"Studies in Gas Chromatography with special reference to Vapour Detectors."

Thesis submitted for the Degree of Doctor of Philosophy in the University of Oxford.

W.J.Shore.

Merton College.

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Introduction:

Chromatographic techniques for the separation of mixtures make use of the differences in the distribution ratios of the components of the mixture between two immiscible phases. The distribution process is effectively repeated many times by causing one phase to move relative to the other. Thus the complete separation of components with only small differences in distribution ratio is made possible. In gas chromatography the moving phase is an inert gas and the substances to be separated are in the form of vapour in the gas phase. The mixture to be separated is introduced into the gas stream, and carried by it along a tube packed with the fixed phase ("the column".) The fixed phase may be a solid (e.g. charcoal of silica gel) or more usually a liquid, involatile at the temperature of operation, on a solid support (e.g. a silicone oil on kieselguhr). Gas-liquid chromatography was originated by James and Martin in 1952 (29).

A component whose distribution ratio, i.e.

$$\frac{\text{Concentration in the gas phase}}{\text{Concentration in the liquid phase}}$$

is high will move through the column at little less than the speed of the carrier gas, while components with lower values will travel correspondingly more slowly. The components of a mixture will therefore generally emerge from the far end of the column separately (provided the column is long enough).

The distribution ratio of a substance in gas-liquid chromatography is determined by its free energy of solution in the liquid phase (30; also 31 & 32.) In the absence of specific interactions between sample and liquid phase, substances tend to emerge from the column in the order of their boiling points: most volatile first.

The vapours emerging in the gas stream enter a detector where their presence and amount is detected and a signal fed to a recorder.

The principal detectors in use in gas chromatography when this work was started (Sept. 1957) were:

		Fig. of merit	Ref.
Katharometer (hotwire)	Thermal conductivity	1	(33)
" (thermistor)	" "	5	(27,34)
Flame & thermocouple	Temperature and height of a hydrogen flame.	10	(35)
Gas Density Balance	Weight of column of carrier gas + vapour compared with that of pure carrier.	50	(36)

(The "figures of merit" are based on the minimum detectable quantity for each detector reported at the time of this work - given in the references cited).

The need for detectors of higher sensitivity had become apparent in all the work being done in this laboratory, i.e.:

1) The use of metal salts as column materials. (37)

Small samples (less than 10^{-5} gms.) are necessary to avoid overloading these columns. Overloading causes

assymmetrical peaks, the positions of whose maxima vary with the sizes of the samples. This complicates the measurement of retention volumes. The katharometers and flame and thermocouple detectors were inadequate, -- the minimum quantities detectable being about 20×10^{-5} gms. and 2×10^{-5} gms. respectively. (33, 30)

2) Silanes, silicon chlorides and later germanes. (39)

Each of these series of compounds was prepared by methods which gave mixtures of several members of the series. (54, 39, 40, 41, 42). The percentages of the higher members present in the mixtures are very small (e.g. Si_4Cl_{10} upwards: total 1% (54)). Thus if the highest members are to be detected on a katharometer, large total amounts of the mixture must be prepared (e.g. 10 gms. of the silicon chloride mixture). The compounds are variously reactive, toxic and explosive, and the use of more sensitive detectors would enable them to be prepared in smaller quantities, which are safer & easier to handle.

3) The volatile material given off by insects.

The amounts of material given off by insects as attractant and repellant scents are extremely small (perhaps as low as 10^{-10} gm.). The material was collected under "natural conditions" by passing a current of air over the insects and then through a trap cooled in liquid oxygen. Volatiles given off by the insects were condensed, and injected on to a gas liquid chromatographic column. Katharometer detectors had been shown too insensitive. (38).

This work was undertaken as a survey of the more sensitive detectors available, with the above applications in mind.

When the work was begun three high sensitivity detectors had been reported:

		Fig. of merit.	Ref.
Vacuum ionisation gauge	Ionisation of sample vapour by accelerated electrons from a hot filament at low pressure.	100	(16)
Discharge tube	Change in voltage drop across a low-pressure discharge, caused by sample vapour.	500	(17,20; also 18,19,21)
Hydrogen flame ionisation	Increase in conductivity of a hydrogen flame caused by sample vapour.	1000-2000	(1, 52)

All three of these detectors were built and operated. The behaviour of the flame ionisation detector when used with organic and inorganic samples (including silanes and silicon tetrachloride) was investigated. It was found easy to construct and operate once a suitable design had been developed. Its sensitivity to all organic compounds is high, and the noise level is low. It can give good results with silicones, silanes, silicon tetrachloride, and stannic chloride, provided samples are kept small - say less than 10^{-4} gms. Larger samples lead to an excessive noise level, the detector often being permanently affected. Sensitivity to this type of compound is increased and the noise level is reduced if the detector is operated with the burner negative - the reverse of normal practice. To some inorganic compounds the detector

gives little or no response. The temperature of the flame at the burners used in this work was measured by the sodium line reversal method.

The vacuum ionisation gauge and the discharge tube were found to be much less satisfactory for routine use, although very sensitive to organic compounds. They require vacuum apparatus, the filament of the ionisation gauge was easily "poisoned" and temporarily lost its emission, and the discharge tube was easily extinguished by an overload and would not relight until the plates had been cleaned.

After the work had begun the argon ionisation detector was reported. In this detector sample vapour is ionised by collision with excited argon atoms formed by bombardment with accelerated electrons. Figure of merit 1500 - 2500. (22,23; also 24,25 & 26). This detector was tested with organic and inorganic samples (silanes, monogermane, phosphine and ammonia - one possible application being an industrial one involving these compounds). The detector is highly sensitive and easy to operate - though it is more complicated to make than the flame ionisation detector and requires a radioactive source and a 1000 - 2000 volt EHT supply. The noise level of the detector was not increased by any of the samples used, and it responded satisfactorily to all, except methane, and amounts of H_2 smaller than 4 micrograms.

The flame ionisation detector has subsequently been in routine use in this laboratory for work on metal salts as column materials (43, 44 & 48), and column materials forming inclusion compounds (45), for silanes (46), moth scents (49 & 53), and borazoles (47). The argon ionisation detector has been used for silanes (in this laboratory (46) and elsewhere), and for work with capillary columns, which can take only very small samples (43 & 44. For capillary columns: 50 & 51).

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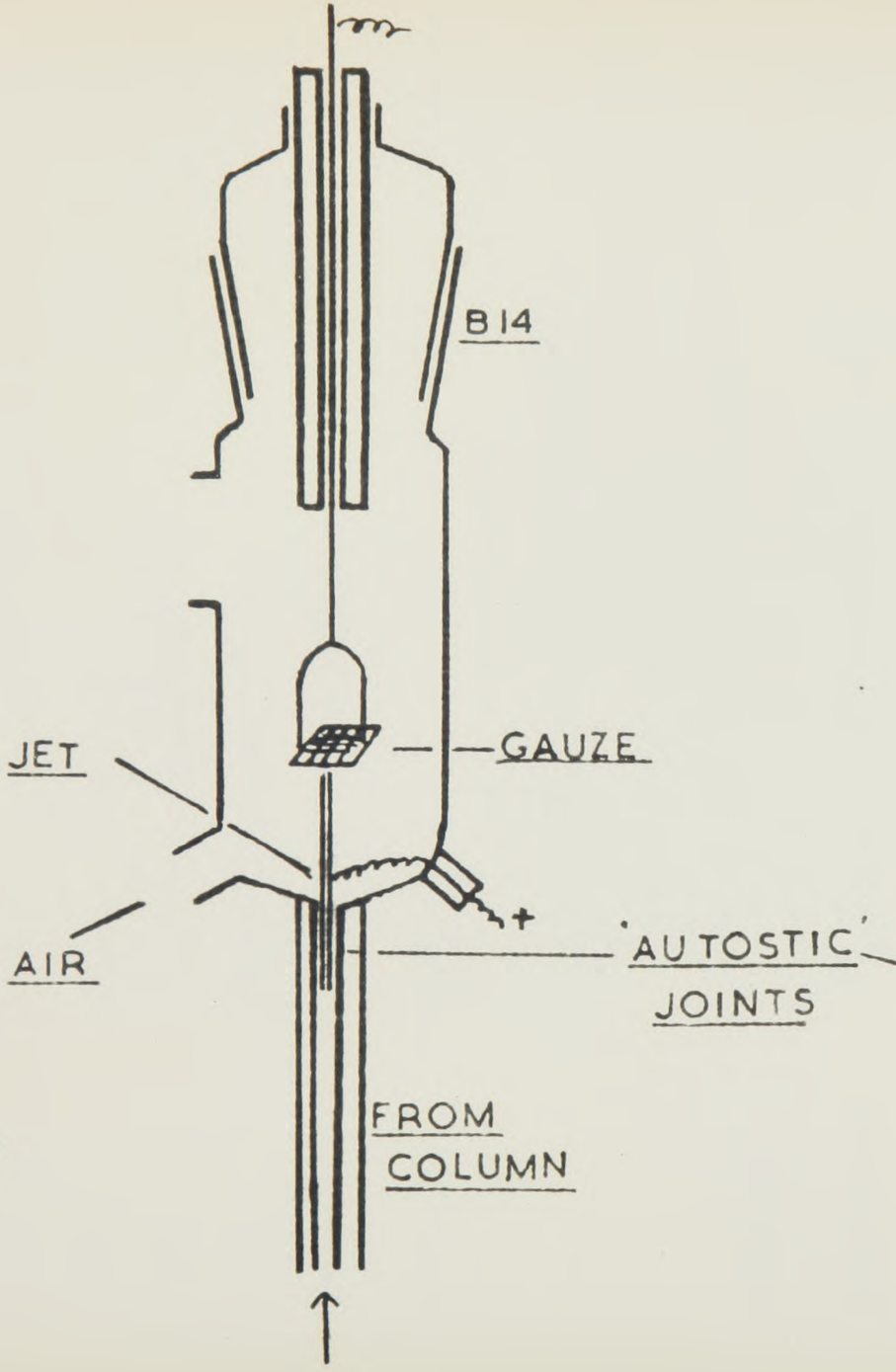

B14
JET
GAUZE
AIR
'AUTOSTIC'
JOINTS
FROM
COLUMN

FIG. 1

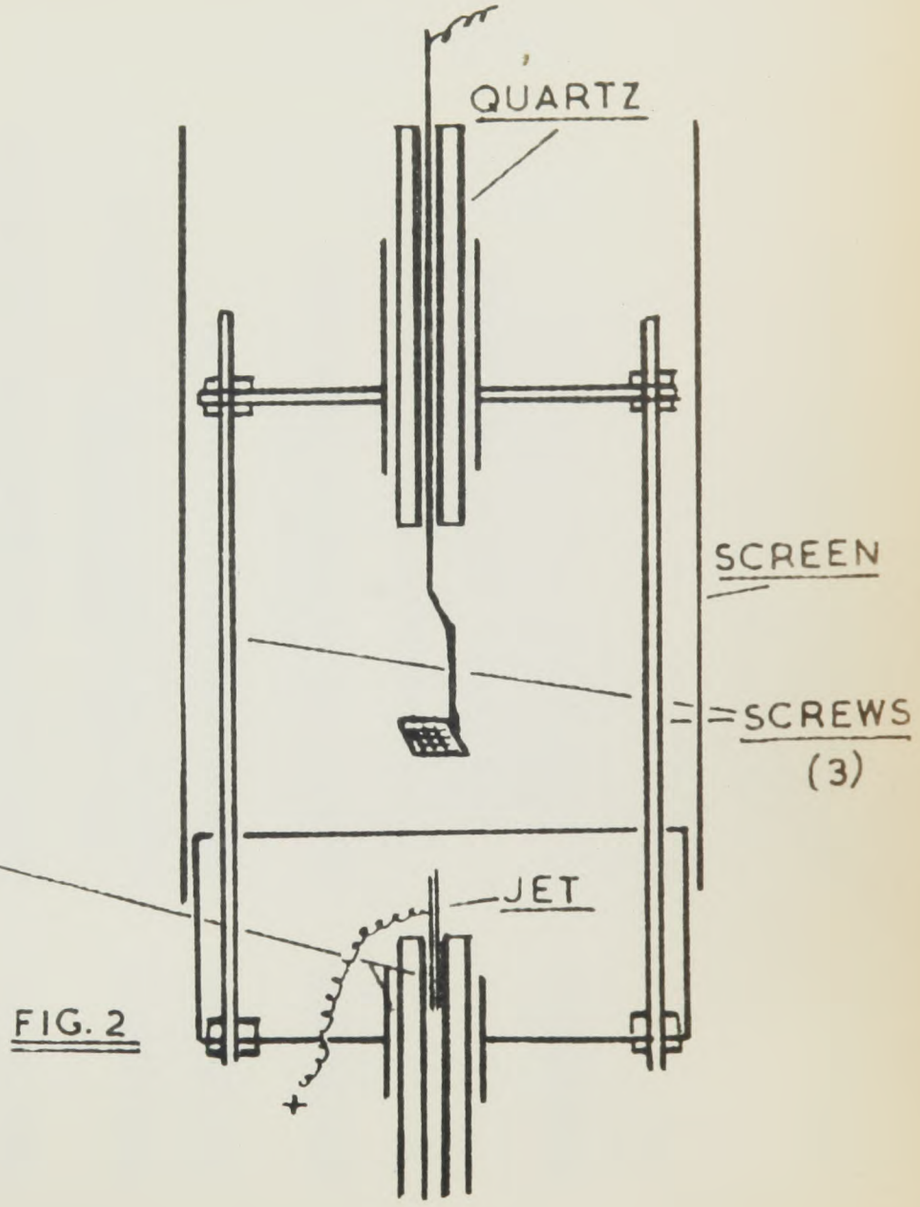

QUARTZ
SCREEN
SCREWS
(3)
JET

FIG. 2

CHAPTER 1

The Hydrogen Flame Ionisation Detector & Associated Equipment.

1.1 The Detector

1.1.1 General

The Hydrogen Flame Ionisation Detector was announced by Harley and Pretorious, (52) and McWilliam and Dewar (1). In its usual form it consists of a metal jet at which hydrogen burns, and some arrangement for introducing the sample to be detected to the flame, where it is thermally ionised. An insulated electrode, (the probe), is supported above or in the flame. A polarising voltage, usually at least 150 volts is applied between the jet and the probe, usually with the probe negative, (the detector will operate with either polarity, but its behaviour is slightly different.) The current flowing between probe and electrode constitutes the output from the detector. The conductivity of a flame burning with pure hydrogen is such that the saturation current is about 10^{-11} to 10^{-10} amp. under typical conditions. (from figures in ref. 1).

