0 VOLTS DC



GRAPH 25: USING A HEATER VOLTAGE OF 6.5 VOLTS DC

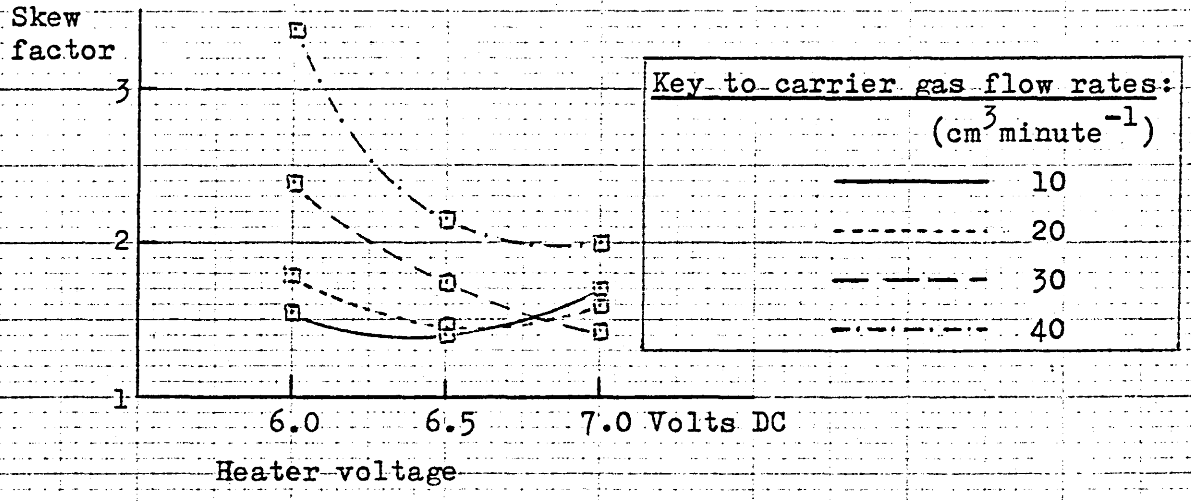


GRAPH 26: USING A HEATER VOLTAGE OF 7.0 VOLTS DC

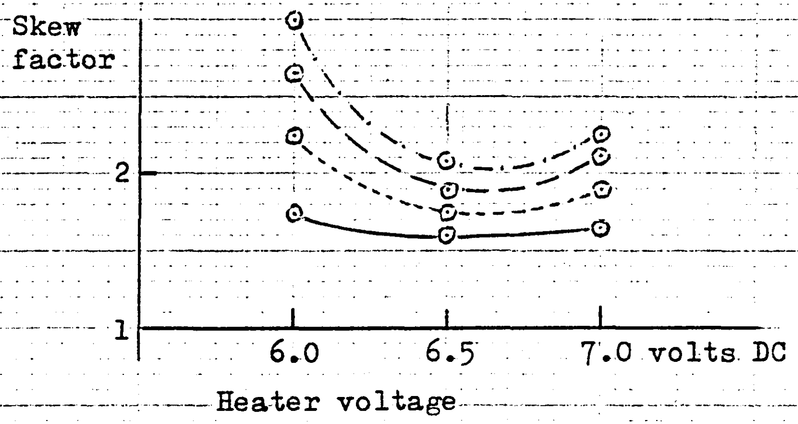


GRAPHS 27-29: VARIATION IN THE SKEW FACTOR OF CHROMATOGRAPHIC PEAKS FOR HYDROGEN, CARBON MONOXIDE AND METHANE WITH HEATER VOLTAGE USING THE T.G.S.711 AT A SERIES OF CARRIER GAS FLOW RATES

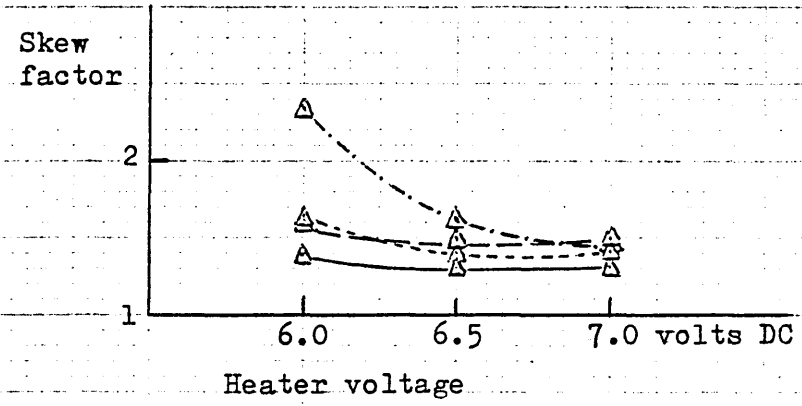
GRAPH 27: VARIATION IN THE SKEW FACTOR FOR HYDROGEN



GRAPH 28: VARIATION IN THE SKEW FACTOR FOR CARBON MONOXIDE

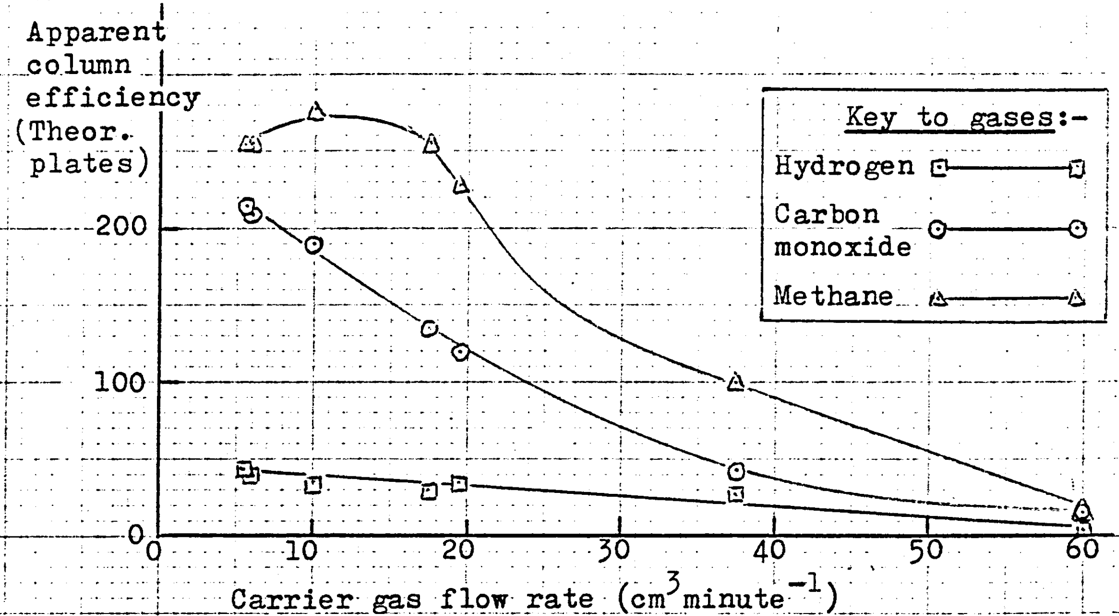


GRAPH 29: VARIATION IN THE SKEW FACTOR FOR METHANE

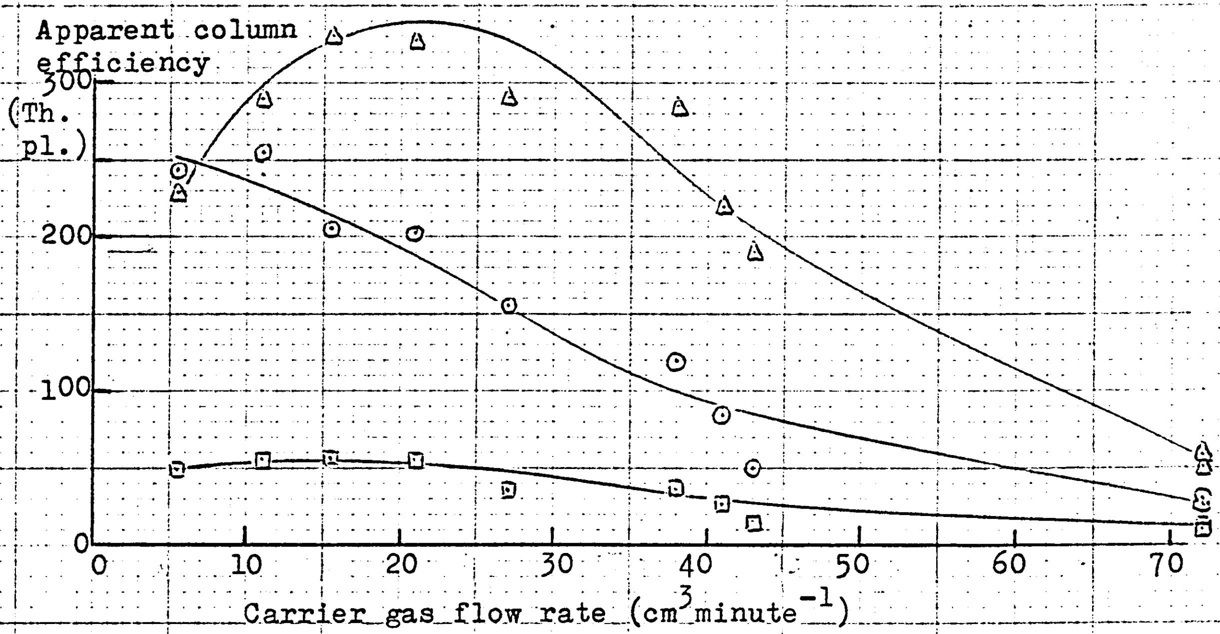


GRAPHS 30-32: VARIATION IN THE APPARENT COLUMN EFFICIENCIES FOR HYDROGEN, CARBON MONOXIDE AND METHANE WITH CARRIER GAS FLOW RATE USING THE T.G.S.711

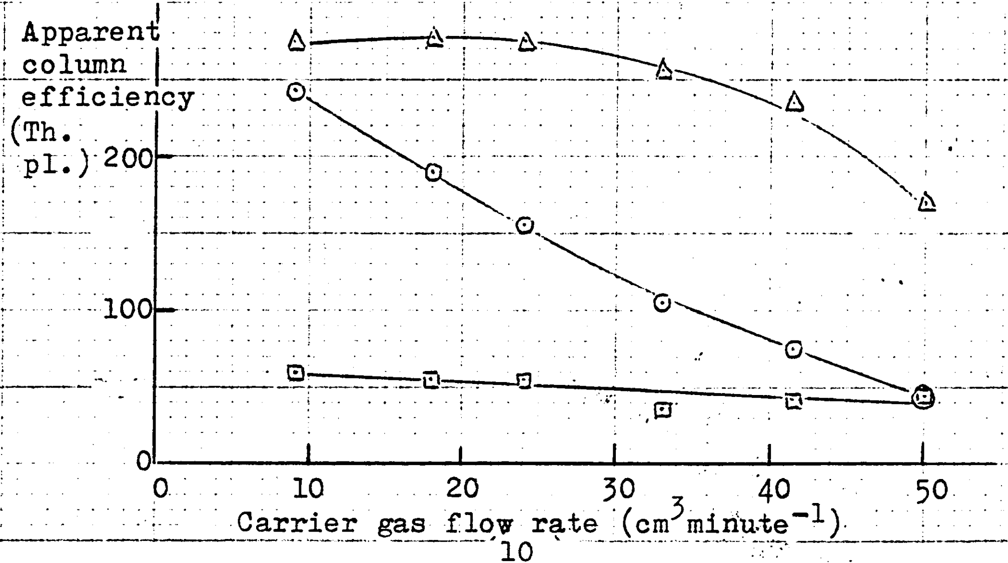
GRAPH 30: EMPLOYING A HEATER VOLTAGE OF 6.0 VOLTS (0.36 watts)