1.1.2 Detectors used in this Work

The first two detectors constructed were demountable glass ones (as in Fig. 1). The need was soon felt for a detector in which the height of the probe could be more easily adjusted, which was more robust and accessible and which could be fitted with a metal screening can (Fig. 2). A further advantage of this design was that there was greater freedom

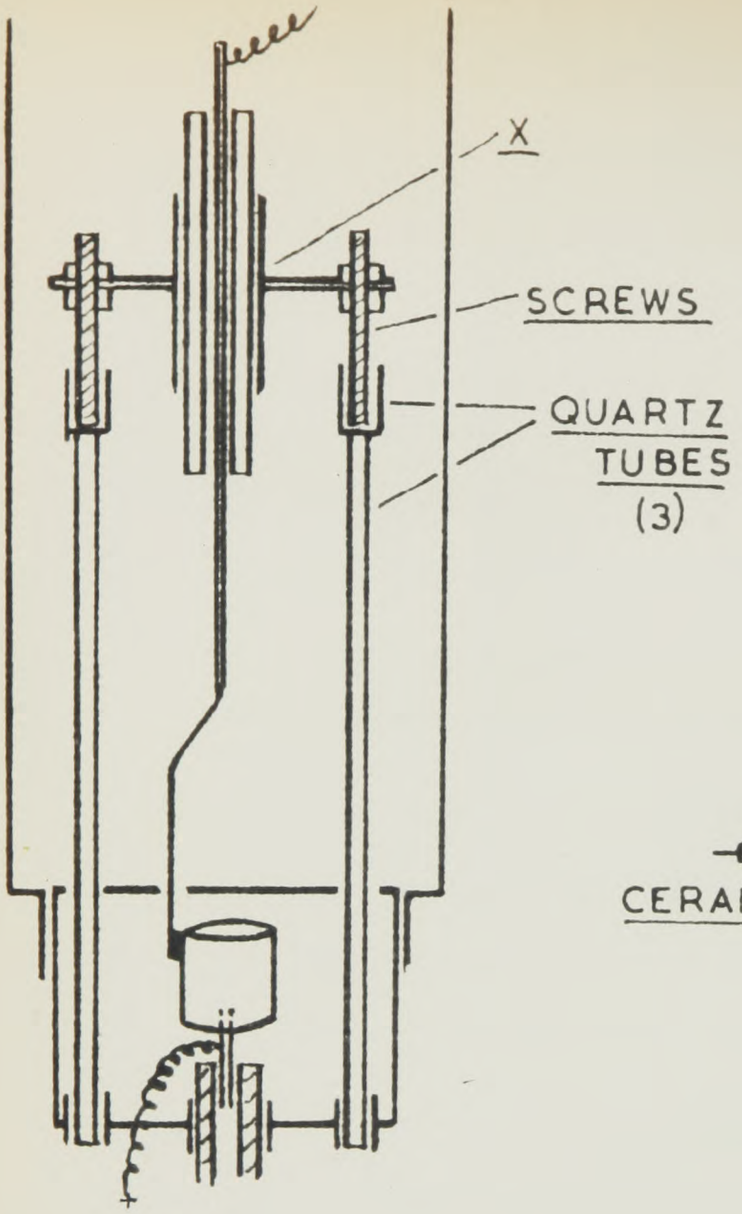


FIG. 3

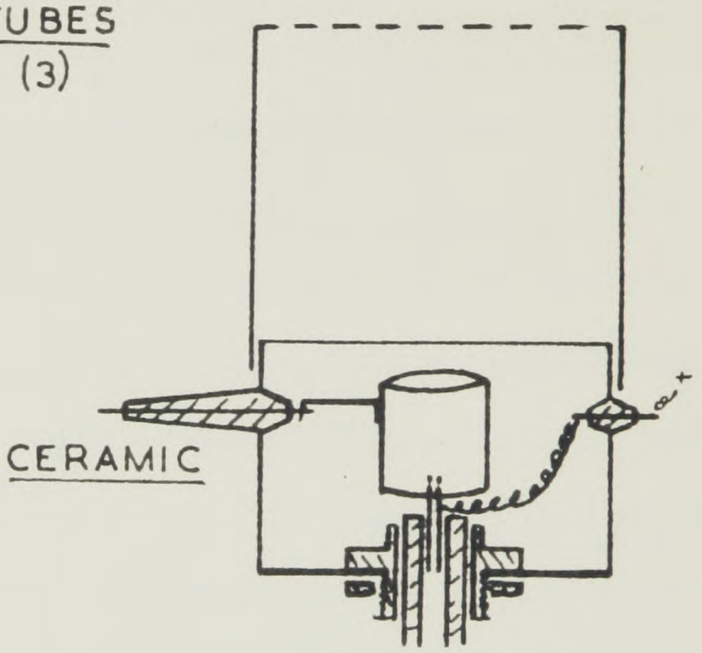


FIG. 4

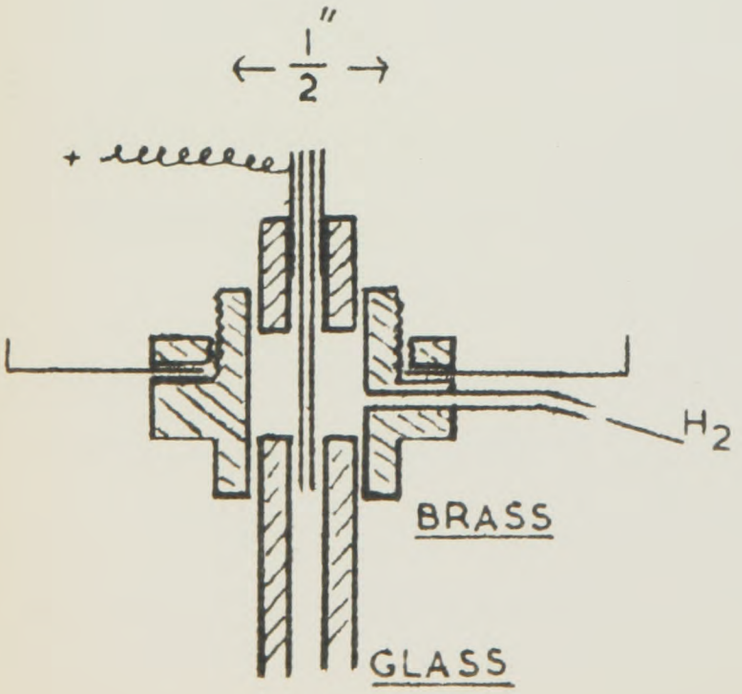


FIG. 5

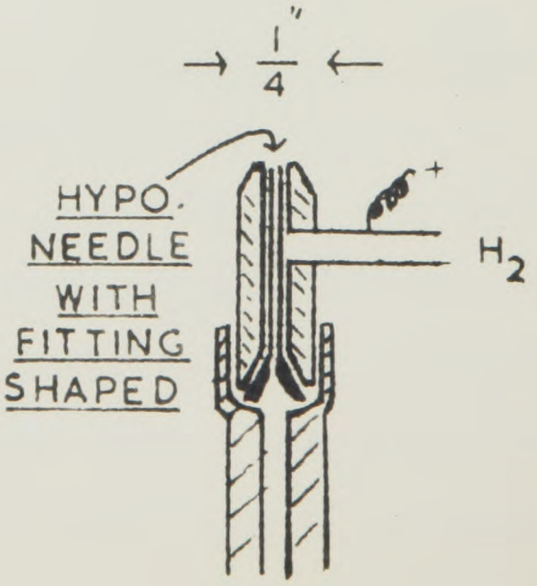
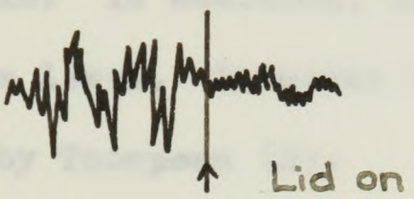


FIG. 6

for the products of combustion to escape, rather than depositing on the insulation and providing a surface leakage path. The effect of screening on the noise level can be seen in this tracing of a section of baseline. An improvement of some threefold is effected by placing a lid on the otherwise open screening can:



Flow rates of hydrogen of more than 40 - 50 cc/min. caused considerable noise of the "grass" type, an example of which is shown:



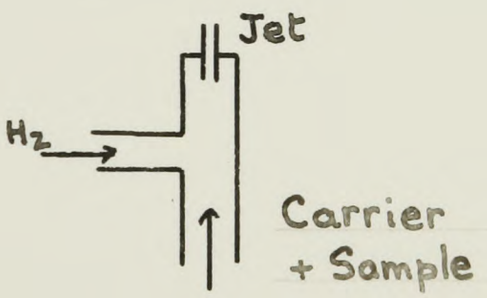
and a high standing signal of about 10 volts(10^{-8} amps). This was felt to be due to the rather short length of quartz insulation in detector II, which was directly above the flame and exposed to the heat and combustion products from it. The background signal fell slowly over a few minutes when the flame was put out, and rose equally slowly when it was relit. Detector III therefore had a greater length of insulation, most of which was not above the flame (Fig. 3).

This version still gave trouble, "spiky" noise appearing on the baseline unless the isolated piece of metalwork 'X' was earthed to the screening. However this solution had the effect of shorting out the new insulation (the 3 quartz tubes).

The most satisfactory design used small ceramic "lead-through" insulators (K.L.G. Sealed Terminals, type CS 115/1 or CS 115/2), (Fig. 4). Ceramic material is a better insulator than glass at higher temperatures, and its polished surface is less likely to become coated with a surface film. In addition, the insulator is kept entirely below flame level. Detector IV is similar to the one described by Thompson (2).

1.1.3 The jet or burner

The detector was to be used with samples including volatile inorganic halides (such as $SiCl_4$, $SnCl_4$) and it was thought that there would be some risk of their being attacked by hydrogen if this were used as carrier gas. The usual technique when some gas other than hydrogen is used as carrier with a flame ionisation detector is to bleed hydrogen into the carrier gas stream just before the detector, thus:



In this system however the samples still come into contact with hydrogen before they reach the flame, and so a different arrangement was adopted. The hydrogen was burnt at a fairly wide jet (about 0.8 mm.), and the gas carrying the sample passed through a metal capillary (23 gauge hypodermic needle) up the middle of the jet directly into the flame. Two main



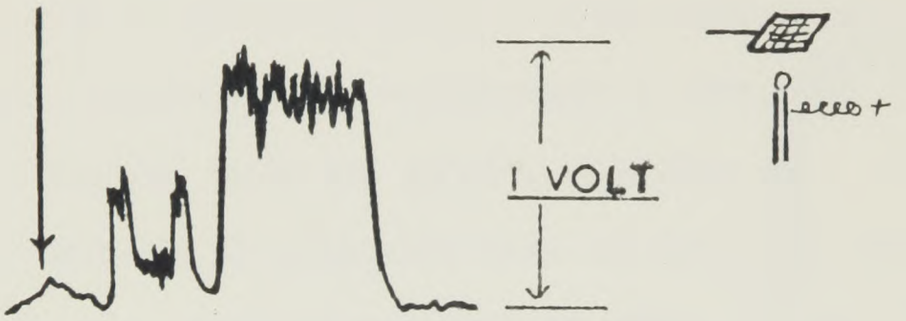
FIG. 7

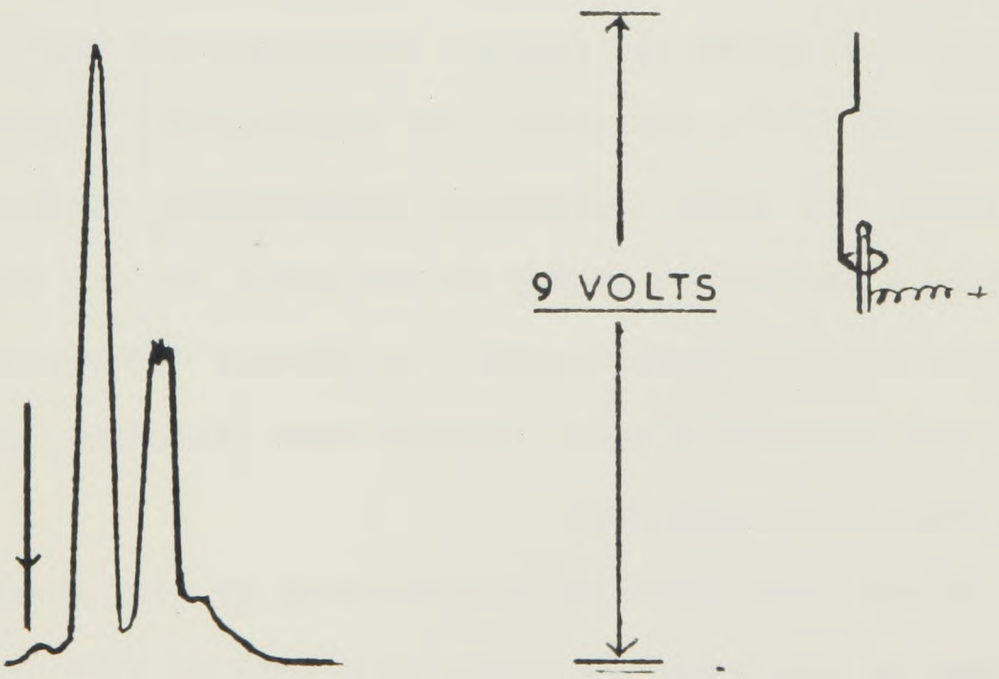
ways of constructing this "concentric jet" arrangement were tried (Figs. 5 & 6), the second proving easier to make and being less prone to leak. The comparatively large mass of brass cooled the flame down slightly, (see Sec.2.2.5.), but this is advantageous since a lowering of the flame temperature is said to result in an improvement in the signal to noise ratio. (5) In addition a large jet does not get as hot as a small one, and this is also effective in reducing noise. (3), Fig. 7 shows the jet constructed as in Fig. 6.

1.1.4 The Probe or Collector

The arrangement of McWilliam and Dewar used a small piece of metal gauze as the collector electrode, and most detectors in routine work use this type of collector. (See Figs. 1 & 2) However there is an important disadvantage. When used with silicone oil columns ("Silicone oil 702") at temperatures of 150°C. and above, the silicone oil distils off the column and enters the flame, forming SiO_2 which is deposited as a fine white powder on the gauze and the jet causing considerable "spiky" noise. A similar deposition of solid, and consequent noise, occurs when silicones, $SiCl_4$ and $SnCl_4$ are run as samples.

It was found that this noise could be very considerably reduced by replacing the gauze by a loop of wire about $\frac{1}{4}$" across positioned round the jet just below the level of its tip. A cylinder (of thin nickel foil) about $\frac{1}{2}$" in diameter and $\frac{1}{2}$" long was also used with success. (See Figs.3&4.)





SAMPLE IN BOTH CASES = APPROX. 1 MGM.

SILICONE OIL MS 200/2CS.

FIG.8

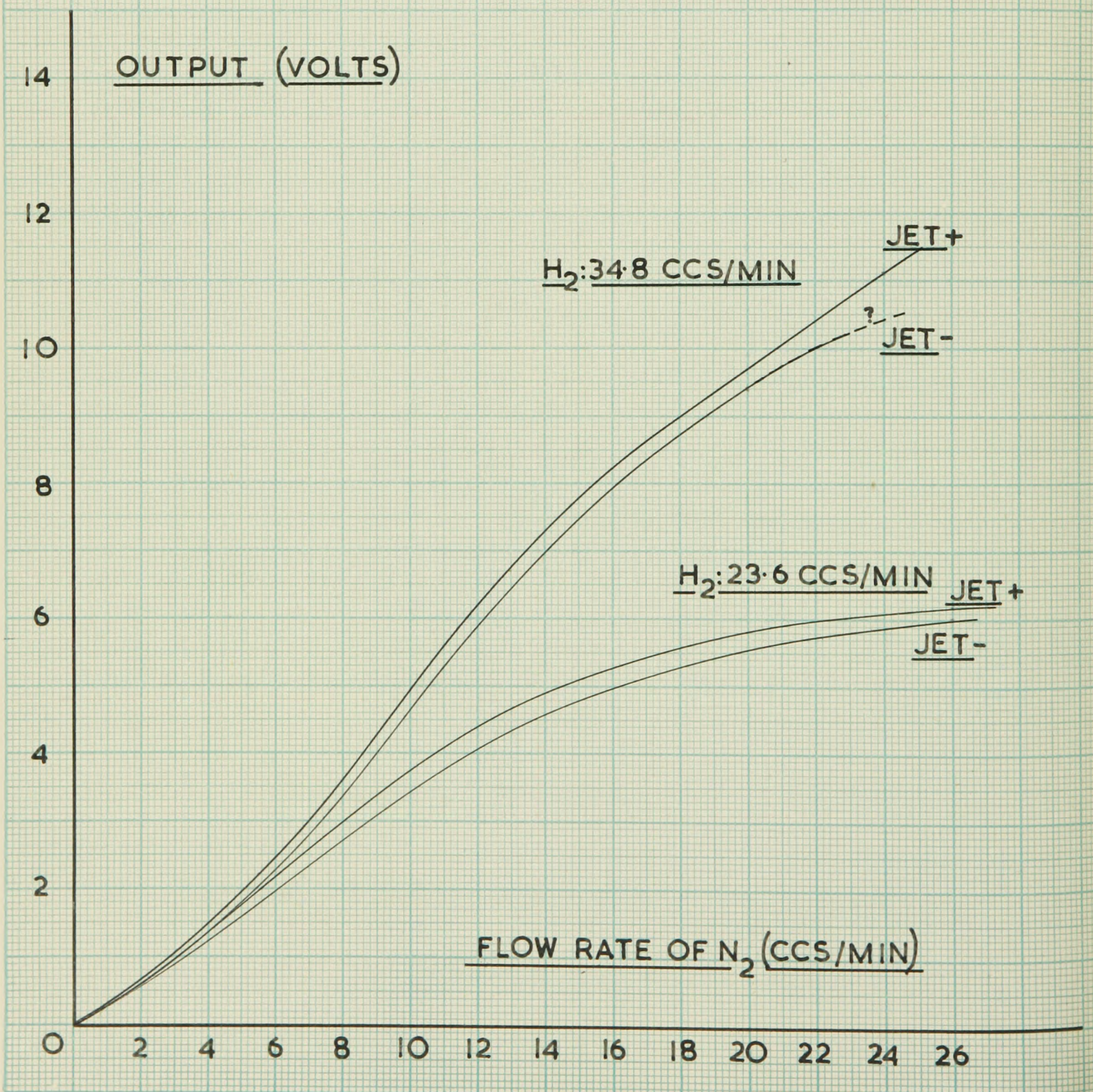
FIG. 9

CCl_4 IN SATR. AT 0·3 C.

V.P.: 33 MM. Hg

LARGE DOUBLE JET.

(FIGS. 20 & 21 COMBINED)



Examples of the improvement in noise are shown in Fig. 8.

1.1.5 Polarity of Polarising Voltage

McWilliam and Dewar only mention a positive polarity for the jet relative to the probe, and much of the routine application by various workers seems to have been with this arrangement. The work of Desty, Goldup and Geach (4) and of Ongkiehong (5) indicates that the sensitivity of the detector is not dependent on polarity provided that the potential is high enough to ensure saturation, i.e. that all the ions formed are being collected. Other things being equal, Desty has shown that the minimum voltage required for saturation with propane samples is higher with the jet positive than with it negative. Some observations in this work on tetralin indicate that a positive jet gives a higher sensitivity by a factor of about 2.

Observations in this work on carbon tetrachloride in relatively high concentration (3-10 molar%) show no major variation in sensitivity with polarity, except possibly at high rates of entry. (Fig. 9).

With lower silicones, from $(SiMe_3)$-O-$(SiMe_3)$ to $(SiMe_3)$-$(O\text{-}SiMe_2)_5$-O-$(SiMe_3)$, there appears to be a difference in sensitivity with differing polarity, a negative jet giving the greater sensitivity by a factor of about 2-2.5. The sample sizes used were of the order of 1 mgm. or less.

With $SnCl_4$ and $SiCl_4$ there is a marked change in response when the polarity is reversed. The response to $SnCl_4$ with the jet negative is 3 - 4 times the response with jet

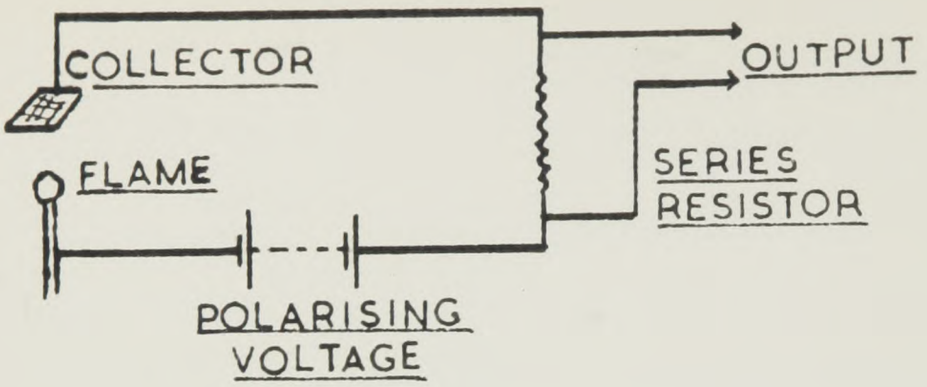


FIG. 10

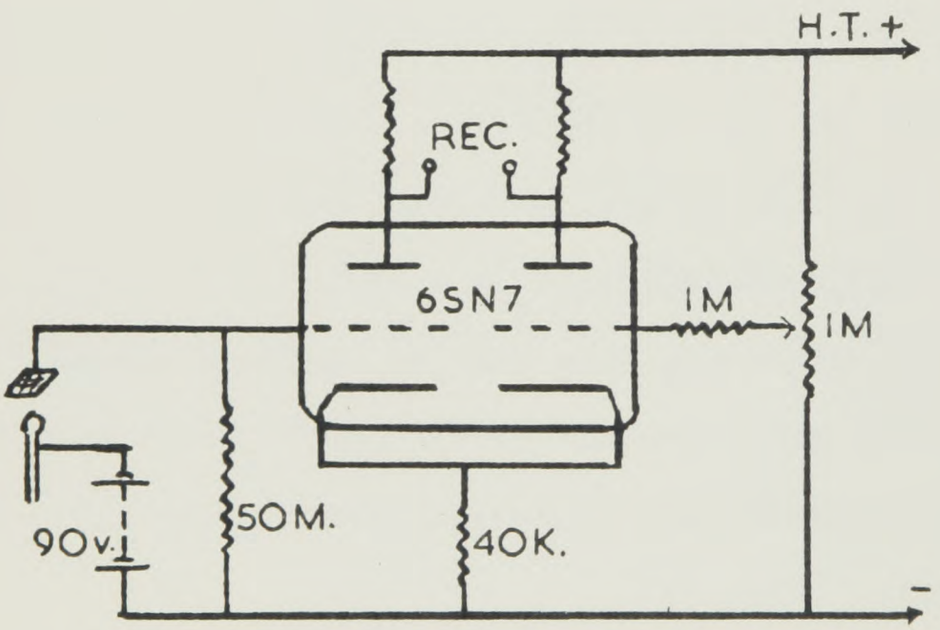


FIG. 11

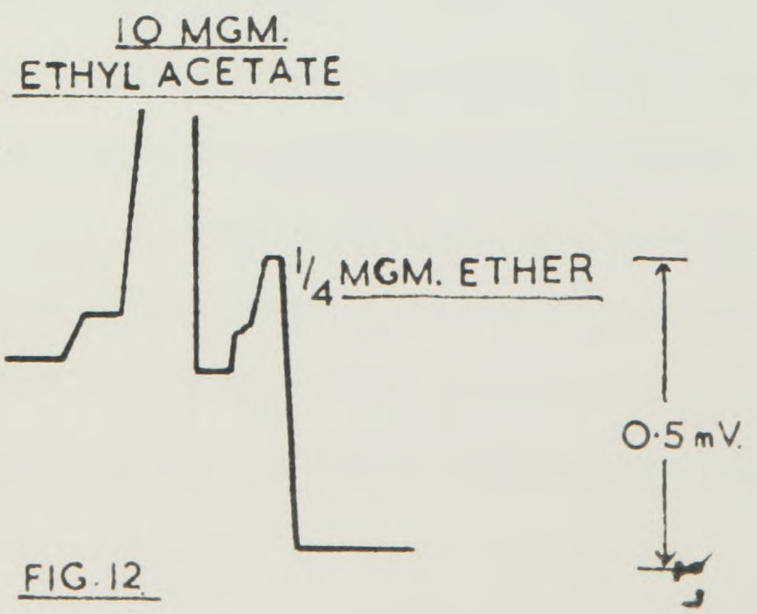


FIG. 12

positive, and there is a large reduction in the noise level. When the jet is positive, long filaments of white solid (presumably SnO_2), tend to "grow" across and bridge the gap between jet and probe, sending the recorder off-scale until the filament is removed. With the jet negative, the solid seems to remain on the jet to a much greater extent (as would be expected if the solid particles were positively charged by thermal ionisation.)

$SiCl_4$ shows similar behaviour, the improvement in noise level being less marked.

Generalisation: Substances giving solid involatile combustion products give a higher ion current with a negative jet and vice versa. The noise level is considerably reduced by a negative jet, and by a ring or cylinder collector instead of a piece of gauze.

1.2 The Impedance Converter:

1.2.1 General

The output from a flame ionisation detector is a very small current, 10^{-8} -10^{-12} amps. This is normally passed through a very high value series resistor (10^8-10^{10} ohms), and the voltage drop across this resistor is made to drive a recorder, usually potentiometric. (Fig.10)

The input impedance of some recorders is of the order of 10,000 ohms or less, and they cannot be connected directly across the series resistor since they would virtually short-circuit it. Other recorders do not work well with more than

about 1000 ohms across their output terminals, becoming sluggish and failing to return to zero when a signal is removed.

There must therefore be an "impedance converter", with high input and low output impedances, between the series resistor and the recorder. A valve has such a high input impedance, drawing very little current from a signal source connected between grid and cathode (provided that the grid is maintained negative with respect to the cathode.) A low output impedance suitable for feeding a recorder can be obtained from a "cathode follower" output stage. (See Footnote *)

1.2.2 Circuits used in this work:

1.2.2.1 Simple Circuit:

The first circuit tried was similar to that given by McWilliam and Dewar (1). See Fig. 11.

Using a polarising voltage of 120 volts from a HT battery, and input resistors of only 1 Megohm or 50 Megohms, broad full-scale peaks could be obtained on a 2mV. recorder with a few microlitres of either injected from a syringe. This circuit has no provision for a low output impedance and peak shapes on the Honeywell-Brown recorder were very poor. (Fig. 12).

(* Recorders (e.g. Honeywell-Brown) are now available with an impedance converter built in, including a high value input resistor, and the input terminals of such a recorder can be connected directly in series with the detector and polarising voltage.)

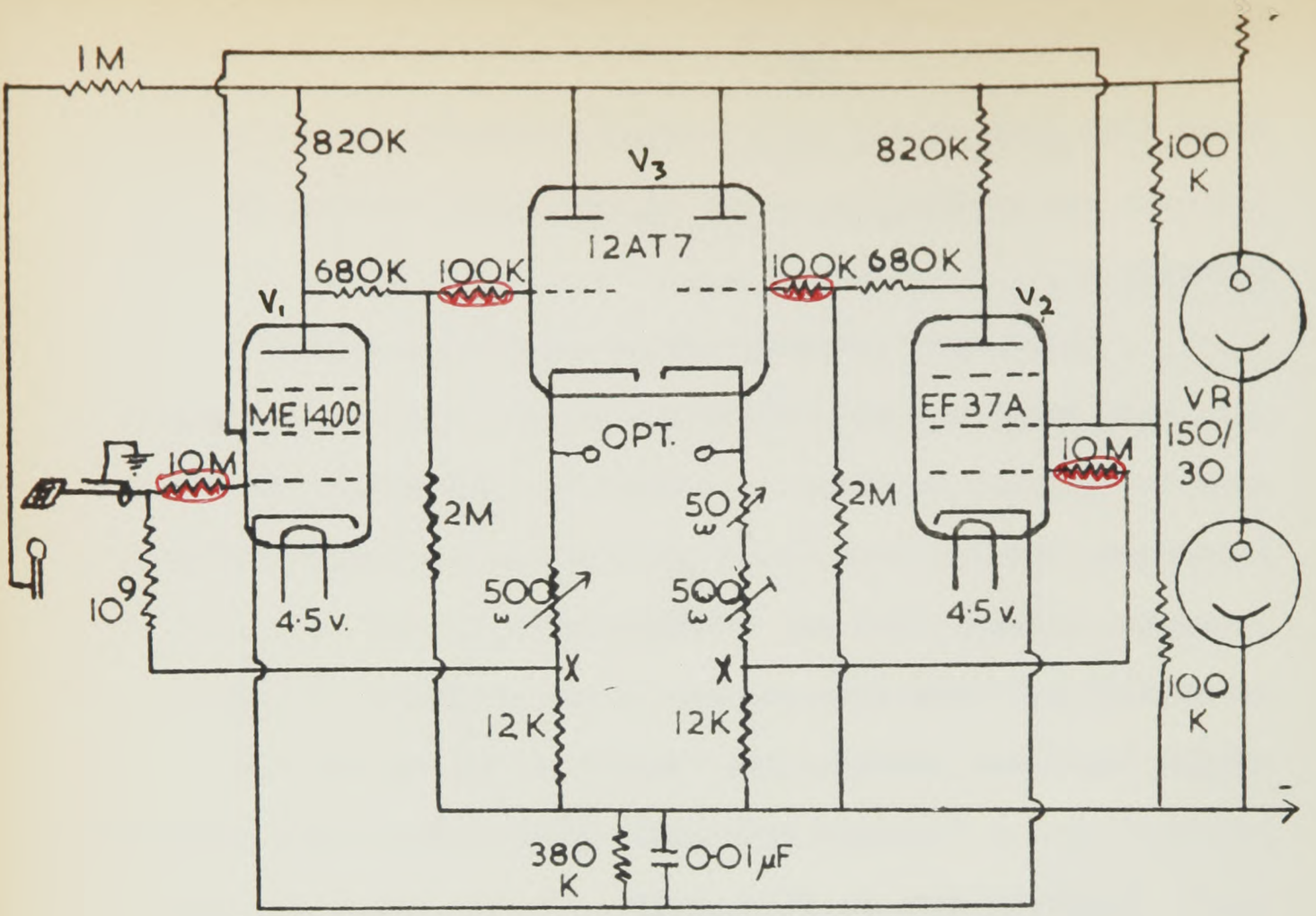

1M
820K
V3
12AT7
820K
100 K
680K
100K
100K
680K
V1
V2
ME1400
EF37A
OPT.
VR 150/ 30
10M
10M
2M
50 ω
2M
10^9
500 ω
500 ω
4·5 v.
4·5 v.
X
X
12K
12K
100 K
380 K
0·01 μF