GRAPH 31: EMPLOYING A HEATER VOLTAGE OF 6.5 VOLTS (0.43 watts)

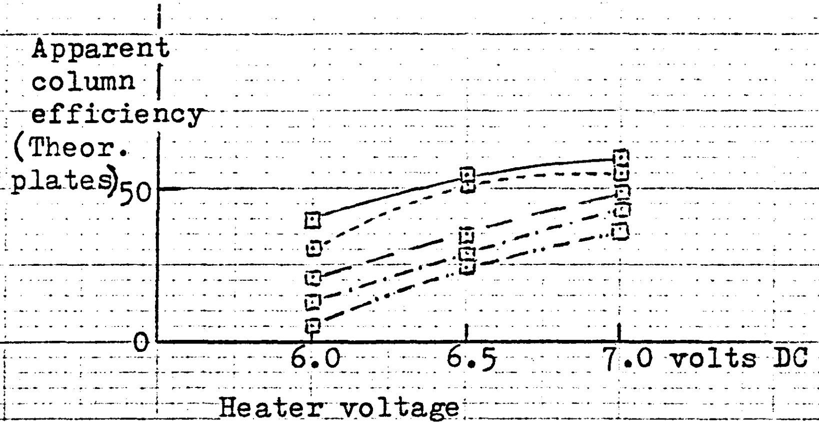


GRAPH 32: EMPLOYING A HEATER VOLTAGE OF 7.0 VOLTS (0.50 watts)

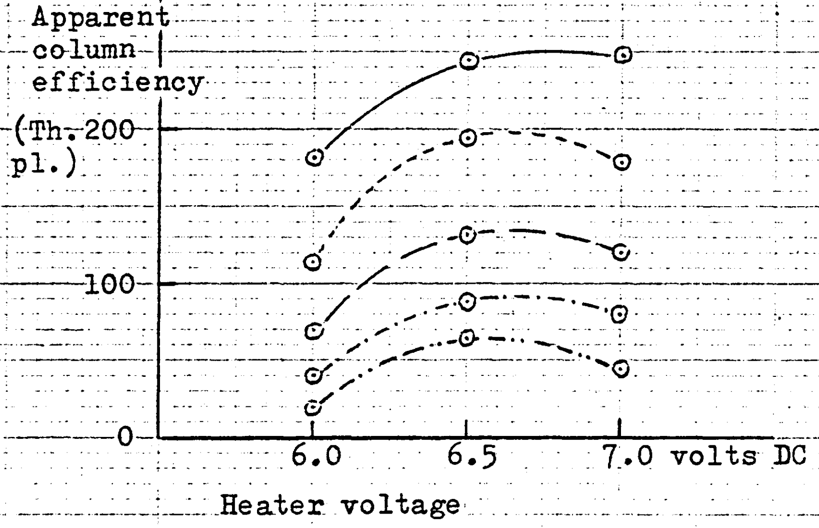


GRAPHS 33-35: VARIATION IN THE APPARENT COLUMN EFFICIENCY FOR HYDROGEN, CARBON MONOXIDE AND METHANE WITH HEATER VOLTAGE USING THE T.G.S.711 AT A SERIES OF CARRIER GAS FLOW RATES

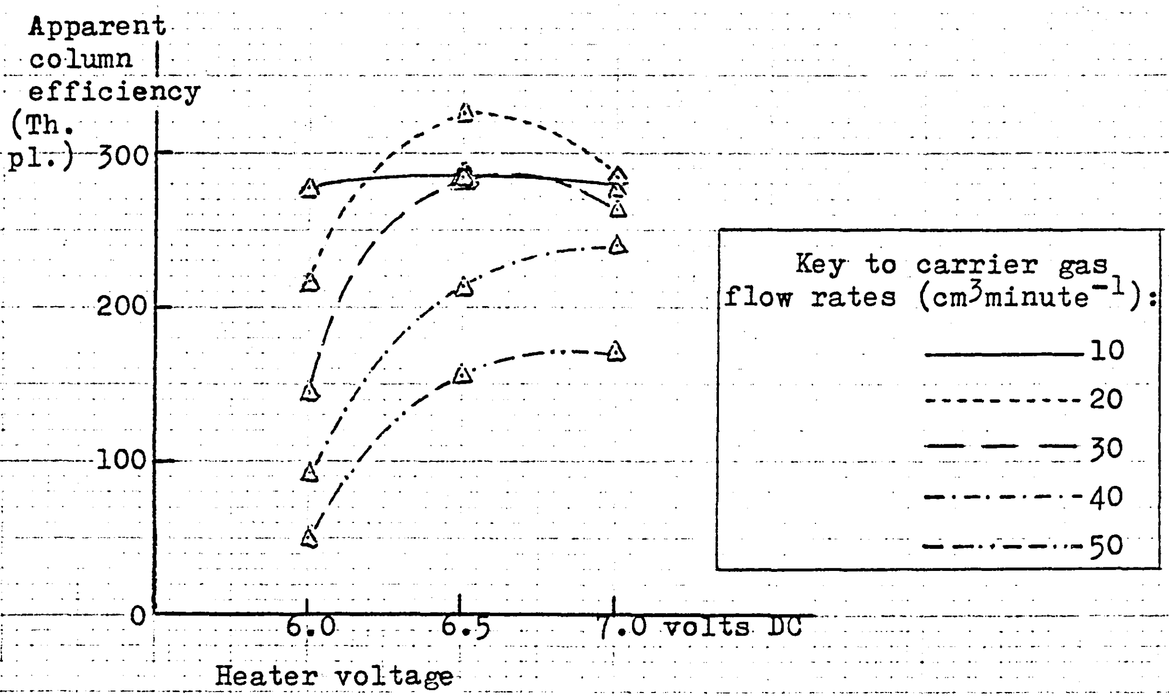
GRAPH 33: VARIATION IN APPARENT COLUMN EFFICIENCY FOR HYDROGEN



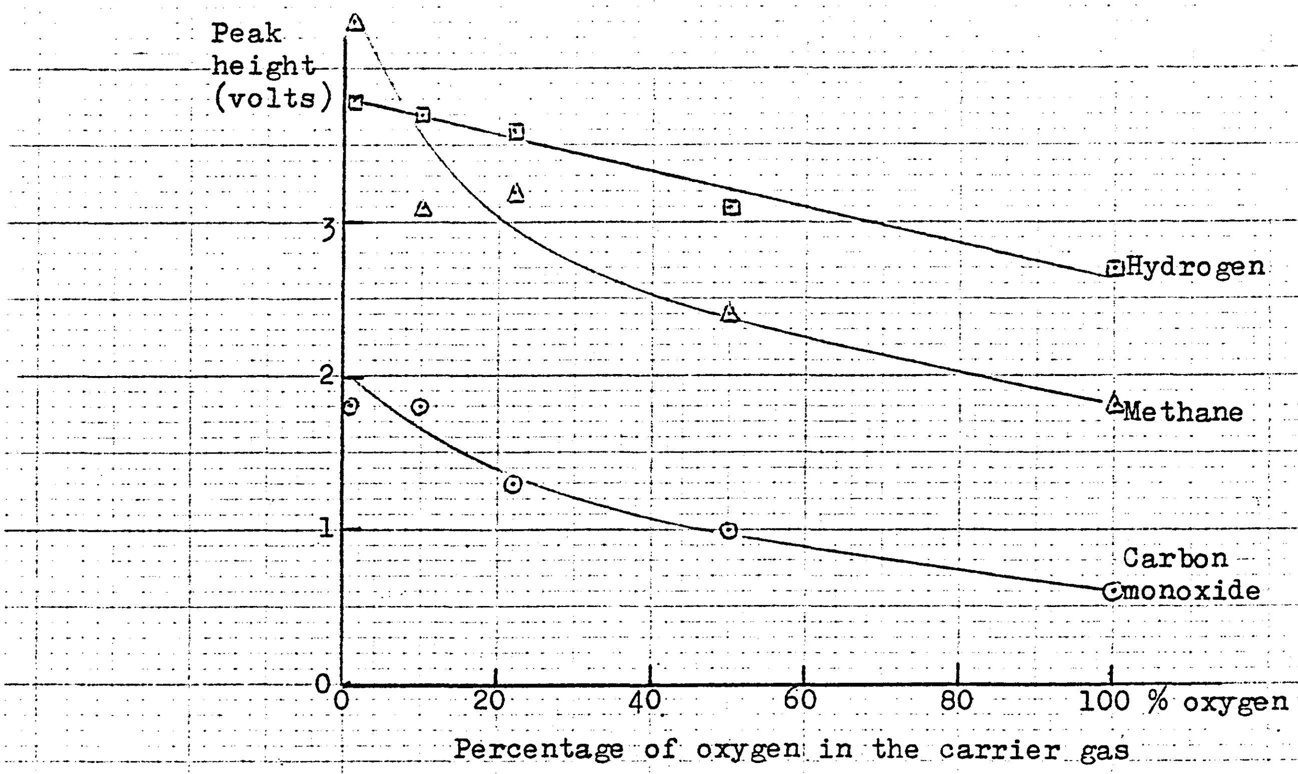
GRAPH 34: VARIATION IN APPARENT COLUMN EFFICIENCY FOR CARBON MONOXIDE



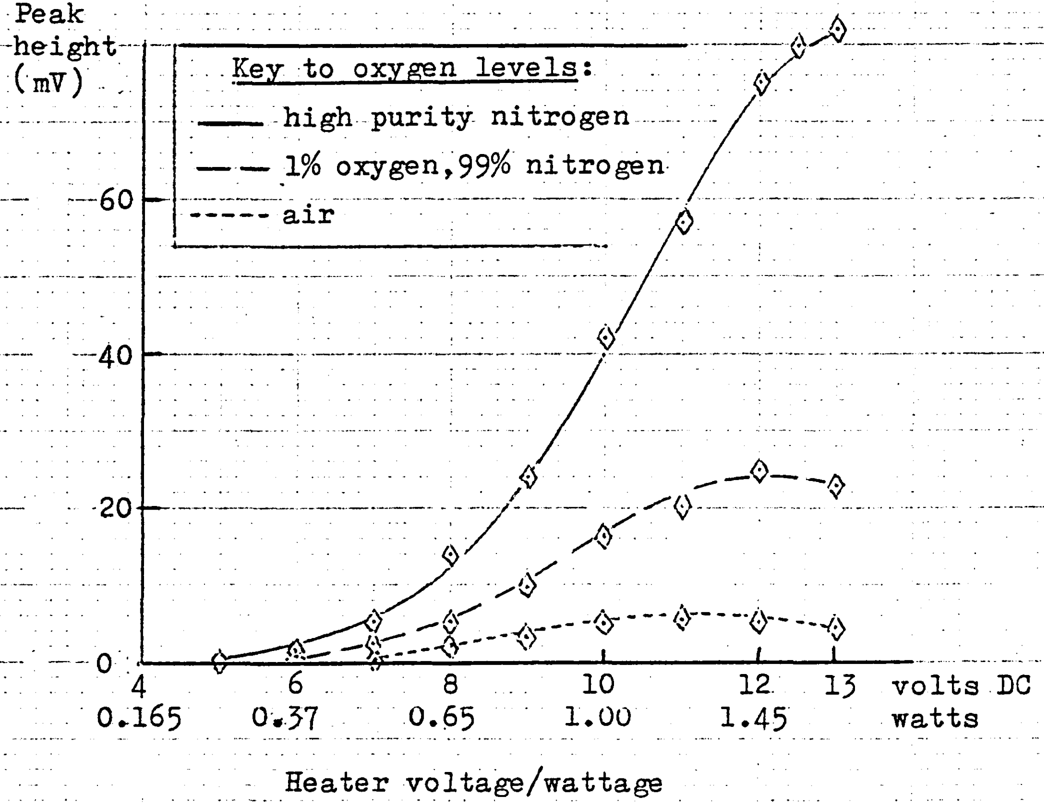
GRAPH 35: VARIATION IN APPARENT COLUMN EFFICIENCY FOR METHANE



GRAPH 36: VARIATION IN THE PEAK HEIGHTS FOR HYDROGEN, CARBON MONOXIDE AND METHANE, USING THE T.G.S.711, AS A RESULT OF VARYING THE PERCENTAGE OF OXYGEN IN THE CARRIER GAS

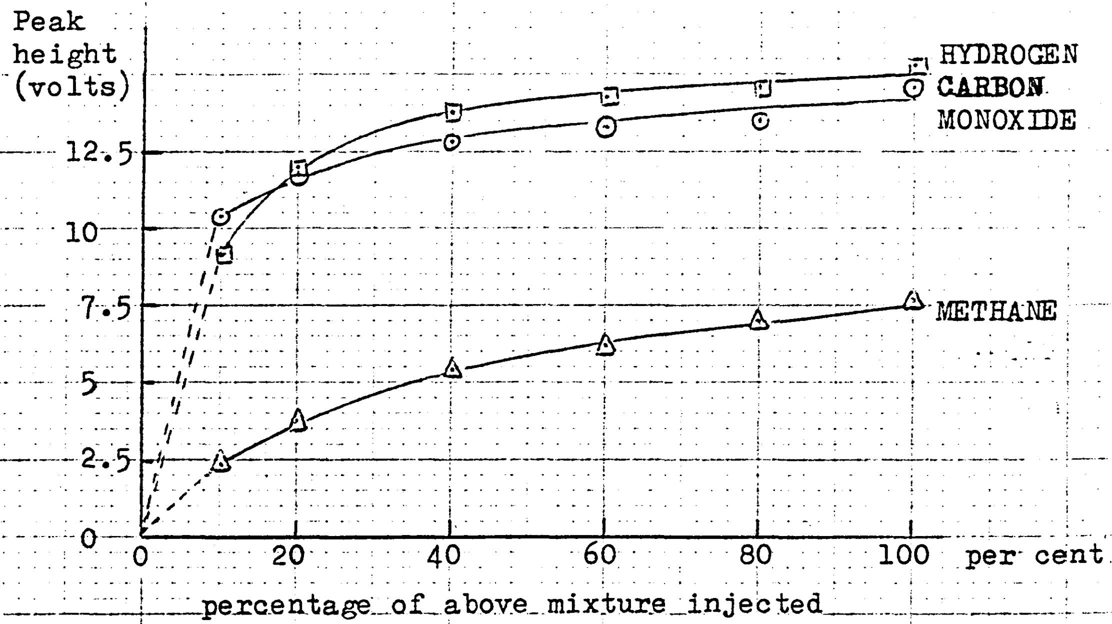


GRAPH 37: VARIATION IN THE PEAK HEIGHT OF ETHENE WITH HEATER VOLTAGE, USING THE T.G.S.711, AND CARRIER GASES CONTAINING THREE DIFFERENT LEVELS OF OXYGEN

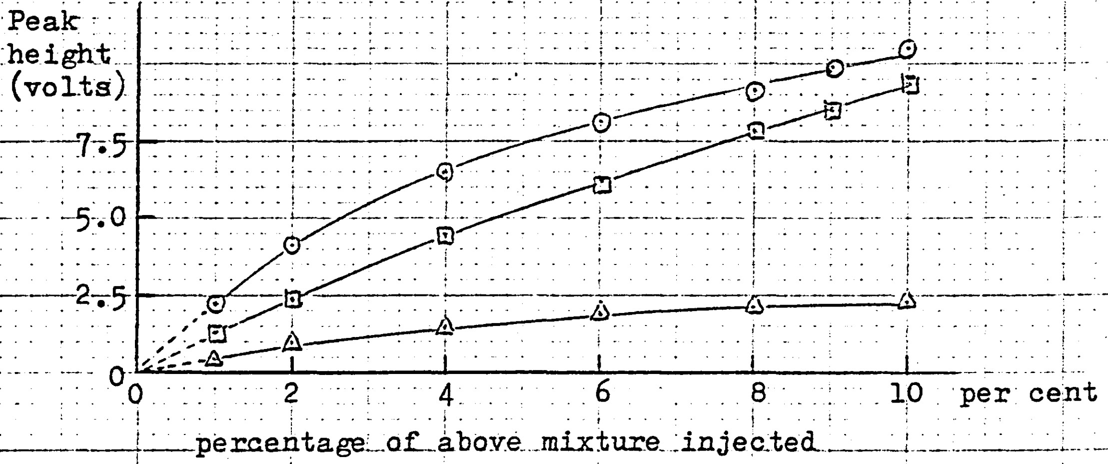


GRAPHS 38-40: CALIBRATION GRAPHS FOR HYDROGEN, CARBON MONOXIDE AND METHANE USING THE T.G.S.711 IN CONJUNCTION WITH THE MODIFIED LOAD RESISTOR CIRCUIT

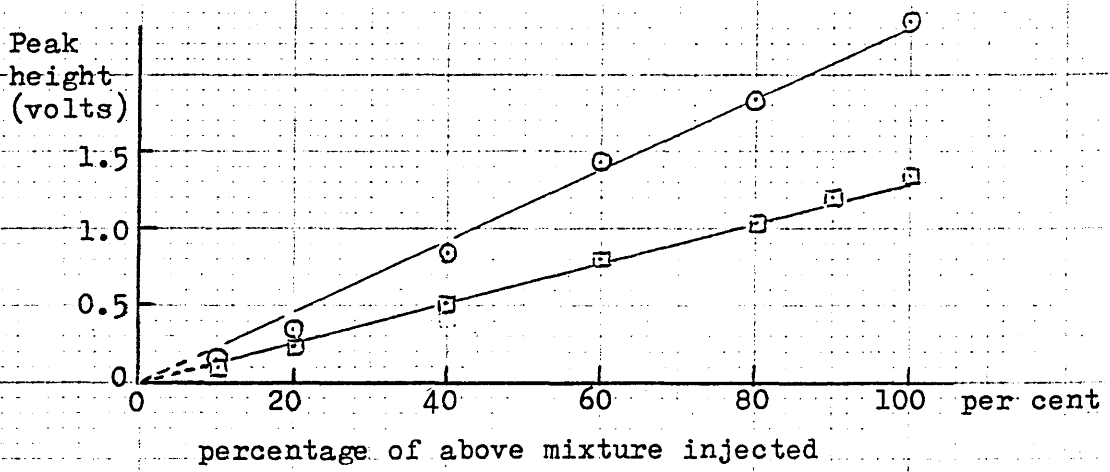
GRAPH 38: HYDROGEN (100 ppm) CARBON MONOXIDE (1200 ppm) AND METHANE (4.0% v/v)



GRAPH 39: HYDROGEN (100 ppm) CARBON MONOXIDE (1200 ppm) AND METHANE (4.0% v/v)

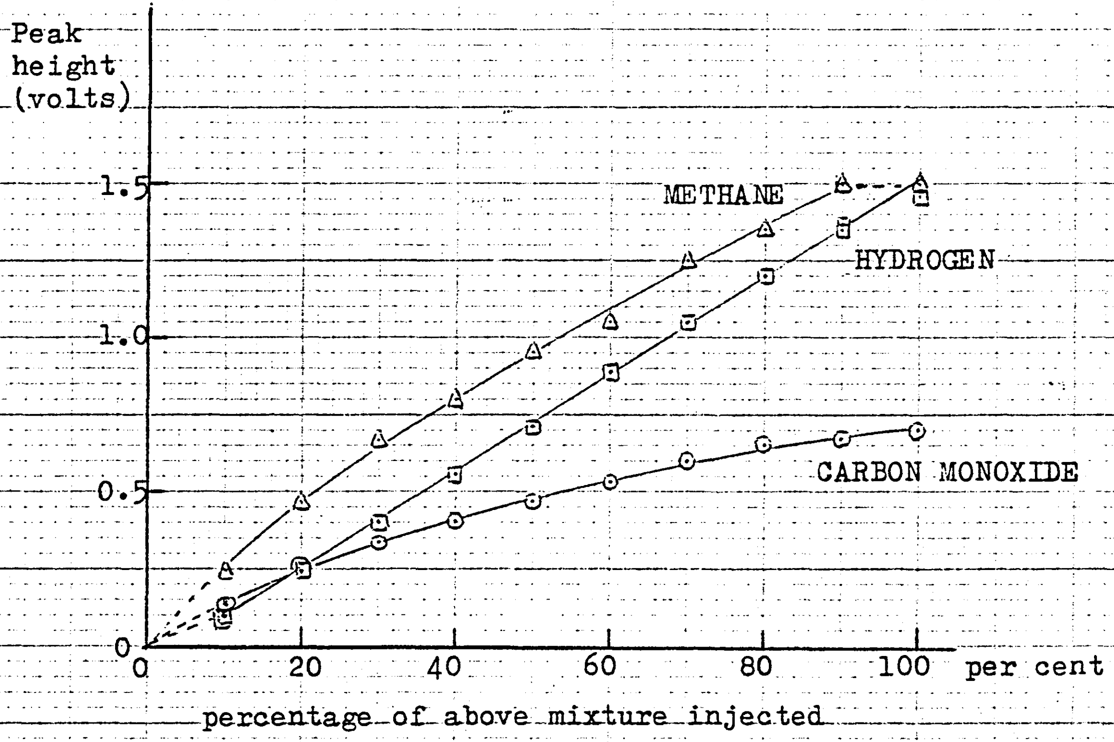


GRAPH 40: HYDROGEN (1 ppm) CARBON MONOXIDE (12 ppm)