FIG. 13

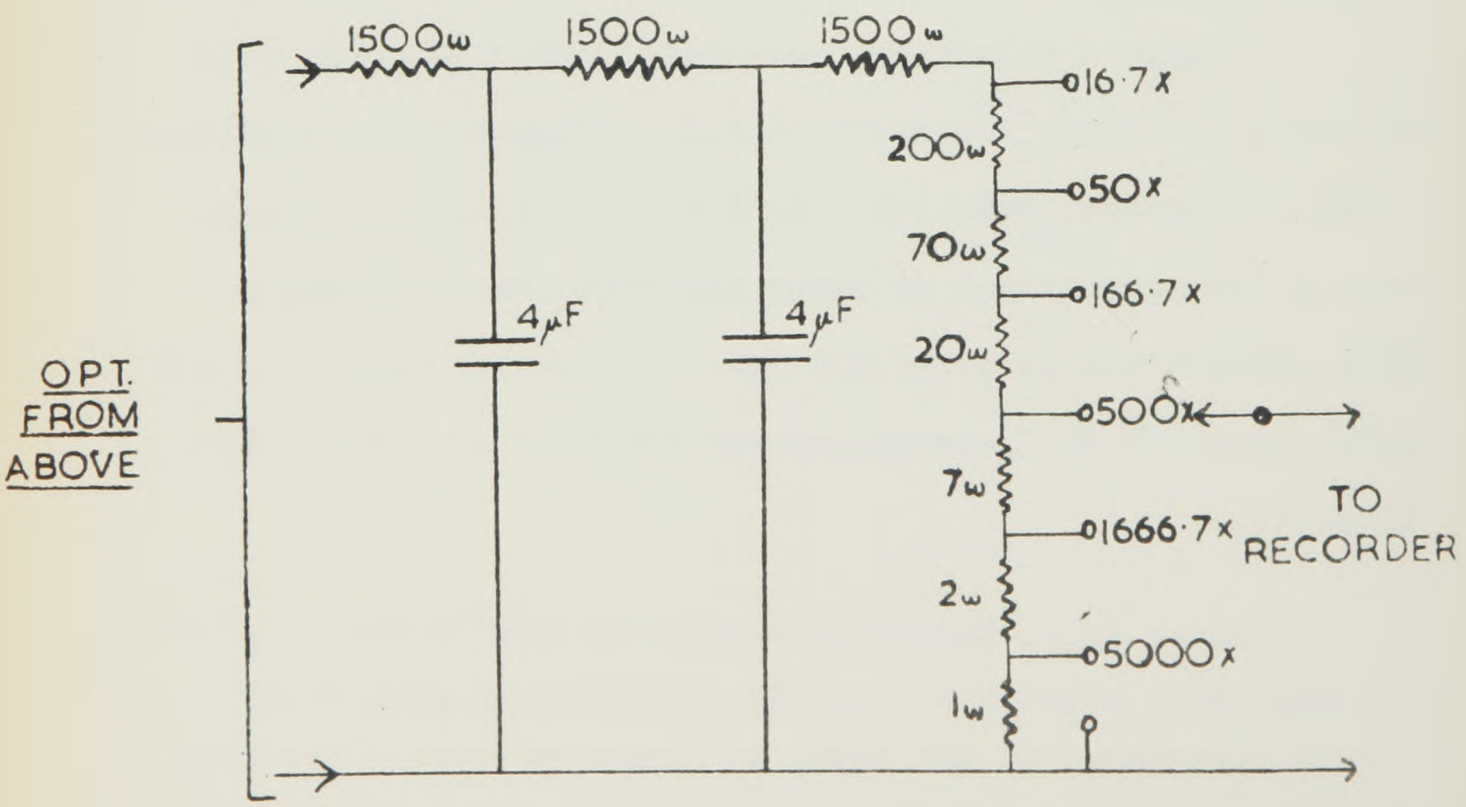

1500ω
1500ω
1500ω
16·7x
200ω
50x
70ω
166·7x
4μF
4μF
20ω
500x
OPT. FROM ABOVE
7ω
1666·7x
TO RECORDER
2ω
5000x
1ω

FIG. 14

1.2.2.2 Improved Circuit:

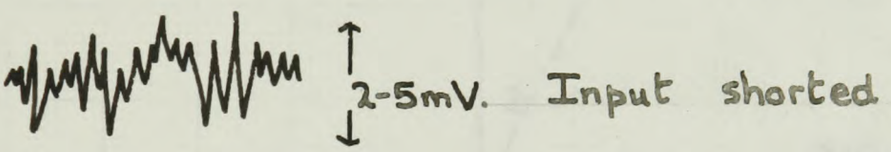
To exploit more fully the potential sensitivity of the detector, a series resistor of some 10^9 ohms or more should be used, and ordinary triode or pentode valves do not operate satisfactorily with such a large grid-cathode resistance. An "electrometer" type valve is much more suitable. A circuit which is stable and fulfils the conditions of output and input impedance is the type described by Scroggie for pH meters (6). Two of these circuits were built to the design of A.E. Thompson, subsequently described by him (2) See Fig.13

Features of this circuit are:

i). Electrometer-type input valve, such that series resistors of at least 10^{10} ohms can be used. The valve ME 1400 is an EF37 specially selected for this application. It is run on a low heater voltage of 4.5 volts, and before use the heater can be aged for 50 - 100 hours at its full 6.3 volts. The valve is metallised, and the top inch or so of the metallising should be scraped away, to lengthen the leakage path along the glass. For the same reason the screening on the input coaxial cable should be stripped back for about 2" at the detector end. Any graphite coating remaining on the bared insulation must be completely removed. An instance was encountered in this laboratory of an apparatus which completely failed to work because this was not done.

ii). The output appears as a difference voltage between the two halves of the circuit, which are identical

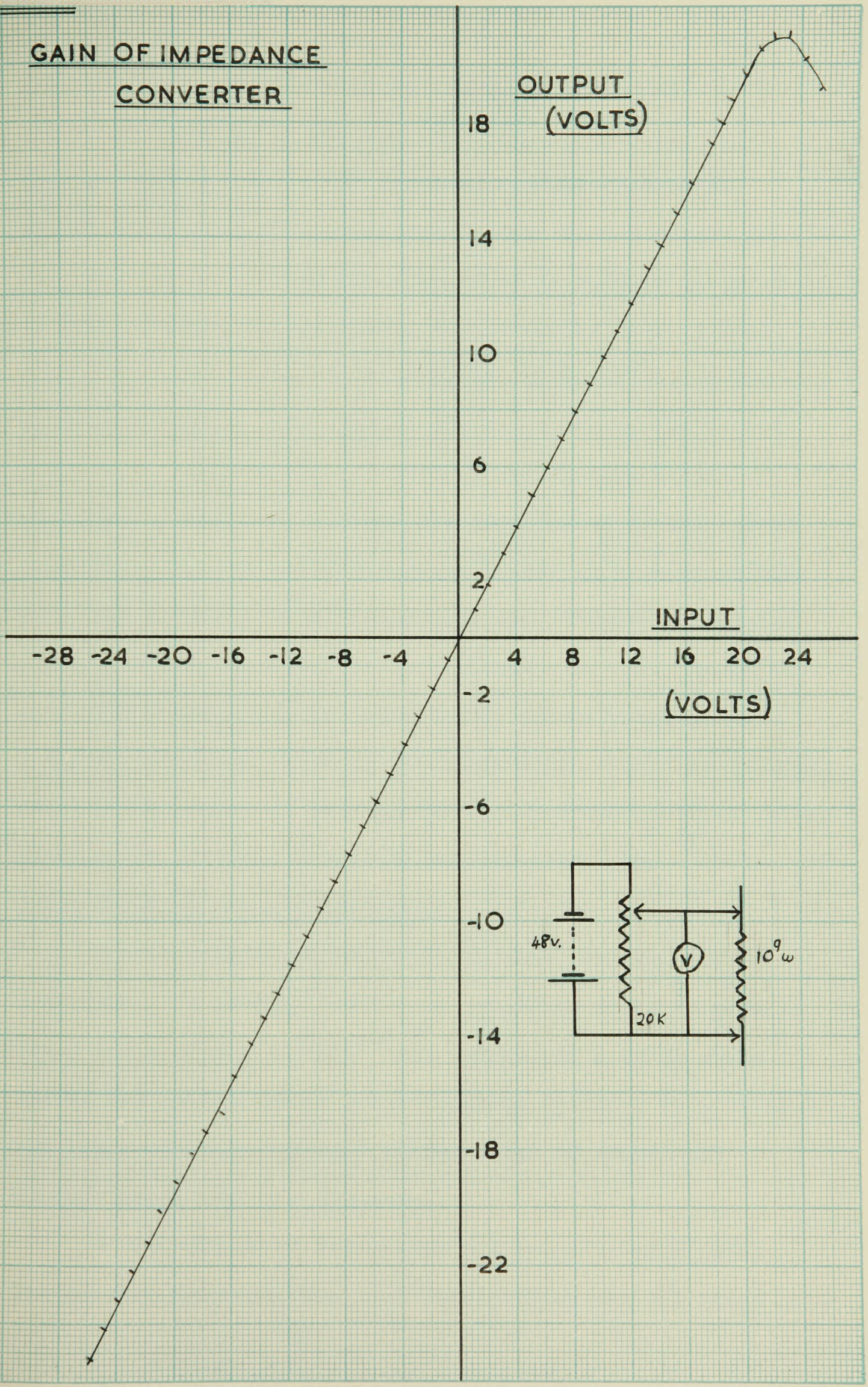
except that one half has no input. This arrangement helps to balance out the effects of variations in ambient temperature, mains voltage etc. The converter was totally enclosed in a small metal box (approx. 6" cube), to promote temperature stability, and the mains voltage was stabilised by a constant voltage transformer and the HT by neon stabilisers. In a preliminary version of the converter the HT was not stabilised, and the noise of the type sketched below decreased by a factor of 50 when stabilisers were later incorporated.



iii). A very high degree of negative feedback is applied to the converter, a proportion of the output being fed back to the input, in opposition to the input voltage. (the "earthy" side of the input and the grid of V_2 are connected to tappings on the output resistors -- points 'X'). This feature reduces the gain of the circuit to approximately unity, ensures that the gain remains constant over the whole range of input voltages and minimises the effect of valve ageing etc. on the performance of the circuit. The constancy of the gain was checked and the results are plotted in Fig. 15.

iv). Electrical screening is very important, since noise can be caused by interference from the surroundings, hand-capacity effects etc. The metal box mentioned earlier must be earthed, and the connection to the probe in the

GAIN OF IMPEDANCE CONVERTER



detector made with good quality coaxial cable with the screening earthed to the case.

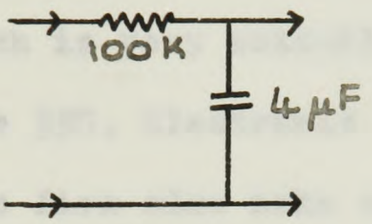
Under certain ill-understood conditions it is possible for this circuit to oscillate. The frequency is too high (50 - 100 c/s) for the effect to be seen directly on the recorder, and the usual manifestation is an output of about 5 - 10 volts which cannot be balanced out by the zeroing controls. The trouble can be caused by the layout adopted in any particular instance; for example in one converter built by the author the positioning of the output attenuator near to the input valve seemed to be responsible. The four resistors in red in Fig.13 are "stoppers" intended to damp out any tendency to oscillation, and their inclusion was effective in several cases in the author's experience. A further possible cause of an output which cannot be balanced out has been found to be a particular specimen of 12AT7 valve. Replacement effected a cure on several occasions.

1.2.3 Attenuator and Smoothing: (Fig. 14)

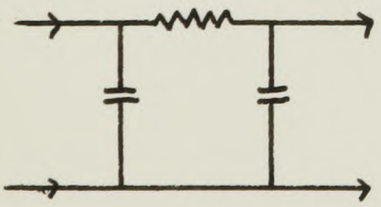
The attenuator/smoothing circuit performs two functions. It reduces the output, which is often as high as 1 - 5 volts with a 10^{-3}-10^{-4} gm. sample, to a value which can be fed into a normal potentiometric recorder (1 - 10 mV.) and the resistance-capacity filter helps to smooth out "spiky" noise from the detector.

The values of resistance and capacity used affect the overall response time, and values which are too large will

alter the shapes of peaks, particularly sharp ones where the signal rises or falls rapidly. A suitable time constant (given, in seconds, by the product of R (megohms) and C (microfarads)), would be about $\frac{1}{2}$ second, e.g. 4 μF and 100,000 ohms. (7)



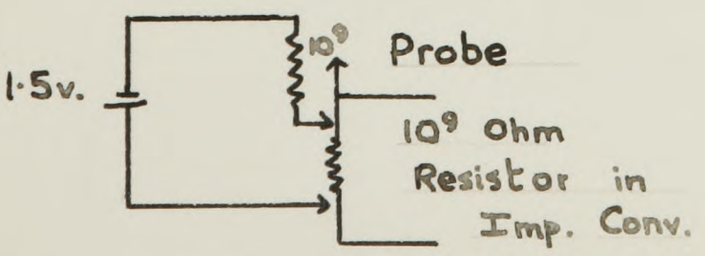
However, since the total resistance of the stepped portion of the attenuator should be less than 1000 ohms, (resistance across recorder terminals - see above), and the minimum division ratio required is about 1/10, a value of only about 10,000 ohms can be tolerated for the "smoothing" resistor. A 40 μF condenser would therefore be needed to give the right time constant - an impossibly high value, since it has to be a paper condenser, not an electrolytic (because of the inherent leakage current of the latter.) The best solution seems to be a'Pi' type of smoothing circuit:



with values as in Fig. 14.

1.2.4 Short-term stability and freedom from noise:

This was checked by applying a constant input as shown:



Drift and noise are negligible when the flame is not lit.

Note 1 : A different impedance converter circuit was used in the work described in Section 3.14., with a ME1403 electrometer valve. See appendix 3.

Note 2 : There is now a commercial "Electrometer Amplifier" available which is very suitable for this application: the "Vibron" (type 33C, Electronic Instruments Ltd., Richmond, Surrey). This firm also make an instrument (56A) which includes various switched series resistors, and a variable "backing-off" potential. A Type 33C was used for a short time and seemed very suitable, except that its maximum input voltage was not as great as that of the converter described above. A further instrument combines the functions of the 33C and 56A, and battery versions are also available.

FIG. 16

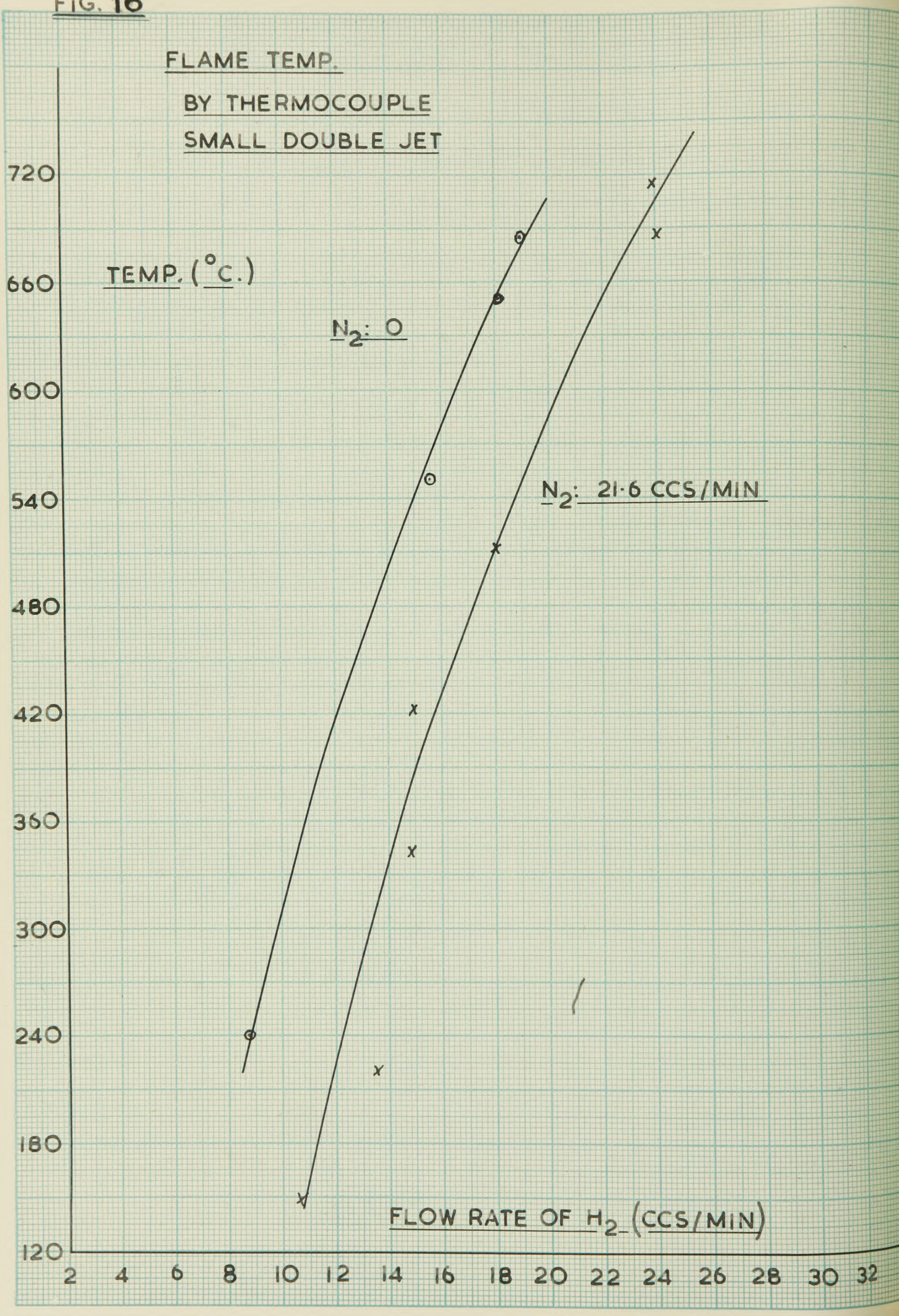
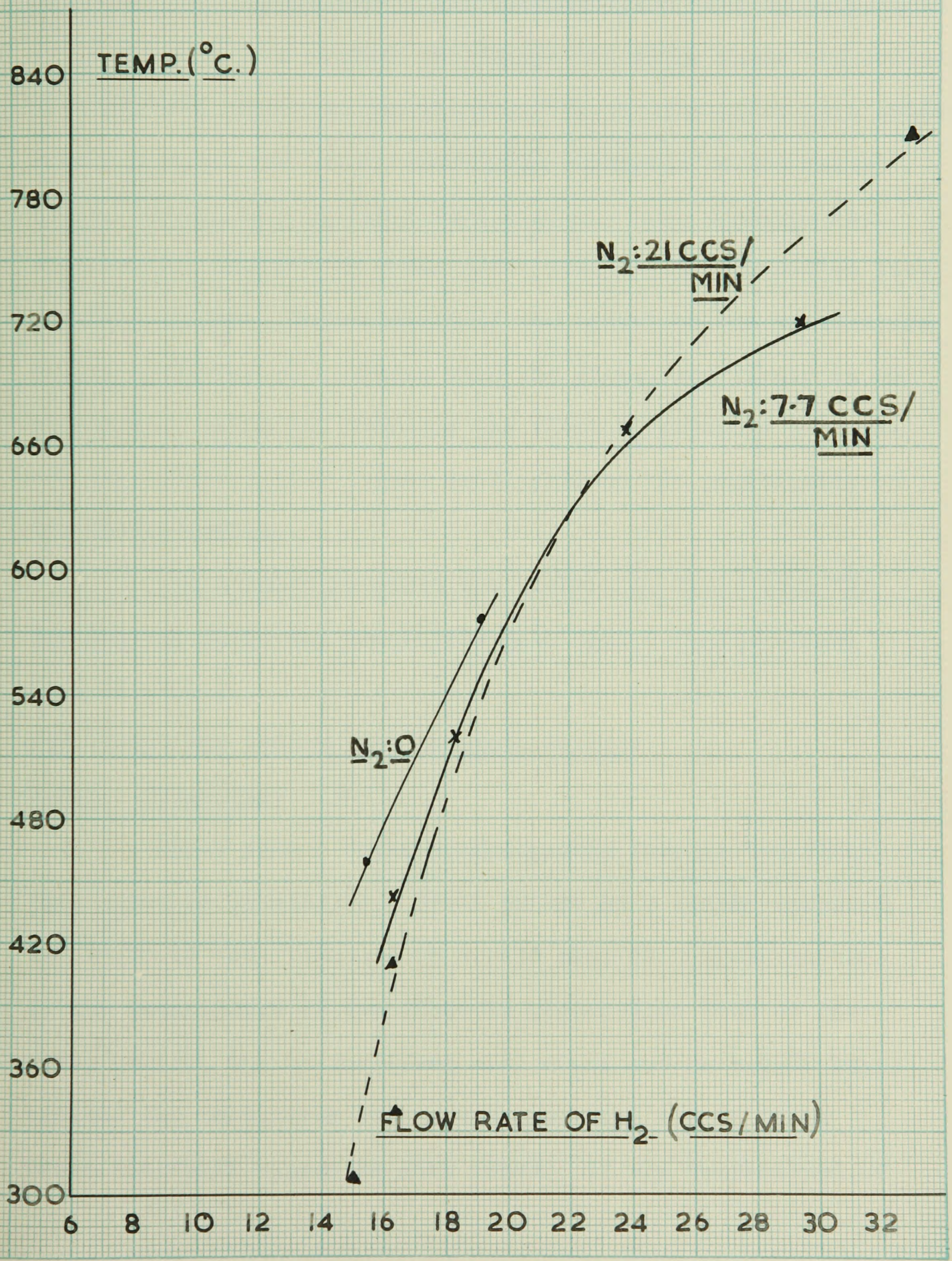

FLAME TEMP.
BY THERMOCOUPLE
SMALL DOUBLE JET
TEMP. (°C.)
720
660
600
540
480
420
360
300
240
180
120
N2: 0
N2: 21·6 CCS/MIN
FLOW RATE OF H2 (CCS/MIN)
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32

FIG. 17

FLAME TEMP.
BY THERMOCOUPLE
LARGE DOUBLE JET



CHAPTER 2

Measurement of the Temperature of the Flame:

2.1 Using Thermocouples: The flames are very small, about 3 mm. high and 2 mm. in diameter, and thermocouples must be very small if they are not to disturb the flames and alter their temperatures. Thin (0.008") platinum and platinum/13% rhodium wires were welded together using two carbon electrodes connected to the mains through a 600 watt electric fire element. The readings are considerably lower than those later obtained by the sodium line reversal method. Measurements of the effect on the temperature of the admission of nitrogen into the flame, are likely to be unreliable, since the shape of the flame is markedly changed, and the readings will depend critically on the positioning of the thermocouples.

The results obtained are plotted in Figs. 16 & 17, for the two different concentric jets used. (Calibration: Fig. 21 (15)).

2.2 Using the Sodium Line Reversal Method:

2.2.1 Principle: (14)

Light from a white source passes through the flame, into which is introduced a small amount of a sodium compound. The light is then focussed on to the slit of a spectrometer. If the temperature of the flame is higher than that of the white source, the sodium lines will stand out as bright lines against the continuous background spectrum, and if it is lower they will appear as dark lines. If the temperature of

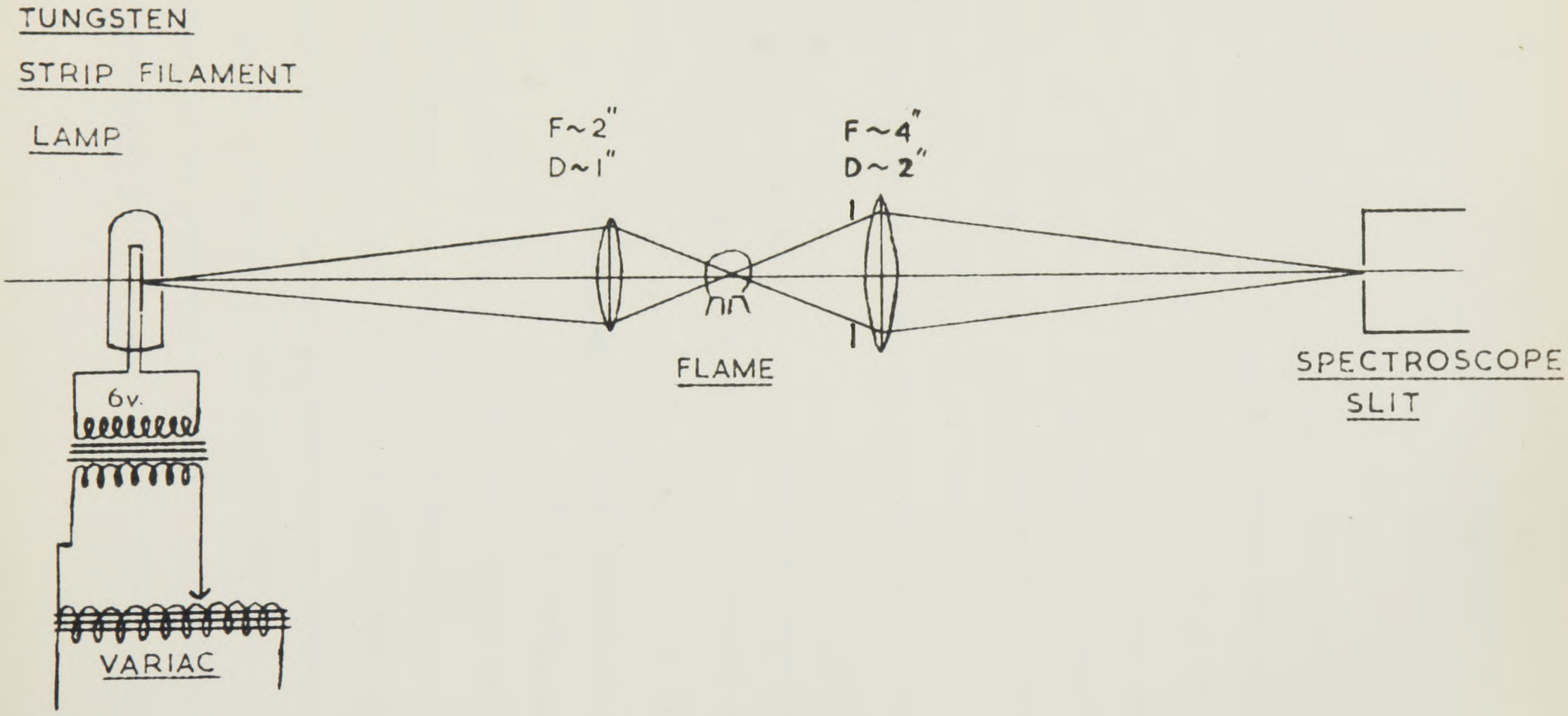

TUNGSTEN
STRIP FILAMENT
LAMP
F~2"
D~1"
F~4"
D~2"
6v.
FLAME
SPECTROSCOPE
SLIT
VARIAC

FIG. 18

the white source can be varied, a point will be found at which the sodium lines merge into the background, and the temperatures of the flame and the white source are then equal. The source can be calibrated using some form of pyrometer.

2.2.2 Method: See Fig. 18.

Light from a tungsten strip-filament lamp, fed from a 6 volt 30 amp. transformer connected to a Variac, was focussed on to the flame, and then on to the slit of a constant-deviation spectrometer. The stop before the second lens is recommended in the reference to ensure that the solid angle of light taken from the flame is the same as that taken from the lamp. (This precaution seems mainly applicable to large flames.) The flame was coloured by placing a small amount of very finely powdered sodium chloride on top of the burner. The lamp was calibrated against a disappearing filament optical pyrometer. In this instrument the source whose temperature is to be measured is viewed as the background to the filament of a bulb in the pyrometer. The current through the filament is varied until it disappears into the background. The current through the bulb then gives a measure of its temperature and therefore of that of the background, and an ammeter calibrated directly in temperature is provided. Filters are included, so that the temperature measured is that for red light.

The pyrometer appears to be designed for measuring the temperatures of extended sources such as furnace interiors, and some difficulty was experienced with the strip lamp, since

the comparison involved was between a hairpin filament and a straight filament. It was found best to arrange the two thus  or thus  and to concentrate attention on the point of crossing. (Results in Fig.22)

2.2.3 Precautions:

1) Alignment of the entire system and accurate focussing are very important. Any error here makes the reversal point indistinct or non-existent.

2) Too little sodium chloride in the flame makes the absorption weak.