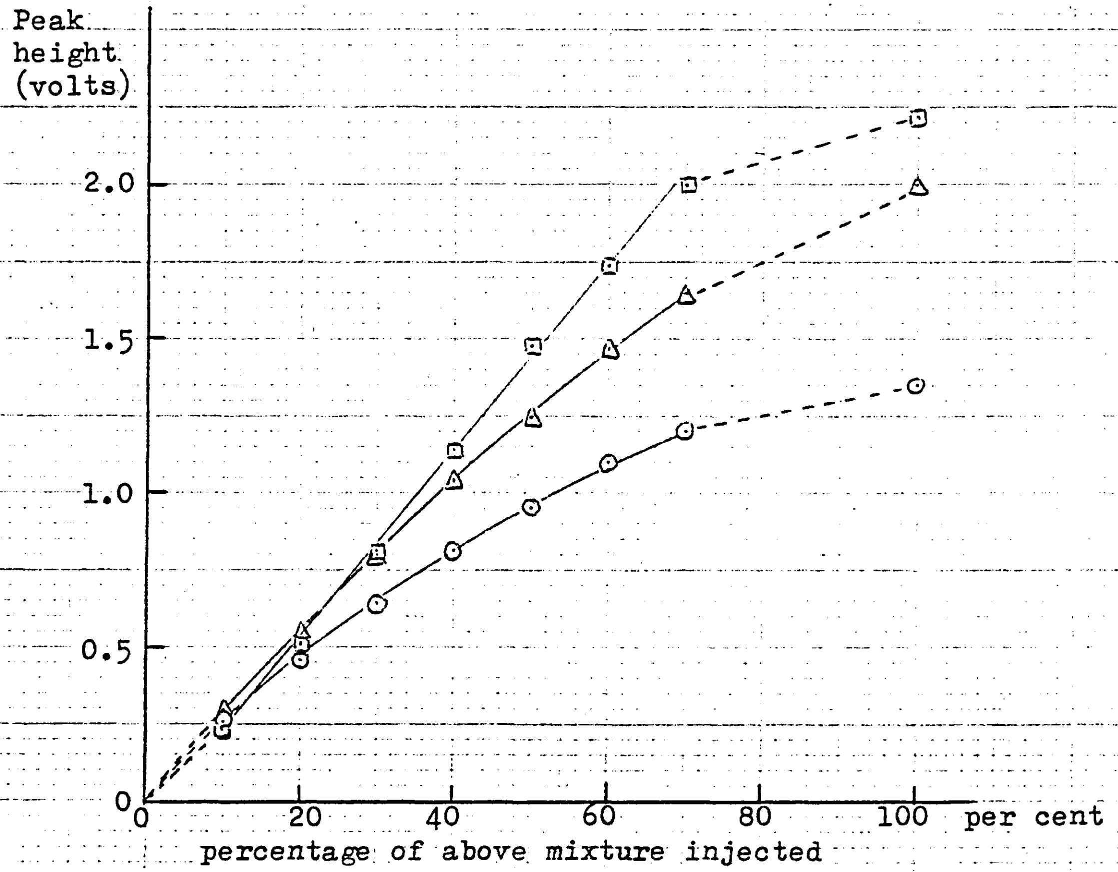


GRAPHS 41-42: CALIBRATION GRAPHS FOR HYDROGEN, CARBON MONOXIDE AND METHANE USING THE T.G.S.711 IN CONJUNCTION WITH THE MODIFIED OPERATIONAL AMPLIFIER CIRCUIT

GRAPH 41: HYDROGEN (100 ppm) CARBON MONOXIDE (1200 ppm) AND METHANE (4.0% v/v) using the T.G.S.711(1)

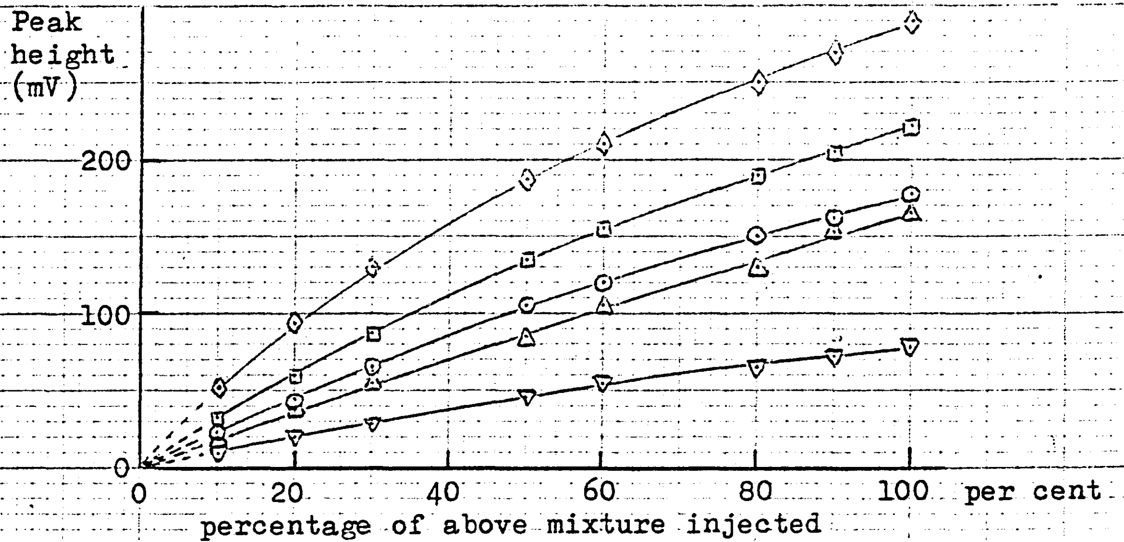


GRAPH 42: HYDROGEN (100 ppm) CARBON MONOXIDE (1200 ppm) AND METHANE (4.0% v/v) USING THE T.G.S.711(2)

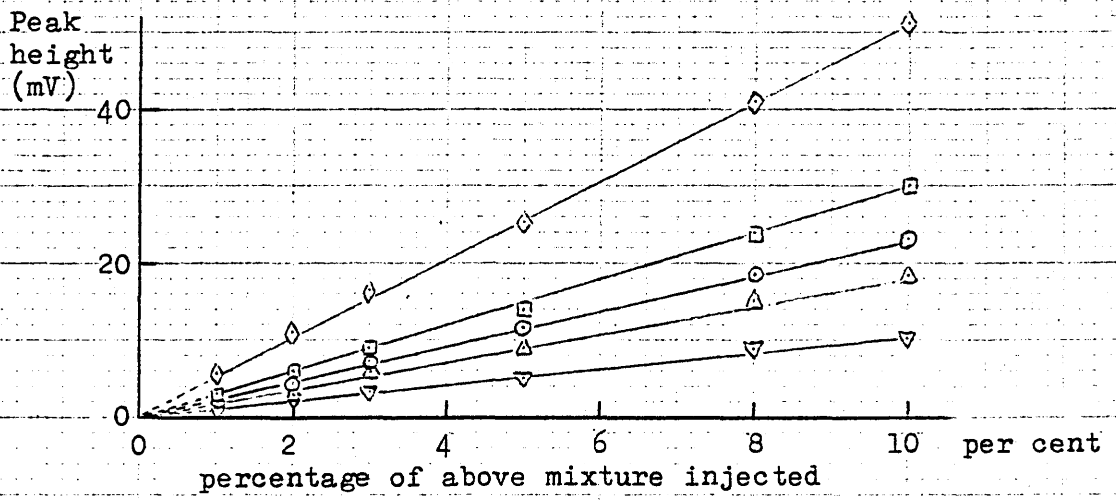


GRAPHS 43-44: CALIBRATION GRAPHS FOR METHANE, ETHANE, ETHENE, PROPANE AND ETHYNE USING THE T.G.S.711(2) IN CONJUNCTION WITH THE MODIFIED OPERATIONAL AMPLIFIER CIRCUIT

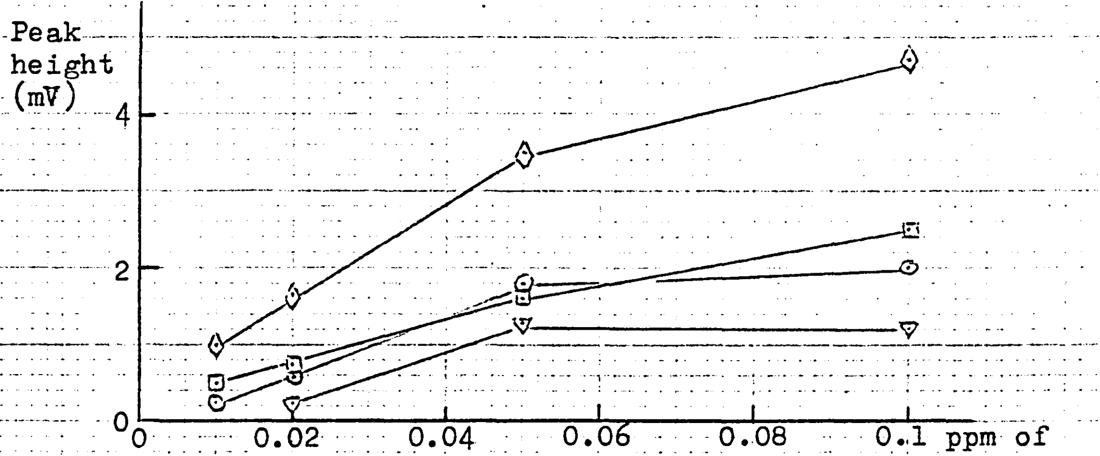
GRAPH 43: METHANE, ETHANE, ETHENE, PROPANE, ETHYNE (100 ppm of each)



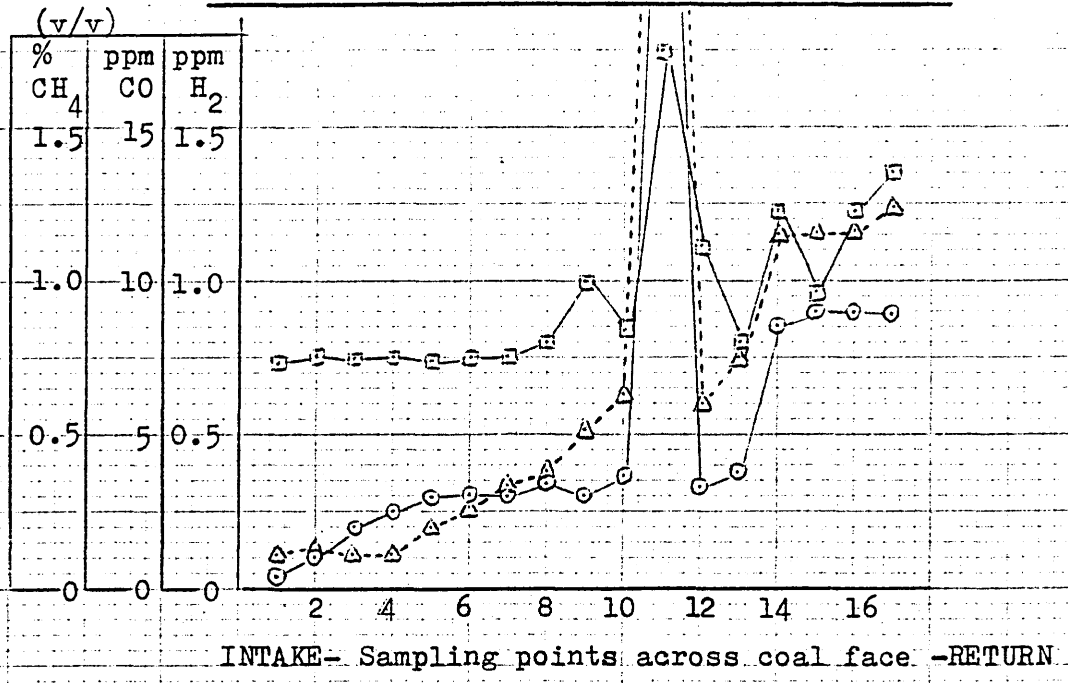
GRAPH 44: METHANE,ETHANE,ETHENE,PROPANE,ETHYNE (100 ppm of each)