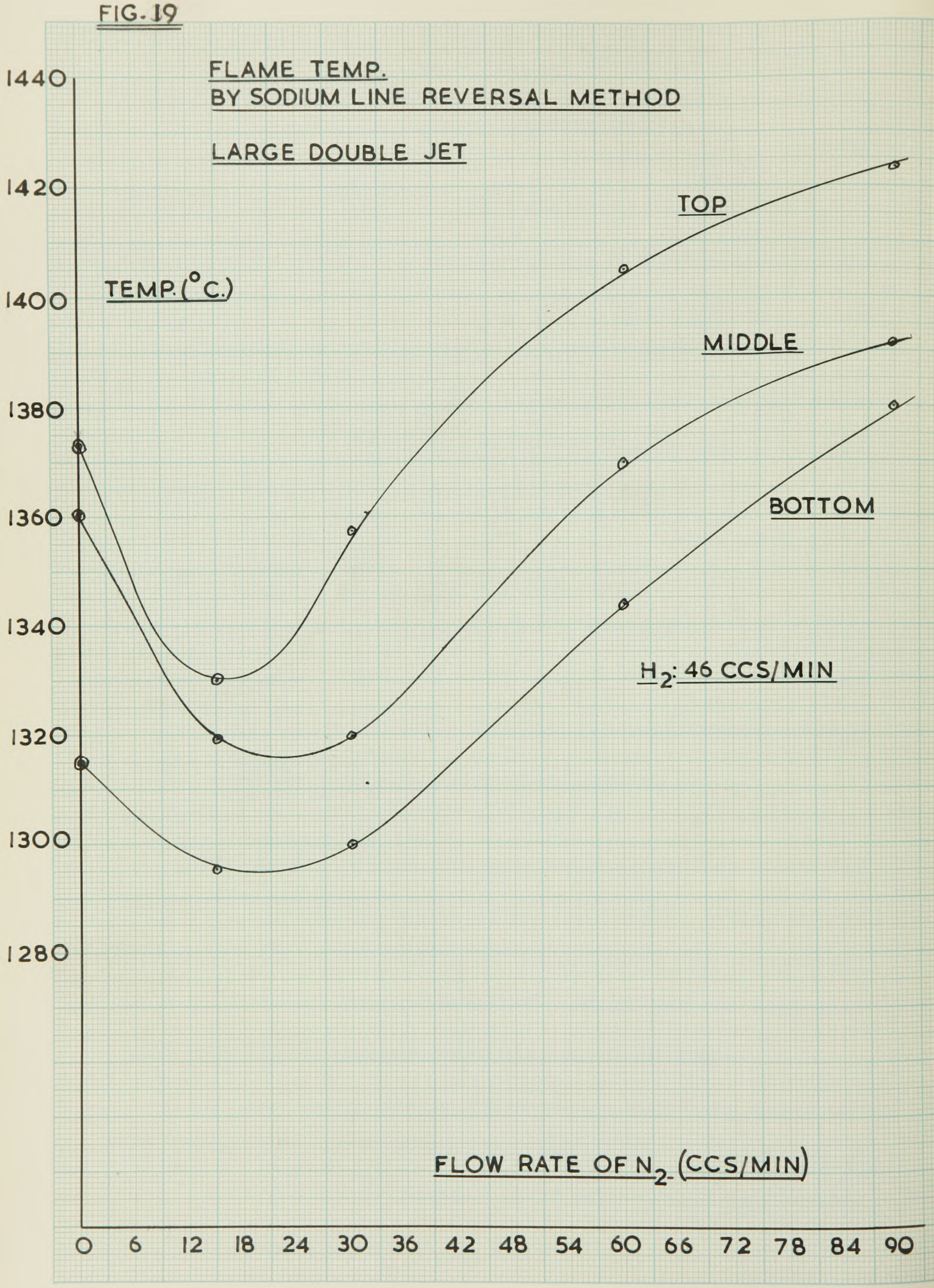
3) The sodium chloride must be kept clear of the actual jet, or changes in the shape of the flame affect the results.

2.2.4 Corrections and Errors: (14)

1) Variation of Emissivity with Wavelength: The comparison between the lamp and the pyrometer is made using red light and that between the lamp and the flame using yellow light. Since the emissivity of tungsten varies with wavelength, the temperature for yellow light will be higher than that for red light. The error resulting is about 10%.

2) Reflection at the Lenses and Refraction in the Flame: The usual procedure is to assume a 10% loss. This error almost exactly cancels out that due to (1). Refraction is unimportant except with thick flames.

FIG. 19


FLAME TEMP.
BY SODIUM LINE REVERSAL METHOD
LARGE DOUBLE JET
TOP
MIDDLE
BOTTOM
TEMP. (°C.)
1440
1420
1400
1380
1360
1340
1320
1300
1280
H2: 46 CCS/MIN
FLOW RATE OF N2 (CCS/MIN)
0
6
12
18
24
30
36
42
48
54
60
66
72
78
84
90

3) Emission from the Flame: the radiation from the flame results in the population of the excited state being slightly less than it ought to be. The correction at atmospheric pressure amounts to about + 3°C. for an air flame. This has been ignored.

4) Departure from Equilibrium in the Flame: Stated to be "probably slight" and therefore ignored.

Accuracy: Below 1500°C.: ± 5°C. for the reversal and ± 5°C. for the temperature calibration = ± 10°C.

Up to 2300°C.: ± 5°C. for the reversal and ± 10°C. for the temperature calibration = ± 15°C. (These figures are quoted from reference 14).

2.2.5 Results

The results obtained with the reversal method are plotted in Fig. 19. It was found by masking off parts of the flame that the top of the sodium line received light from the top of the flame and similarly for the other parts of it. Separate measurements of temperature could thus be made for the top, middle and bottom of the flame by observing the reversal points for the corresponding parts of the sodium lines.

No systematic study of the effect of the flow rate of hydrogen on temperature was made, but it was found that an increase from 50 - 100 cc/min. caused an increase in temperature from 1375° to 1775° at the top of the flame, while the bottom stayed constant at about 1315°C.

For flames burning at smaller and narrower burners, e.g. a fine hypodermic needle, the temperature is higher by

FIG. 20

No N_2 -



N_2 INTRODUCED



about 350 - 400°C.

An attempt was made to pass the light through the outer mantle of the flame only. For what it is worth, the temperature found was 1460°, 100° hotter than the top of the flame measured in the normal way.

To see if the addition of vapours had any effect on the temperature, the nitrogen (at 20 cc/min.) was bubbled through tetralin or benzene at room temperature. The effect was marginal in both cases: an increase from 1350 - 1356°C.

For calculations a temperature of 1360 - 1390° seems reasonable. (In view of the nature of these observations, several of them were checked by another worker, and confirmed).

The effect on the introduction of nitrogen in causing an increase in the flame temperature, after an initial fall, was unexpected, since it was expected to have merely a diluting, and therefore cooling, effect. Two possible explanations can be suggested. The shape of the flame changes markedly when the nitrogen is introduced, (see Fig.20), and the way it does so suggests either that extra air is being drawn in by the updraught of nitrogen or that the flame is being drawn inwards into a more compact shape resulting in a higher temperature.

(The author wishes to thank Dr. R.F. Barrow of the Physical Chemistry Laboratory, Oxford, for helpful advice and for the loan of apparatus).

FIG. 21

CALIBRATION CURVE FOR

THERMOCOUPLE (Pt / Pt+13%Rh)

(COLD JUNCTION AT 20°C)

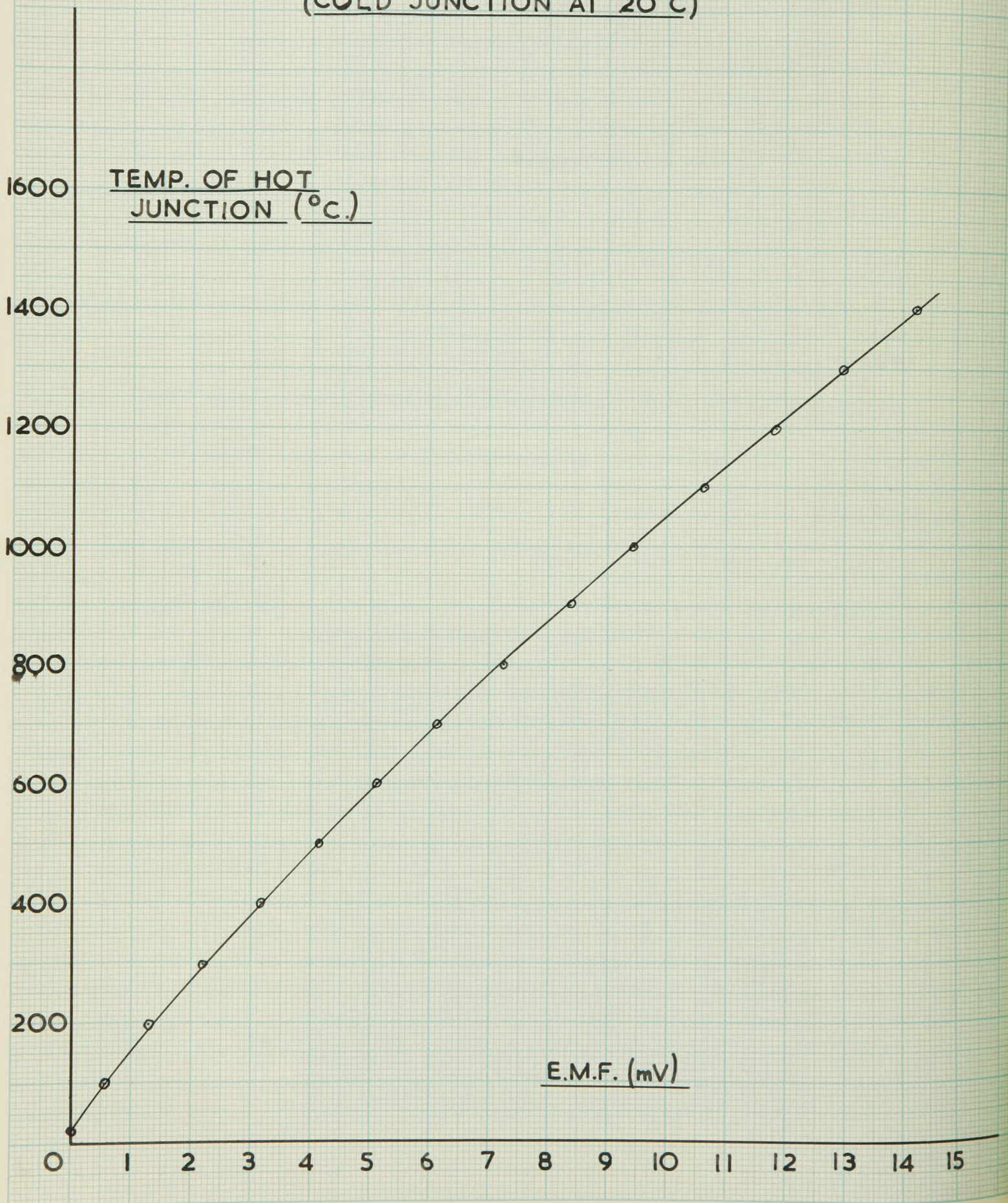
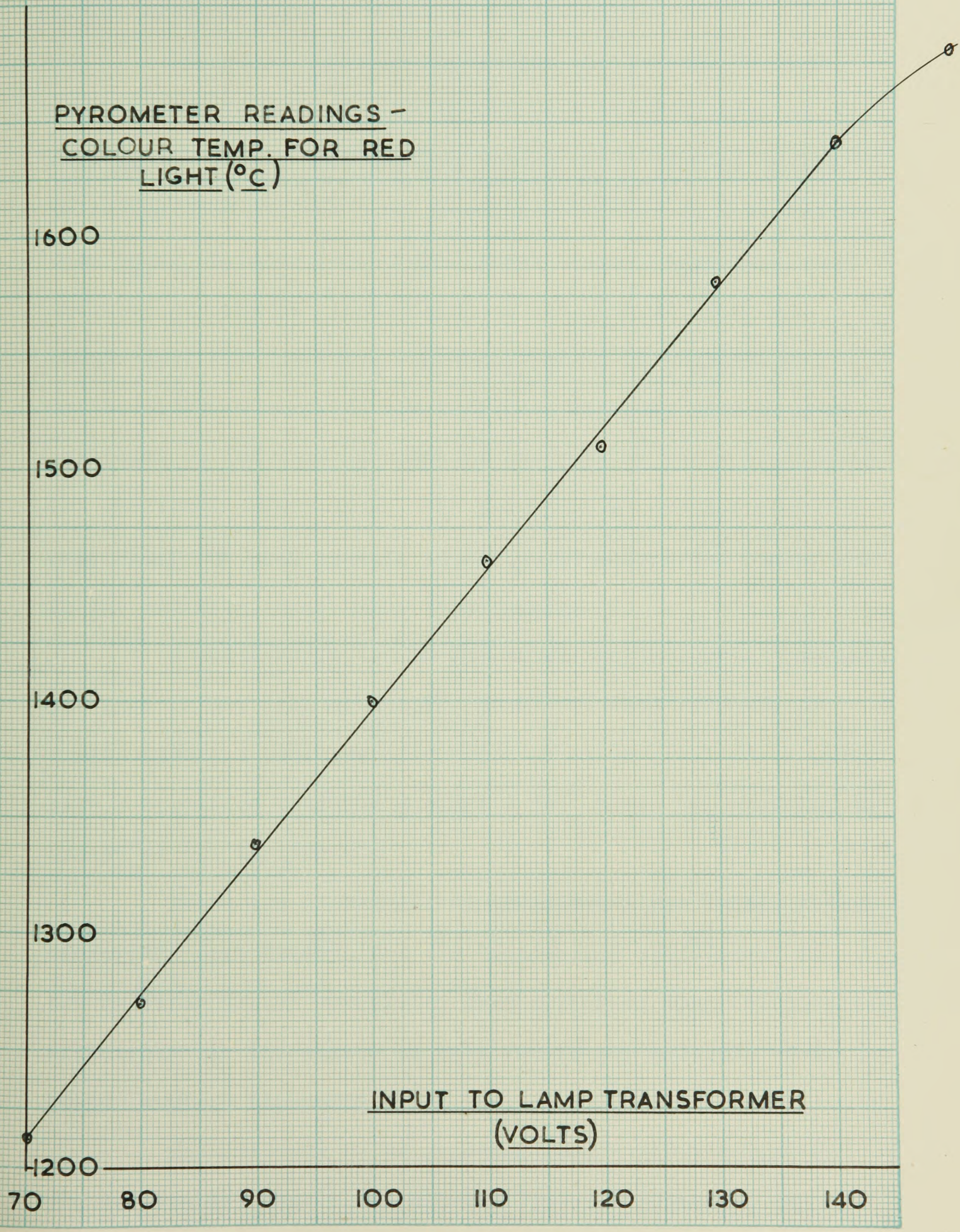


FIG. 22

CALIBRATION CURVE FOR BAND LAMP



CHAPTER 3

The Response of the Flame Ionisation Detector to Various Substances:

3.1.1 Introduction:

For given detector conditions the current through the detector is proportional to the rate of production of ions in the flame. The applied voltage must be high enough to ensure that all the ions formed are collected, i.e. greater than about 80 volts (4). For a given sample, therefore, the detector current is proportional to the rate of entry of sample into the detector. The peak height is proportional to the detector current, and therefore the peak area is proportional to the time integral of the rate of entry of sample: ie. the total sample size. The flow rate of carrier gas will only alter the peak area in so far as it alters the conditions in the detector, e.g. flame temperature.

Sensitivities can be expressed as peak areas (coulombs) per gram or per mole of sample, or as the rate of entry of sample into the detector (gms./sec. or moles/sec.) which would give a specified detector current - 10^{-9} amps. for example, in excess of the background.

These two statements of sensitivity are easily interconverted (see below), and the "ionisation efficiency" of the detector can be calculated from either of them ("Ionisation efficiency" is the number of ions formed per molecule of a given sample.) (Appendix 6)

The response to be expected from a given apparatus can be obtained from a sensitivity figure. Allowance can be

made for variations in the temperature of the flame, which should be stated where possible in giving sensitivities.

3.1.2 Deriviation of Sensitivity from Peak Areas:

A peak area of A volt.mins. on the recorder chart corresponds to $A.10^{-9}$ .60 amp.secs., or coulombs. (the gain of the impedance converter being unity, and the input resistor 10^9 ohms). If the sample size is m gms., then the sensitivity is $\frac{6A.10^{-8}}{m}$ coulombs/gm.