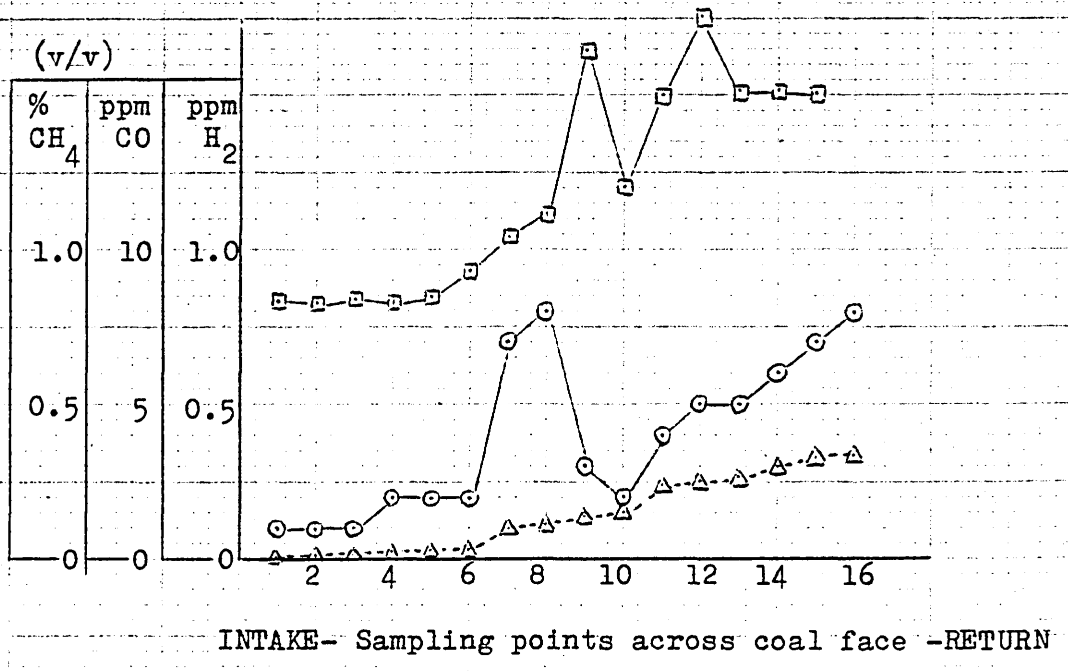
GRAPH 45: CALIBRATION GRAPHS FOR ETHANE, ETHENE, PROPANE AND ETHYNE NEAR THEIR LIMITS OF DETECTION, USING THE T.G.S. 711(2) AND THE MODIFIED OPERATIONAL AMPLIFIER CIRCUIT



GRAPH 46: VARIATION IN THE CONCENTRATIONS OF HYDROGEN, CARBON MONOXIDE AND METHANE FOUND IN SAMPLES TAKEN DURING A TRAVERSE OF 82's COAL FACE AT COLLIERY "A"



GRAPH 47: VARIATION IN THE CONCENTRATIONS OF HYDROGEN, CARBON MONOXIDE AND METHANE IN SAMPLES TAKEN DURING A TRAVERSE OF K 14's FACE AT COLLIERY "B"



Key to gases :-

HYDROGEN ⊡—⊡—⊡

CARBON MONOXIDE ⊙—⊙—⊙

METHANE △--△--△

PLATE 1

Taguchi semiconductor gas sensor Type 711 > as received

PLATE 2

T.G.S.711 with cover removed

PLATE 5

T.G.S.711 modified for use as a gas chromatographic detector, showing gas inlet from column.

PLATE 4

T.G.S.711 modified for use as a gas chromatographic detector, exterior view.

PLATE 5

Matsushita semiconductor gas sensor, with cover removed.

PLATE 6

Matsushita sensor, as received and with cover removed.

PLATE 7 I.S.T. sensor with sintered covers in position.

PLATE 8 I.S.T.sensor with sintered covers removed

PLATE 9 I.S.T. sensor - close up view.

PLATE 10

sensor, modified for use as a gas chromatographic detector, showing sensor bead and housing.

PLATE 11

sensor, modified for use as a gas chromatographic detector, with sensor inside detector housing

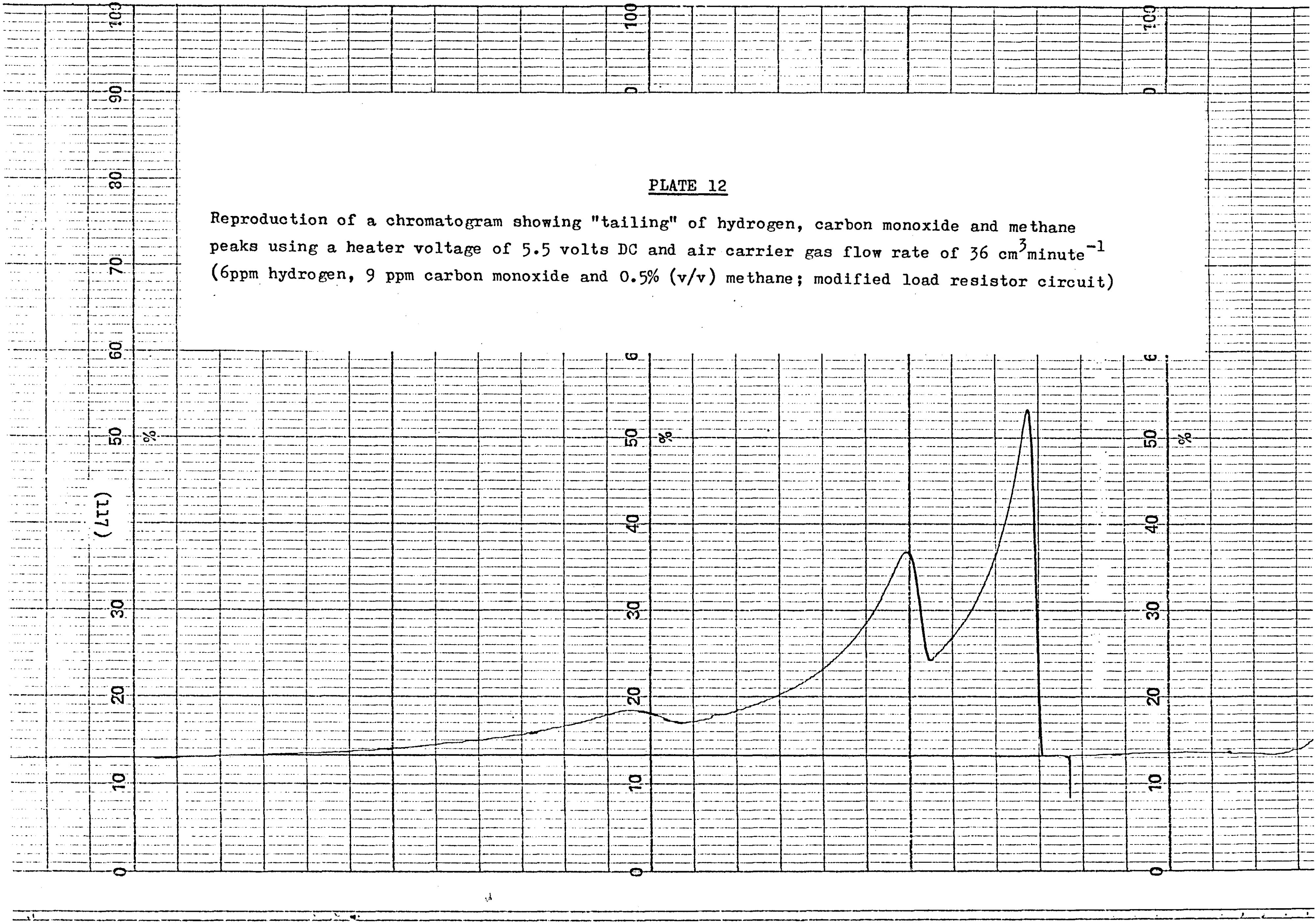
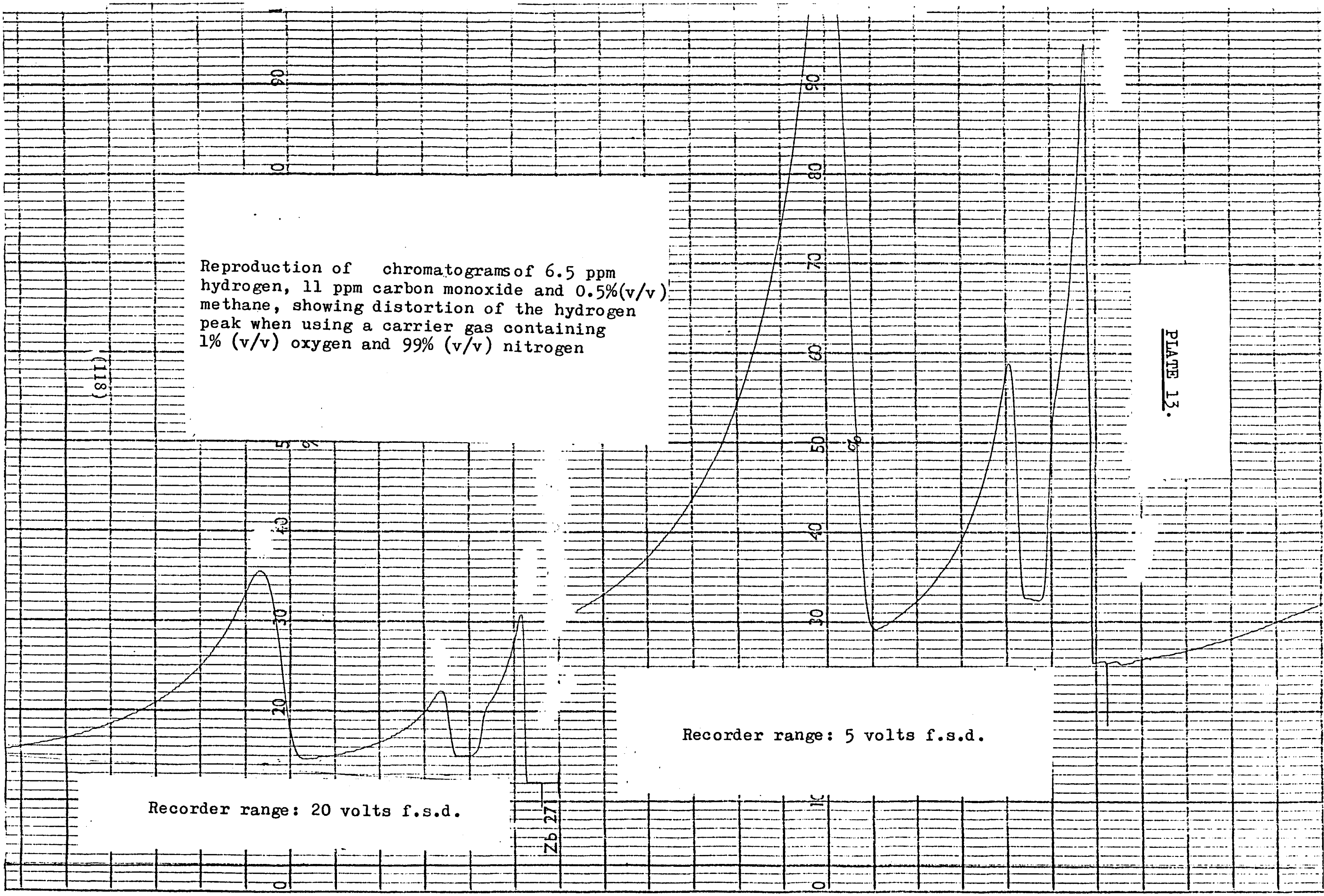


PLATE 12

Reproduction of a chromatogram showing "tailing" of hydrogen, carbon monoxide and methane peaks using a heater voltage of 5.5 volts DC and air carrier gas flow rate of 36 $cm^3 minute^{-1}$ (6ppm hydrogen, 9 ppm carbon monoxide and 0.5% (v/v) methane; modified load resistor circuit)

PLATE 13.



Recorder range: 20 volts f.s.d.

Recorder range: 5 volts f.s.d.

Reproduction of chromatograms of 6.5 ppm hydrogen, 11 ppm carbon monoxide and 0.5%(v/v) methane, showing distortion of the hydrogen peak when using a carrier gas containing 1% (v/v) oxygen and 99% (v/v) nitrogen

PLATE 14

Reproduction of a portion of the chromatographic record from the automatically operated hydrogen/carbon monoxide/methane semiconductor chromatograph, showing build up of gas leakage from behind a stopped-off area. in samples continuously pumped to the surface.

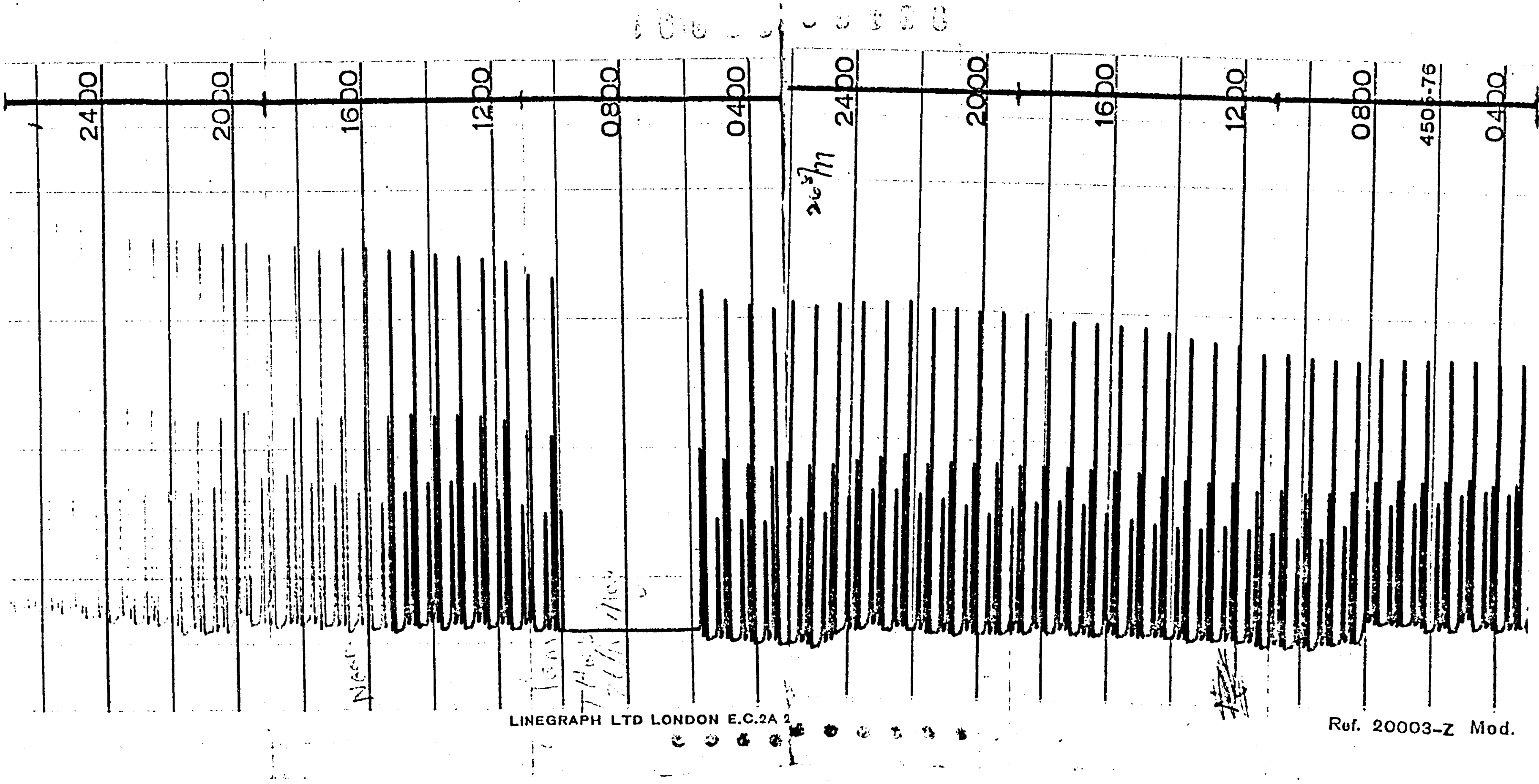


PLATE 15

Reproduction of a portion of the chromatographic record from the automatically operated hydrogen/carbon monoxide/methane semiconductor chromatograph, during the period of gas leakage from behind the stopped-off area, in samples continuously pumped to the surface.

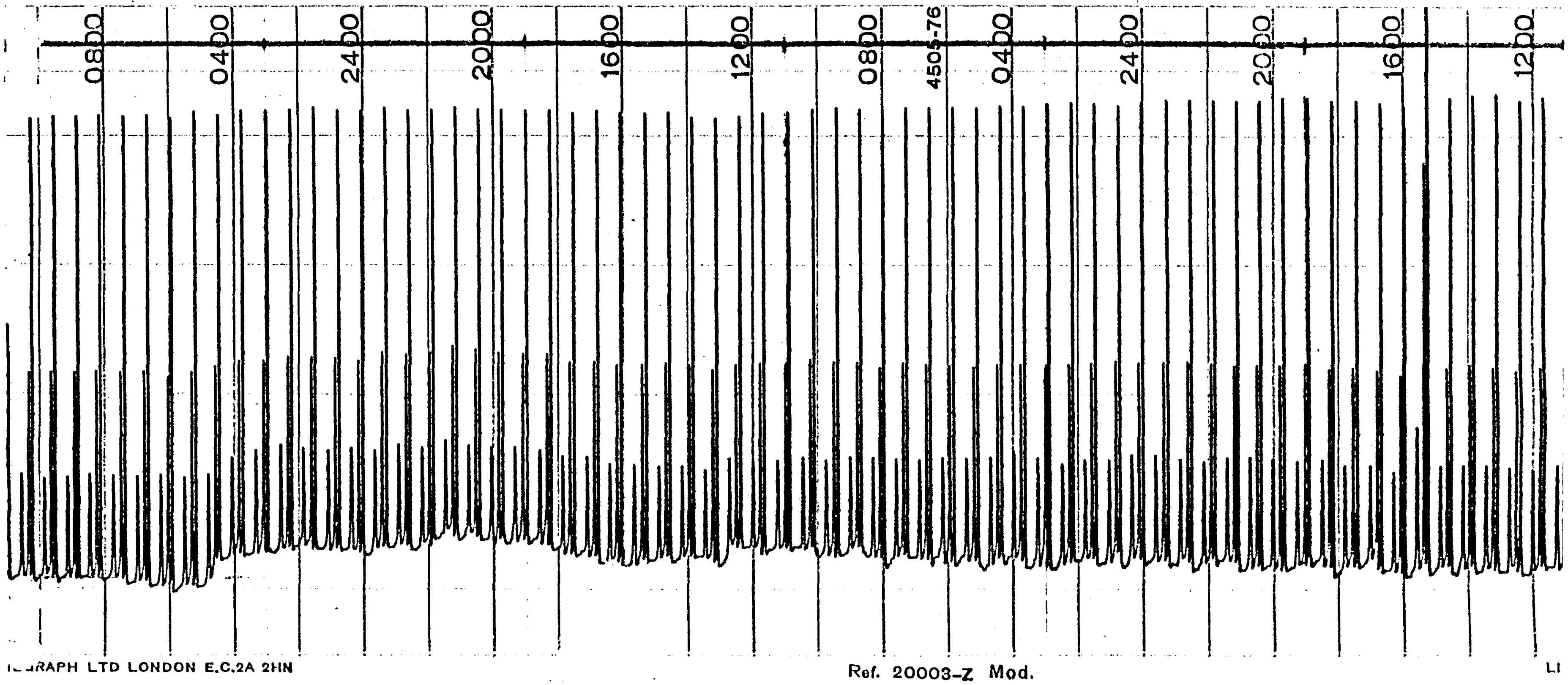
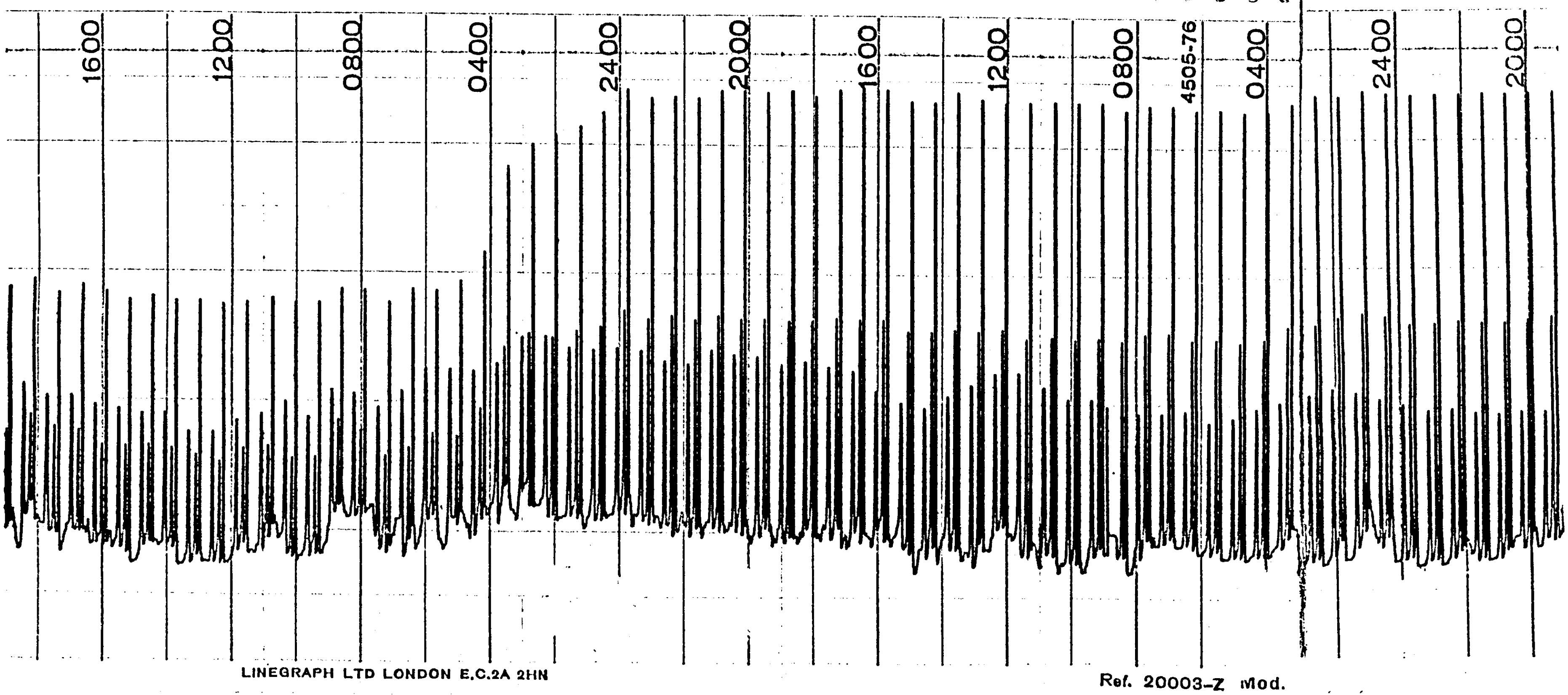


PLATE 16

Reproduction of a portion of the chromatographic record from the automatically operated hydrogen/carbon monoxide/methane semiconductor chromatograph, showing reduction in gas leakage after repairs to stopping, in samples continuously pumped to the surface.