If the sensitivity in coulombs/gm. = S, and the sample size is 1 gm., the peak area will be S coulombs. If the peak is imagined as rectangular with a height corresponding to 1 amp. detector current, the peak width will be S secs. The sample will then be entering the detector at the rate of 1/S gms./sec. to give a current of 1 amp. The sensitivity can be stated as the rate of entry which would give some specified current, say, 10^{-9} amp., in this case 10^{-9}/S gms./sec.

The points to be investigated in a study of the detector were: sensitivity to various types of compound; noise level, and the effect on it of various samples; effect of polarity of applied voltage; linearity; the constancy of sensitivity over a range of sample sizes; ease of operation and construction, and robustness.

3.2 Response to Hydrocarbons etc.

The detector shows high sensitivity to organic compounds in general; samples actually tested include hydrocarbons, ketones, halogen compounds, amines (primary, secondary and tertiary), all these in both the aliphatic and the aromatic series; also alcohols, ethers, nitrobenzenes, and pyridines. In subsequent work no wholly organic compound has been found to which the detector does not show high sensitivity.

The response of the detectors used in this work to aromatic hydrocarbons was of the order of 2×10^{-3} coulombs/gm.

or a rate of entry of 5×10^{-7} gms./sec. for a current of 10^{-9} amp. Flame Temp. about 1600°C. Polarity had a small effect, if any. (See Sec. 1.1.5).

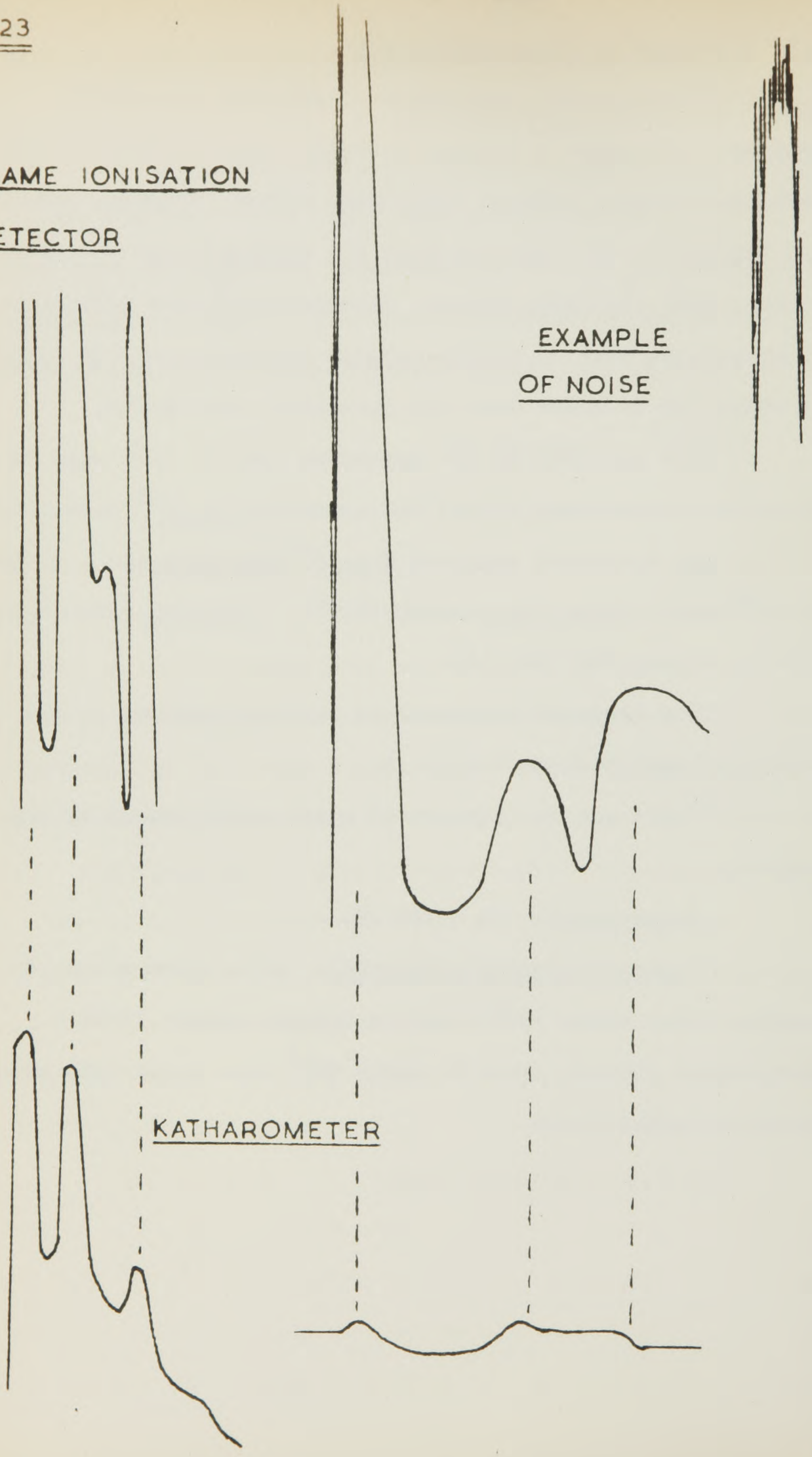
The response increased in rough proportion to the number of carbon atoms (1, 3).

There was no increase of noise level caused by the samples.

Noise Level: 50 - 100 mV.

Minimum Detectable Quantity: of a hydrocarbon of boiling point about 100°C. with a typical column (1600 theoretical plates) would be about 10^{-6} gms. for a peak height twice the noise level.

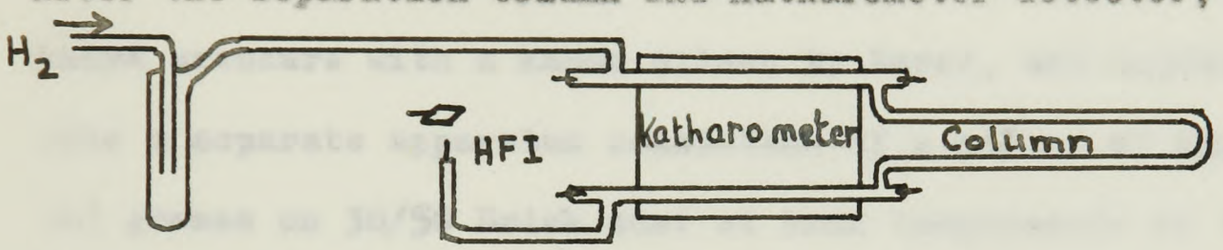
FIG. 23



3.3 Response of Flame Ionisation Detector to Silanes: (Si_nH_{2n+2})

3.3.1 Preliminary Experiments

These were carried out with an all-glass detector (Fig. 1). A worker in the same laboratory (K.Borer) was engaged in work on the silanes using gas-liquid chromatography, and the flame ionisation detector was attached to his apparatus after the separation column and katharometer detector, thus:



In this way the peaks from the flame detector could be compared with those from the katharometer.

There was good correlation between peaks from the two detectors corresponding to silanes from SiH_4 to Si_4H_{10} or Si_5H_{12}. Those from the katharometer were much smaller than corresponding ones from the flame ionisation detector. Peaks appearing only as small "humps" on the sides of larger peaks on the katharometer, or as small movements of the baseline, sometimes correlated with well-defined peaks on the flame detector (Fig. 23). The flame generally showed a yellow tinge when a silane was passing through, and no abnormal appearance on hydrocarbon peaks.

The jet tended to block with a white deposit, presumably silica, when the sample size was too large (about 0.05 gms.). In one of the early experiments the jet apparently blocked and then the trapped monosilane escaped and exploded, damaging the detector. On another occasion when the jet

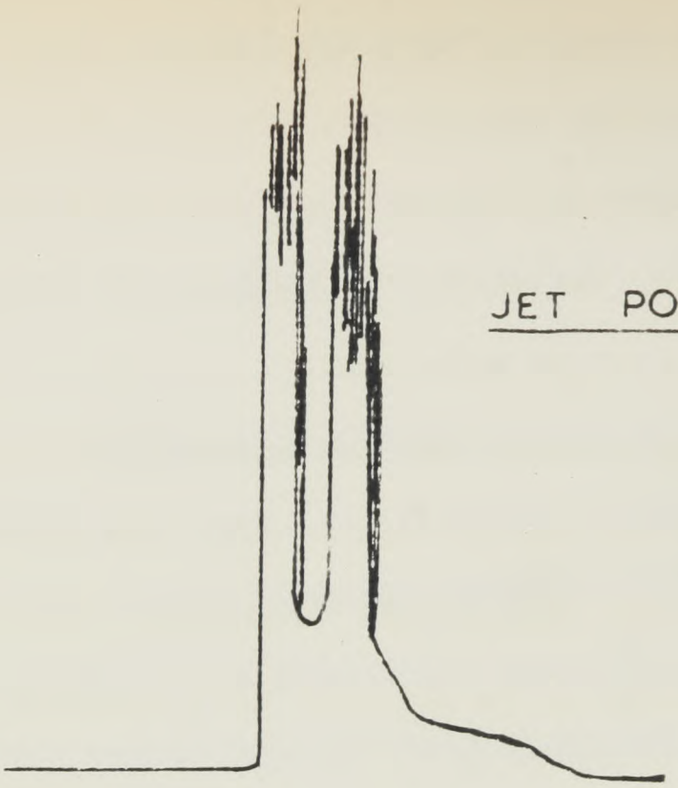
blocked, the gas escaped round the base of the jet, caught fire and continued to burn there, the detector still giving a response. A wider jet (about 1.5 mm.) was fitted but the trouble persisted. Noise on the large peaks was often bad (Fig. 23).

3.3.2 Injection of known samples from traps.

Small sample traps (vol. 7 cc.) were filled to a known pressure with a known silane by Borer, and injected into a separate apparatus consisting of a column of Apiezon 'L' grease on 30/50 Brick dust at room temperature or 176°C., and a detector as shown in Fig. 2, but with a nickel foil cylinder instead of a piece of gauze. For more details of apparatus and methods of injection see Appendix 1.3.

Si_3H_8 and Si_2H_6

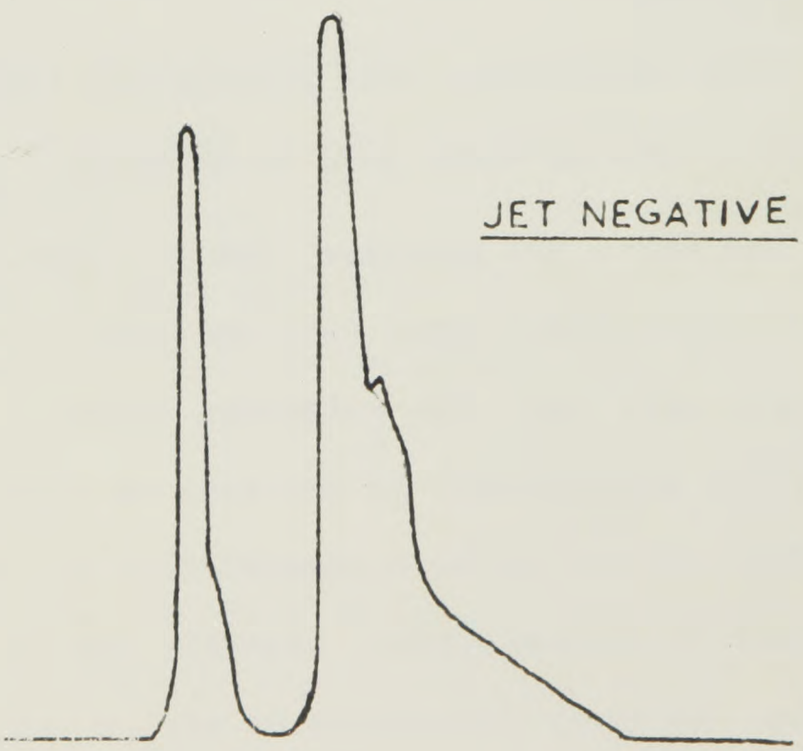
Four experiments were carried out (326 - 329), all with samples from K. Borer said to be Si_3H_8. The jet polarity was: 326 and 327:- jet positive, 328 and 329:- jet negative. The first sample (326), gave only one peak, as expected, while all the rest gave two. The retention volume of the second peak in these experiments is the same as that of the single peak in 326, and it has been assumed that the new peak is Si_2H_6 formed by decomposition, possible due to a little air leaking in. To check the effect of air, a little was deliberately let into the trap containing the silane, and no further peaks appeared.



JET POSITIVE

COMPARISON OF NOISE WITH SILANE SAMPLES

AT DIFFERENT POLARITIES.



JET NEGATIVE

FIG. 24

A sensitivity to Si_3H_8 has been worked out (see below) from 326. This value has then been used tomwork out the amount of Si_3H_8 corresponding to the second peak in 327. Since the total amount of sample in 327 is known, the amount of Si_2H_6 can be found, and a value for the sensitivity to Si_2H_6 calculated.

If it is now assumed that the degree of decomposition in 328 and 329 is about the same as that in 327, the ratio Si_2H_6 to Si_3H_8 can be taken as the same in all these three experiments. Thus sensitivity figures can be obtained for a negative jet from 328 and 329.

(For the difference in noise level due to different polarity see Fig. 24.)

Results

Expt. No.		326	327	328	329
Jet Polarity		+	+	-	-
Peak Areas (sq. ins.)	Si_2	-	0.30	0.34	0.46
	Si_3	1.5	0.66	0.89	0.82
Total sample size (moles x 10^{-6})		3.8	3.8	4.0	3.8
Sample size for each compound (gms. x 10^{-4})	Si_2	-	1.2	1.3	1.2
	Si_3	3.5	1.7	1.8	1.7
Peak Areas (coulombs x 10^{-7})	Si_2	-	0.5	0.56	0.76
	Si_3	2.3	1.1	1.5	1.4
Sensitivity (coulombs/gm. x 10^{-4})	Si_2	-	4.2	4.3	6.33
	Si_3	6.6	6.6	8.3	8.2
Sensitivity as Rate of Entry for current of 10^{-9} amps. (gms./sec. x 10^{-6})	Si_2	-	2.4	2.3	1.6
	Si_3	1.5	1.5	1.2	1.2

Flow Rate of H_2 = 42 ccs/min.; Flame Temp. = approx. 1600°C.

A sensitivity to Si_3H_8 has been worked out (see below) from 326. This value has then been used to work out the amount of Si_3H_8 corresponding to the second peak in 327. Since the total amount of sample in 327 is known, the amount of Si_2H_6 can be found, and a value for the sensitivity to Si_2H_6 calculated.

If it is now assumed that the degree of decomposition in 328 and 329 is about the same as that in 327, the ratio Si_2H_6 to Si_3H_8 can be taken as the same in all these three experiments. Thus sensitivity figures can be estimated from 328 and 329 for a negative jet.

(For the difference in noise level due to different polarity see Fig.24.)