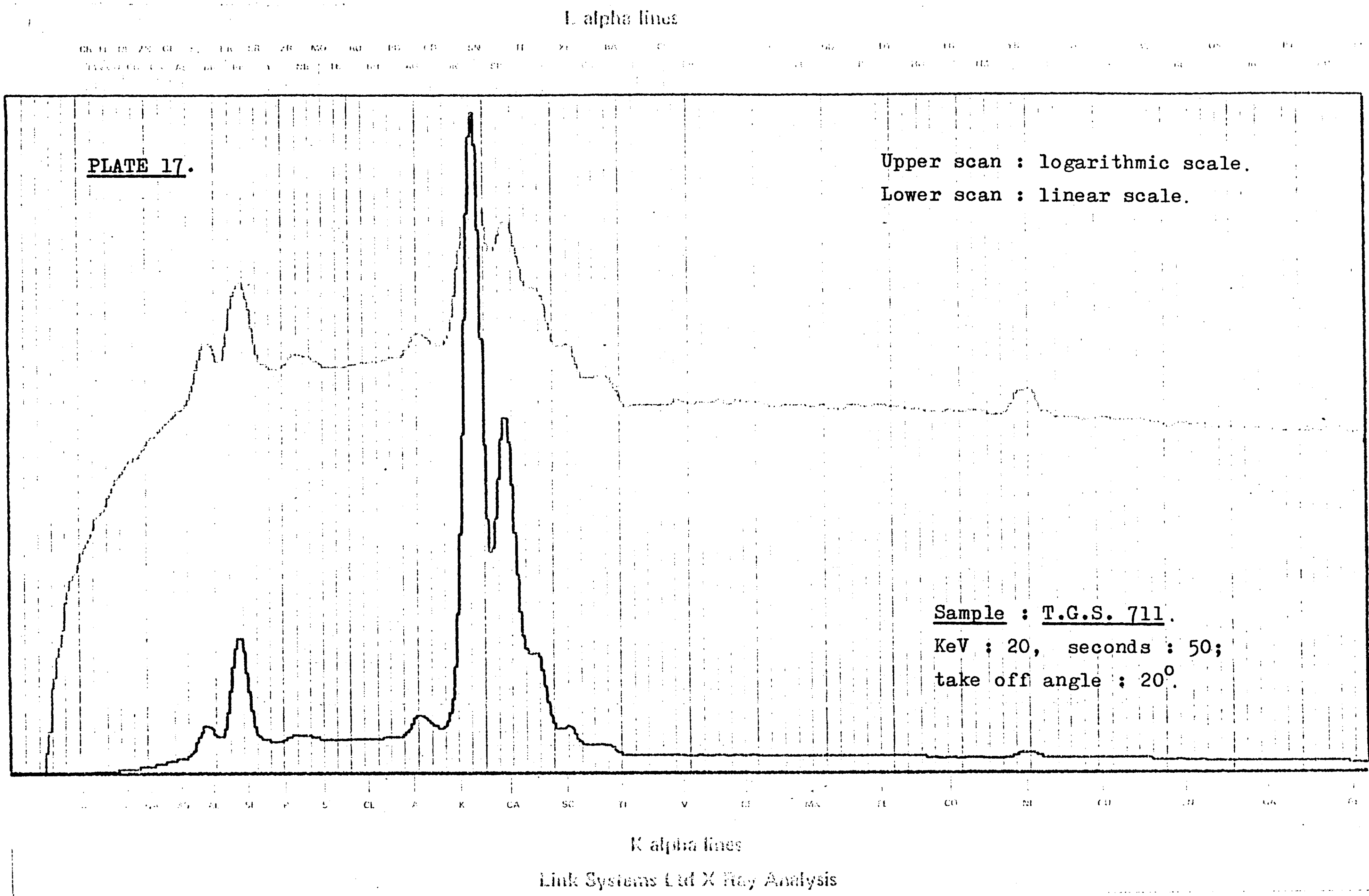


PLATE 17.

Upper scan : logarithmic scale.

Lower scan : linear scale.

Sample : T.G.S. 711.

KeV : 20, seconds : 50;

take off angle : 20°.

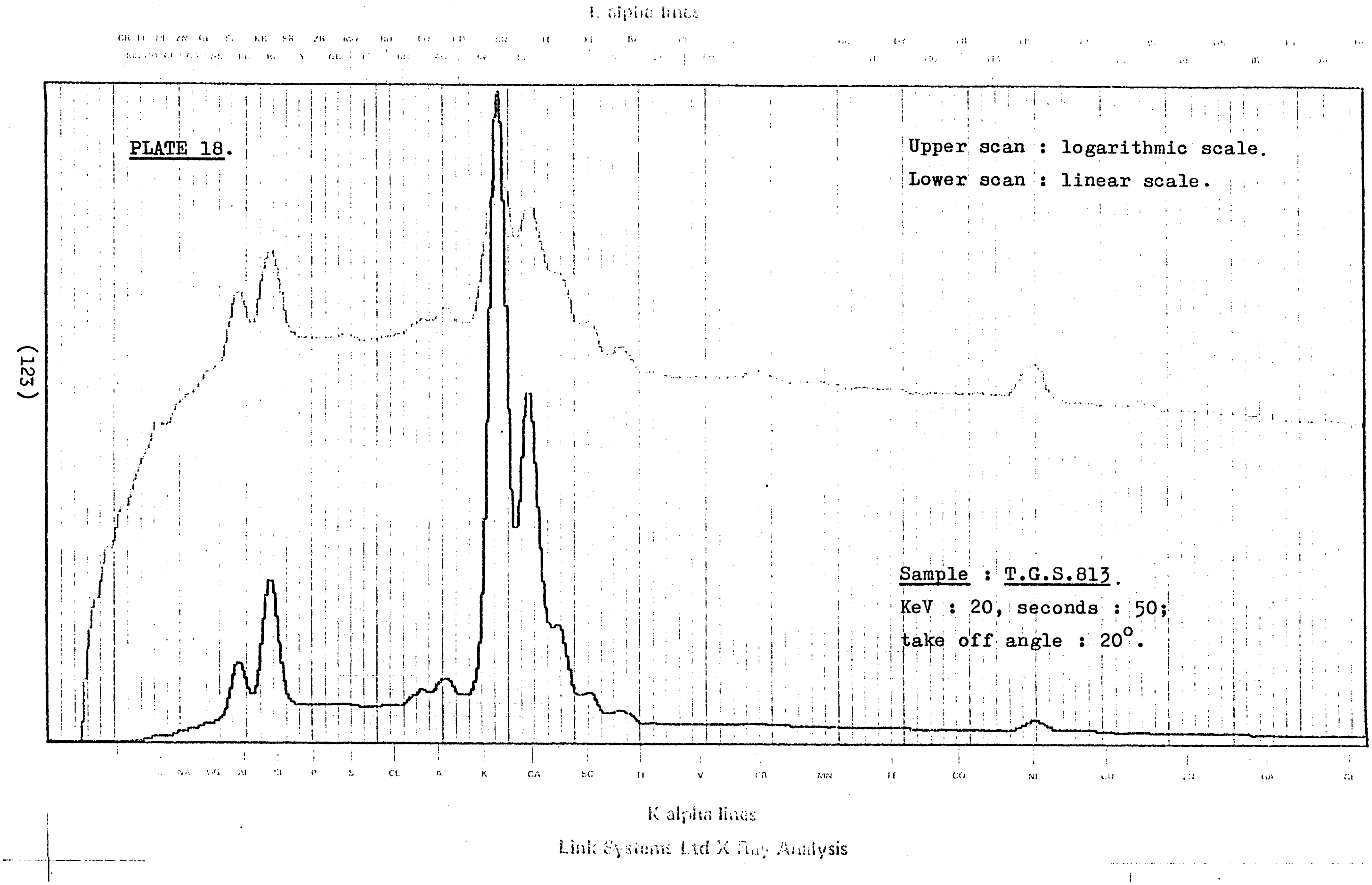
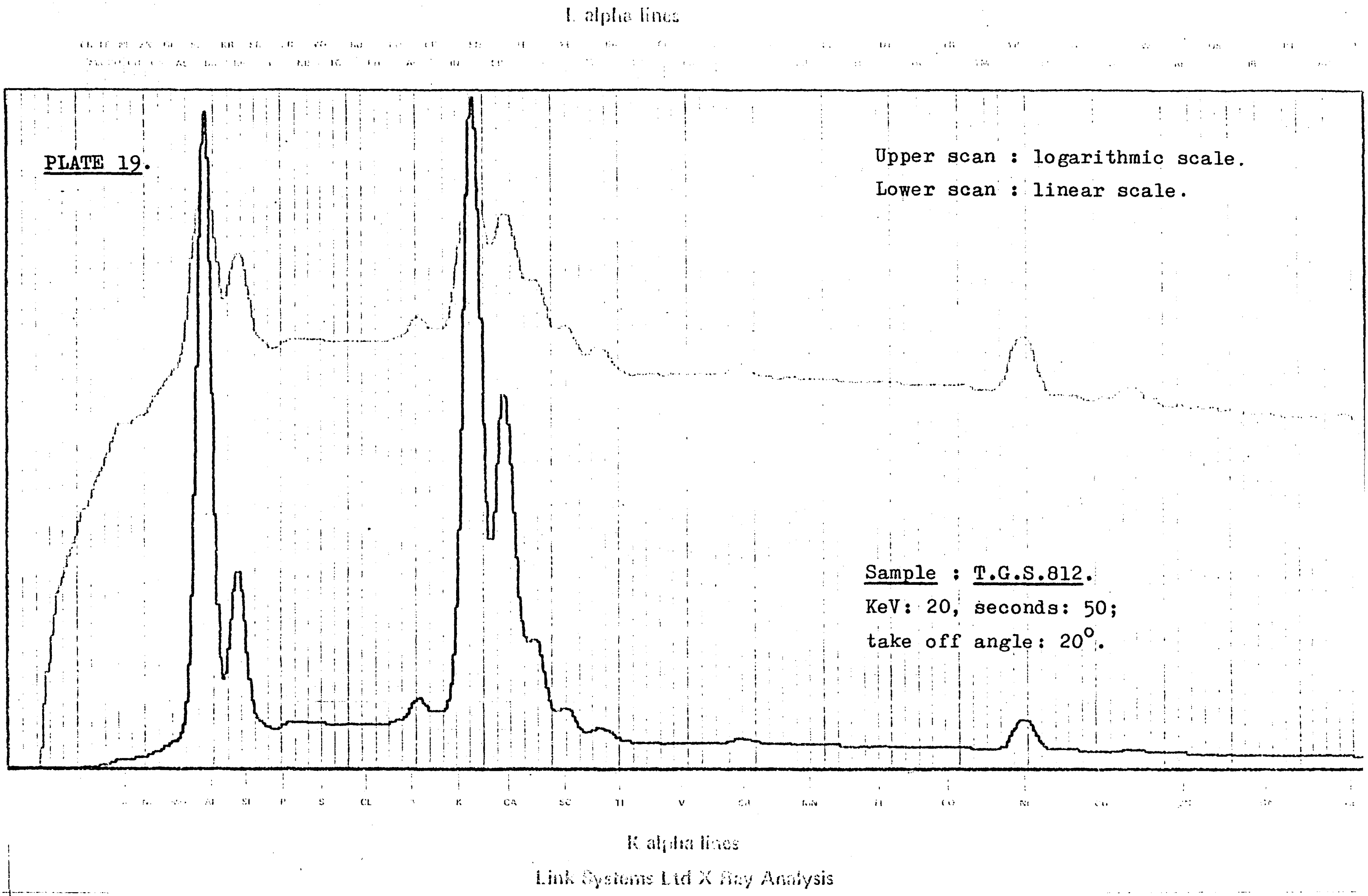


PLATE 18.

Upper scan : logarithmic scale.
Lower scan : linear scale.

Sample : T.G.S.813.
KeV : 20, seconds : 50;
take off angle : 20°.

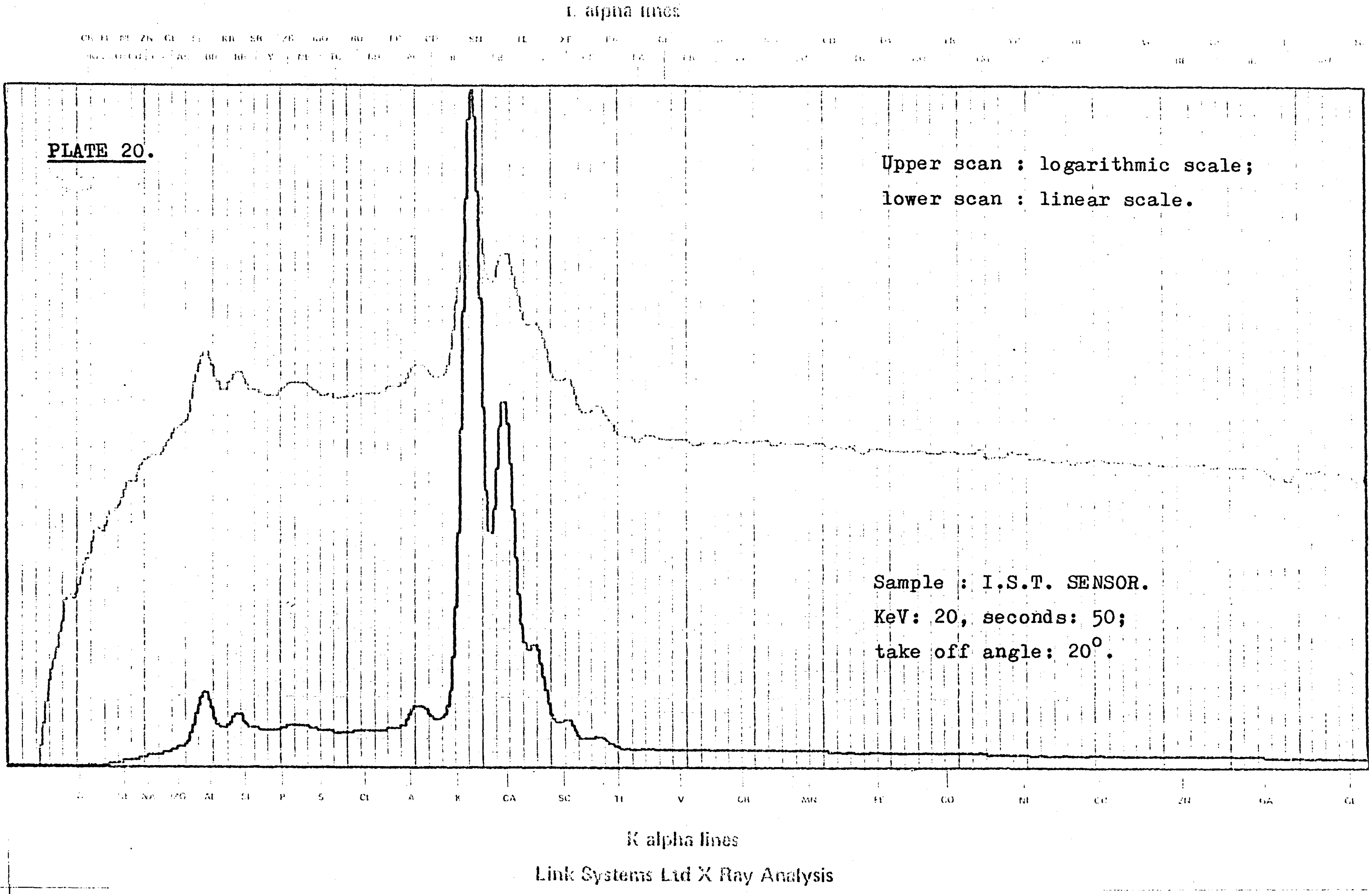
PLATE 19.



Upper scan : logarithmic scale.
Lower scan : linear scale.

Sample : T.G.S.812.
KeV: 20, seconds: 50;
take off angle: 20°.

PLATE 20.

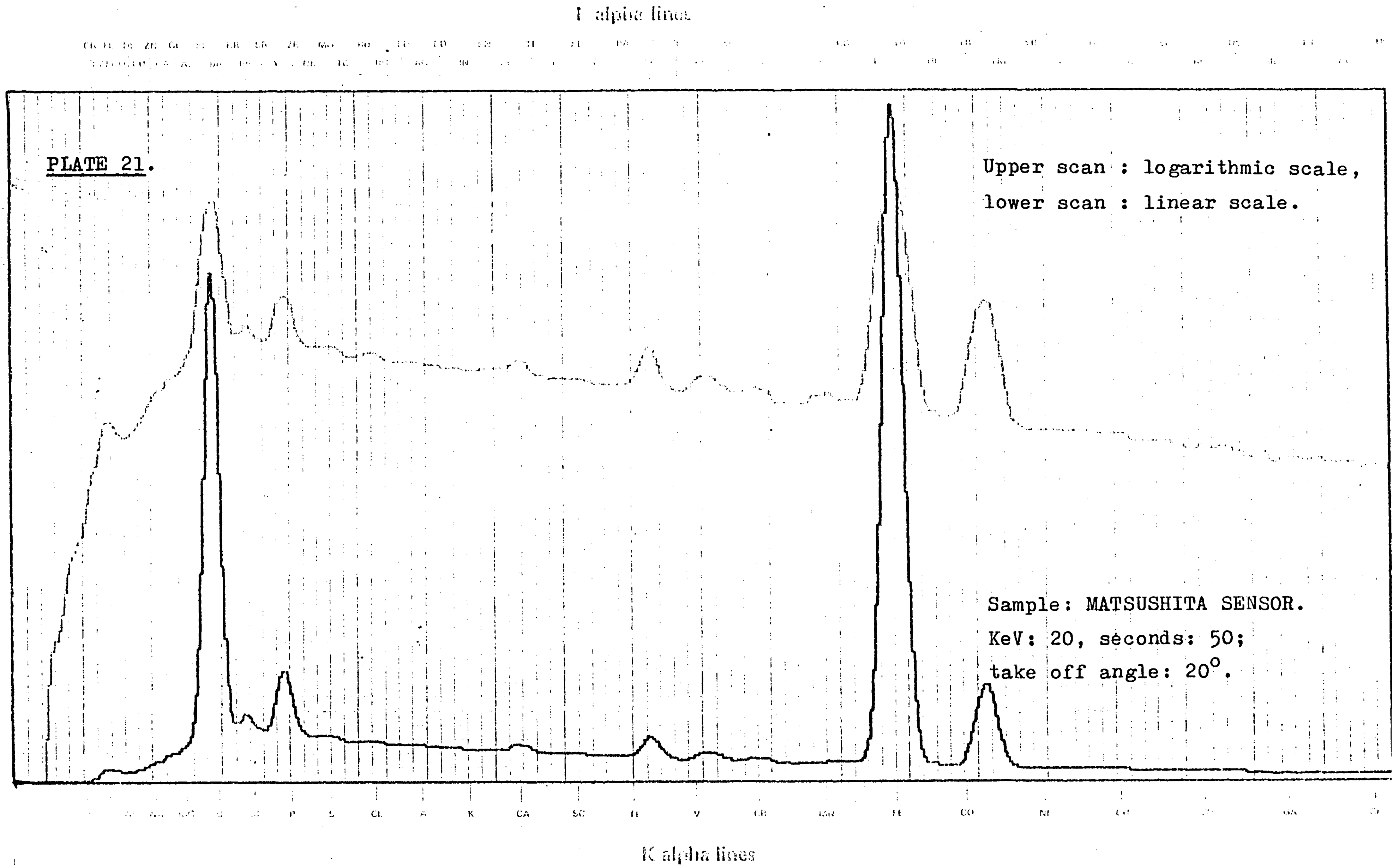


Upper scan : logarithmic scale;
lower scan : linear scale.

Sample : I.S.T. SENSOR.
KeV: 20, seconds: 50;
take off angle: 20°.

Link Systems Ltd X Ray Analysis

PLATE 21.



Upper scan : logarithmic scale,
lower scan : linear scale.

Sample: MATSUSHITA SENSOR.
KeV: 20, seconds: 50;
take off angle: 20°.

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APPENDIX

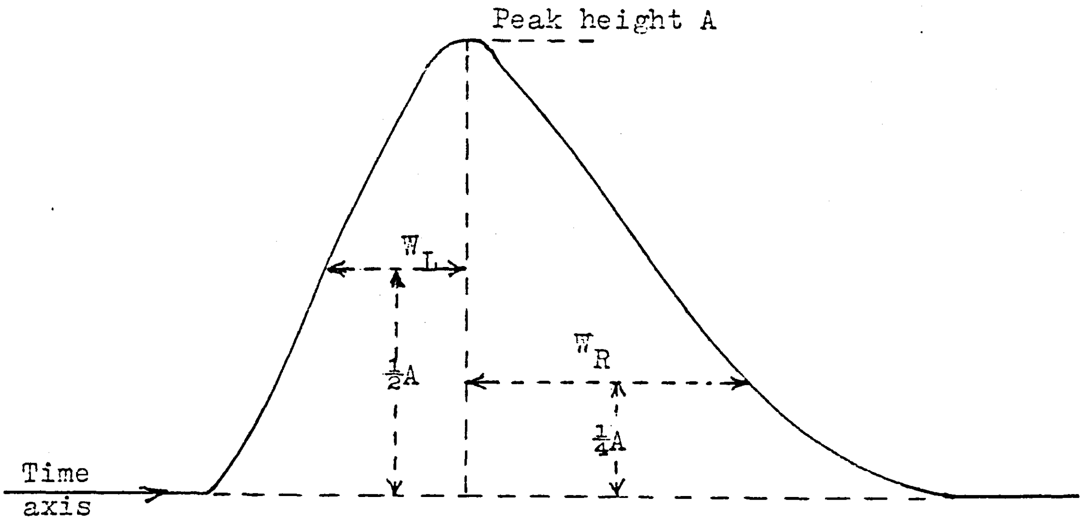
Brief review of methods of measuring asymmetry of gas chromatographic peaks proposed by other workers.

One of the earliest suggestions for measuring the skewness of gas chromatographic peaks was proposed by Cruikshank et.al.(58). They defined the skewness ratio, η , as the ratio of the magnitude of the slopes of the trailing and leading edges of the peak at the points of inflection.

Roberts et.al.(59) proposed a skew factor which was defined as the difference between the half peak width measured at $\frac{1}{4}$ peak height on the tail and the half peak width measured at $\frac{1}{2}$ peak height on the leading edge, i.e. skewness factor,

$$\tau = W_R - W_L \quad \dots \dots \dots \dots \dots \text{Equation 4}$$

Figure 7 Parameters of a gas chromatographic peak required to determine the skew factor, - after Roberts et.al.(59)



Kirkland et.al.(60) state that peak broadening involves the contribution of independent factors, for example those due to poor sample injection, badly packed columns, long time constant for the detector, and so forth. These can be treated as additives in their second moments, or variances, σ^2, according to the relationship :

$$\sigma^2_{TOTAL} = \sigma^2_{COLUMN} + \sigma^2_{DETECTOR} + \sigma^2_{OTHER}$$

Each peak may be regarded as having :

(a) a Gaussian component, having a standard deviation σ, and

(b) an exponential modifier, defined by its time constant, τ .

Peak tailing increases with the ratio τ/σ and peak skewness is defined as :

$$\text{Peak skew} = \frac{2(\tau/\sigma)^3}{[1 + (\tau/\sigma)^2]^{3/2}} \quad .. \quad .. \quad .. \quad .. \quad \text{Equation 5}$$

τ and σ values were assigned to each peak on the basis of computer operated iterative curve fitting.