Results

Expt. No.		326	327	328	329
Jet Polarity		+	+	-	-
Peak Areas (sq.ins.)	Si_2	-	0.30	0.34	0.46
	Si_3	1.5	0.66	0.89	0.82
Total Sample Size (moles x 10^{-6})		3.8	3.8	4.0	3.8
Sample Size for each compound (gms.x 10^{-4})	Si_2	-	1.2	1.1	1.0
	Si_3	3.5	1.7	2.1	2.0
Peak Areas (coulombs x 10^{-7})	Si_2	-	5.0	5.6	7.6
	Si_3	2.3	1.1	1.5	1.4
Sensitivity (coulombs/gm.x 10^{-4})	Si_2	-	4.2	5.3	7.6
	Si_3	6.6	6.6	7.0	6.7
Sensitivity as Rate of Entry for current of 10^{-9}amp. (gms./sec. x 10^{-6})	Si_2	-	2.4	1.9	1.3
	Si_3	1.5	1.5	1.4	1.5

Flow Rate of H_2 = 42 cc./min.; Flame Temp. = approx.1600°C.

Average Sensitivities from above:

	Si_2H_6	Si_3H_8
Jet Positive	4.2×10^{-4} coul./gm. 2.3×10^{-6} gms./sec for 10^{-9} amps. detector current.	6.6×10^{-4} coul./gm. 1.5×10^{-6} gms./sec. for 10^{-9} amps. detector current.
Jet Negative	5.3×10^{-4} coul./gm. 1.6×10^{-6} gms./sec. for 10^{-9} amps. detector current.	8.3×10^{-4} coul/gm. 1.2×10^{-6} gms./sec. for 10^{-9} amps detector current.

Variation in Sensitivity with Polarity:

Si_2H_6 : Ratio (+/-) = ~~0.6~~ 0.8

Si_3H_8 : Ratio (+/-) = ~~1~~ 0.8

Alternative Derivation of a Value for this Ratio:

Run No.	Jet Polarity	Peak Areas (Si_2)		Peak Areas (Si_3)	
327	+	0.30		0.66	
328	-	0.34	) mean =	0.89	) mean=
329	-	0.46	) 0.40	0.82	) 0.86
	Ratio (+/-):	0.75		0.77	

This estimate is based on the fact that the sample sizes are almost the same in the three experiments. and the ratio Si_2/Si_3 is assumed to be the same.

3.3.3 Si_6H_{14} :

A sample of mixed branched-chain hexasilanes from the same source as above was injected by the same method. It was not possible to measure the size of the sample in the same manner since hexasilane has too low a vapour pressure at room temperature. The column was jacketed with nonyl alcohol vapour (178°C).

One large off-scale peak was obtained with three much smaller peaks as 'satellites'. (This is the expected number since there are four branched-chain isomers of Si_6H_{14}).

The size of the sample has been roughly estimated from the size of the peak it gave on the katharometer before it was collected and given to the author. The area of the peak given by a known amount of mesitylene under similar conditions is known, and since the carrier gas was hydrogen, it can be assumed that the sensitivity of the katharometer in terms of molar concentrations is the same for all substances.

The hexasilane peak on the flame ionisation detector is off-scale but an estimate of its height has been made by extrapolation of the sides of the peak.

The polarity was "jet negative", the detector as above (3.3.2), and the peaks well-shaped and noise-free.

Results:

Katharometer:

1 mgm. of mesitylene (0.008 millimoles) gave a peak area 2 sq. ins. The Si_6H_{14} gave a peak area of 5.3 sq.ins. which corresponds to:

$$\frac{0.008 \times 5.3}{2} \text{ millimoles of silane.}$$

$$= \frac{0.008 \times 5.3 \times 182}{2} \text{ mgms.}$$

$$= 3.86 \text{ mgms.}$$

$$\doteq 4 \text{ mgms.}$$

Peak Area on flame detector (estimated) = 2.5 sq.ins. or 2.1×10^{-7} coulombs.

Sensitivity = 5×10^{-5} coulombs/gm. or 2×10^{-5} gms./sec. for a current of 10^{-9} amps.

These values are an order of magnitude less than those obtained for the other silanes above.

3.3.4 Characteristics of the Flame Ionisation Detector with Silane Samples.

Approximate sensitivity to Si_2 and Si_3 as compared with Hydrocarbons

Jet positive:	$\frac{\text{hydrocarbon}}{\text{disilane}}$	= 4.8
	$\frac{\text{Hydrocarbon}}{\text{trisilane}}$	= 3.0
Jet negative	$\frac{\text{hydrocarbon}}{\text{disilane}}$	= ~~3.0~~ 1.9
	$\frac{\text{hydrocarbon}}{\text{trisilane}}$	= ~~2.0~~ 1.2

Noise:

For examples of the noise levels with the different polarities see Fig. 24. It is evident that a negative jet gives considerably better results.

Collector:

There seems to be little difference in noise level between peaks obtained with a piece of gauze and with a cylinder, both being noisy when the polarity of the jet is positive. No results are available for a gauze with the jet negative. A cylinder or ring is, however, preferable, being less prone to become coated with silica.

Recommendations:

The recommended conditions for work with silanes are therefore:

i) Jet negative
ii) Cylinder (or ring) as collector
iii) Samples not larger than about 10^{-3} gms.

Under these conditions satisfactory results can be obtained.

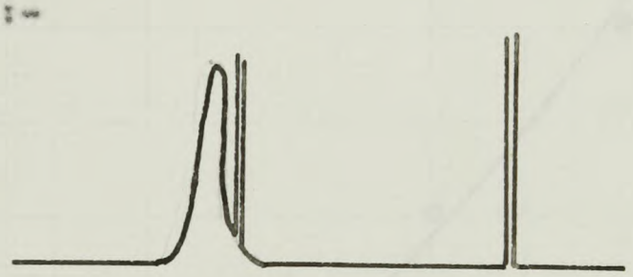
~~The flame ionisation detector has since been used for work on silanes in this laboratory using capillary columns (which take very small samples - about 10^{-6} gms.) and results were satisfactory (46).~~

Note:

Another worker in this laboratory has since passed samples of mixed silanes through a capillary column and into a flame ionisation detector. The general appearance of the chromatograms is similar to those in the experiments already described: quite a lot of random noise as:-



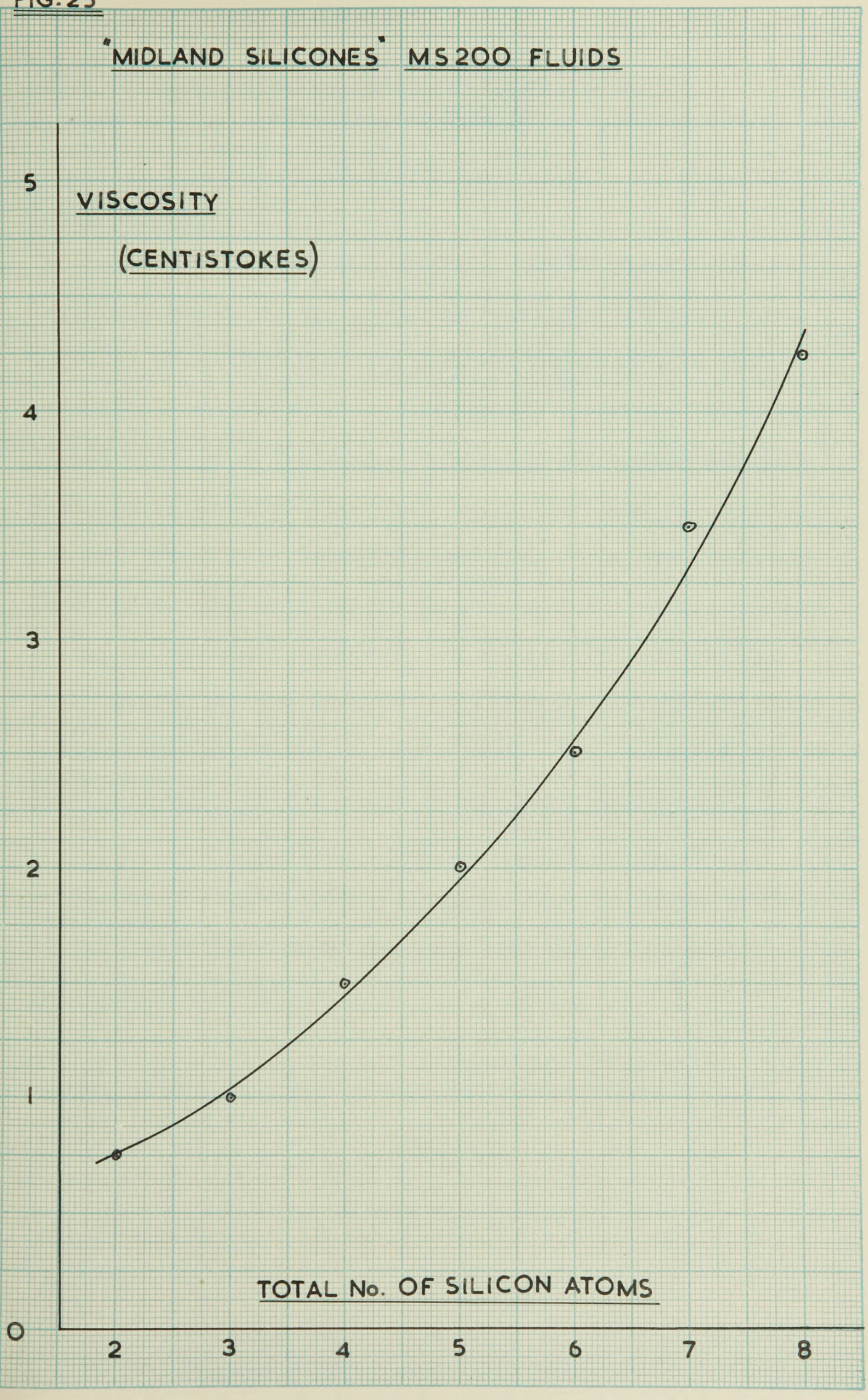
and occasional random off-scale "spikes" on the tops of peaks, and elsewhere:-



Peaks given by hydrocarbons on the same apparatus were "clean". There is some indication that the peaks due to the lower members of the silane series are "cleaner" than those due to later ones.

The sample sizes were of the order 1.5×10^{-4} gms. to 0.5×10^{-4} gms. (total). This is about 1/10 of the size used in the experiments described here. (46)

FIG. 25


"MIDLAND SILICONES" MS 200 FLUIDS
VISCOSITY
(CENTISTOKES)
5
4
3
2
1
0
TOTAL No. OF SILICON ATOMS
2
3
4
5
6
7
8

3.4 Response of the Flame Detector to Silicones:

$$(Si(Me)_3)\text{-}(\text{-}O\text{-}Si(Me)_2\text{-})_n\text{-}O\text{-}(Si(Me)_3)$$

$$n = 0 \text{ to } 4$$

3.4.1 Method:

Samples of MS 200 silicone oils (Midland Silicones) were injected on to the column by capillary injection (see Appendix 1). These silicone oils are labelled with their viscosities in centistokes, and are all mixtures. The three lowest members of the series (n = 0,1 & 2), showed one main peak and up to three very small peaks, and only the main one has been taken into consideration. The other two silicones (n = 3 & 4) each give two peaks of comparable sizes, and the amount of the minor component has been estimated from the peak size, using the sensitivities already determined, and subtracted from the total sample size. The remainder has then been taken as the amount of the main component.

The manufacturers publish figures giving the viscosity of various pure silicones, and this is the basis of the identification of the main components in the oils used. (see graph, Fig. 25)

3.4.2 Results:

Flame Temperature ≑ 1700°C.

Experiment No.	278	279	280	281
Sample	MS200/0.65cs	MS200/1cs	MS200/1.5cs	
Value of 'n'	0	1	2	
Peak Area (coulombs)	0.12×10^{-7}	0.13×10^{-7}	0.13×10^{-7}	0.15×10^{-7}
Sample Size (gms)	0.8×10^{-3}	0.8×10^{-3}	0.8×10^{-3}	
Sensitivity (coul./gm.)	1.5×10^{-5}	1.6×10^{-5}	1.8×10^{-5} (mean)	
Sensitivity (gms/sec. (for 10^{-9} amps.)	6.7×10^{-5}	6.2×10^{-5}	5.6×10^{-5}	

Experiment No.	282 & 284 (identical results)		287		
Sample	MS200/2cs		MS200/3cs		
Values of 'n'	2	3	2	3	4
Peak Areas (coul.)	0.09×10^{-7}	0.22×10^{-7}	0.033×10^{-7}	0.05×10^{-7}	1.2×10^{-7}
Total Sample Size (gms.)	0.8×10^{-3}		0.8×10^{-3}		
Sample Size	$\underline{0.42\times10^{-3}}$	0.38×10^{-3}	$\underline{0.2\times10^{-3}}$	$\underline{0.1\times10^{-3}}$	0.5×10^{-3}
Sensitivity (coul./gm.)	-	4.8×10^{-5}	-	-	2.4×10^{-4}
Sensitivity (gms/sec for 10^{-9} amps.)	-	2.1×10^{-5}	-	-	4.2×10^{-6}

"Sample sizes" underlined in the table are those calculated as explained above.

Apparatus:

1) Detector as in Fig. 4, with simple jet (not concentric).

2) Polarity: Jet positive.

3) Collector: ring (see Fig. 8 and see below).

3.4.3 Characteristics of the Detector with Silicone samples:

1) Sensitivity rather low. ~~Figures relative to n-butane:~~

n	Total No. of Si atoms.	Formula	Sensitivity (coul./gm.)	Relative Sensitivities.	Hydrocarbon silicone
0	2	$Si_2C_6H_{18}O$	1.5×10^{-5}	1	130
1	3	$Si_3C_8H_{24}O_2$	1.6×10^{-5}	1.1	130
2	4	$Si_4C_{10}H_{30}O_3$	1.8×10^{-5}	1.2	110
3	5	$Si_5C_{12}H_{36}O_4$	4.8×10^{-5}	3.2	42
4	6	$Si_6C_{14}H_{42}O_5$	2.4×10^{-4}	16	8.4

The sensitivity is much lower than the number of carbon atoms or of silicon atoms might suggest. (The sensitivity of the detector to hydrocarbons is stated to be proportional to the carbon number) (1, 3).

2) Noise

With a gauze probe the noise was bad, but with a ring probe normal clean peaks were obtained (except for a little noise on the tops of peaks from the higher silicones). See Fig. 8 and Section 1.1.4. Noise "spikes" seemed to tally with the appearance of tiny puffs of white smoke from the flame.

3) Polarity: No results are available with the jet negative.

3.5. Response of the Flame Ionisation Detector to Phosphorus Chloronitriles: $(PNCl_2)_3$ and $(PNCl_2)_4$ (from Albright and Wilson).

The compounds were injected as solutions in carbon tetrachloride, by capillary.

No response at all was obtained, even with strong solutions.

A small crystal of each of the compounds was then placed actually on top of the burner, in the flame. The only effects were a slight shift in the baseline and a small increase in the noise level.

Apparatus: Detector as in Fig. 4, with a piece of gauze as collector.

Polarity: Trimer with both polarities, tetramer with jet positive only.

Note: It has since been found that the flame ionisation detector gives no response to chloroborazoles, though it responds to other borazoles (47). The structure of these compounds is similar to that of the phosphorus chloronitriles.

FIG. 26

CCl_4 IN SATR. AT 0·3°C.

V.P.: 33 MM. Hg.

LARGE DOUBLE JET

JET NEGATIVE

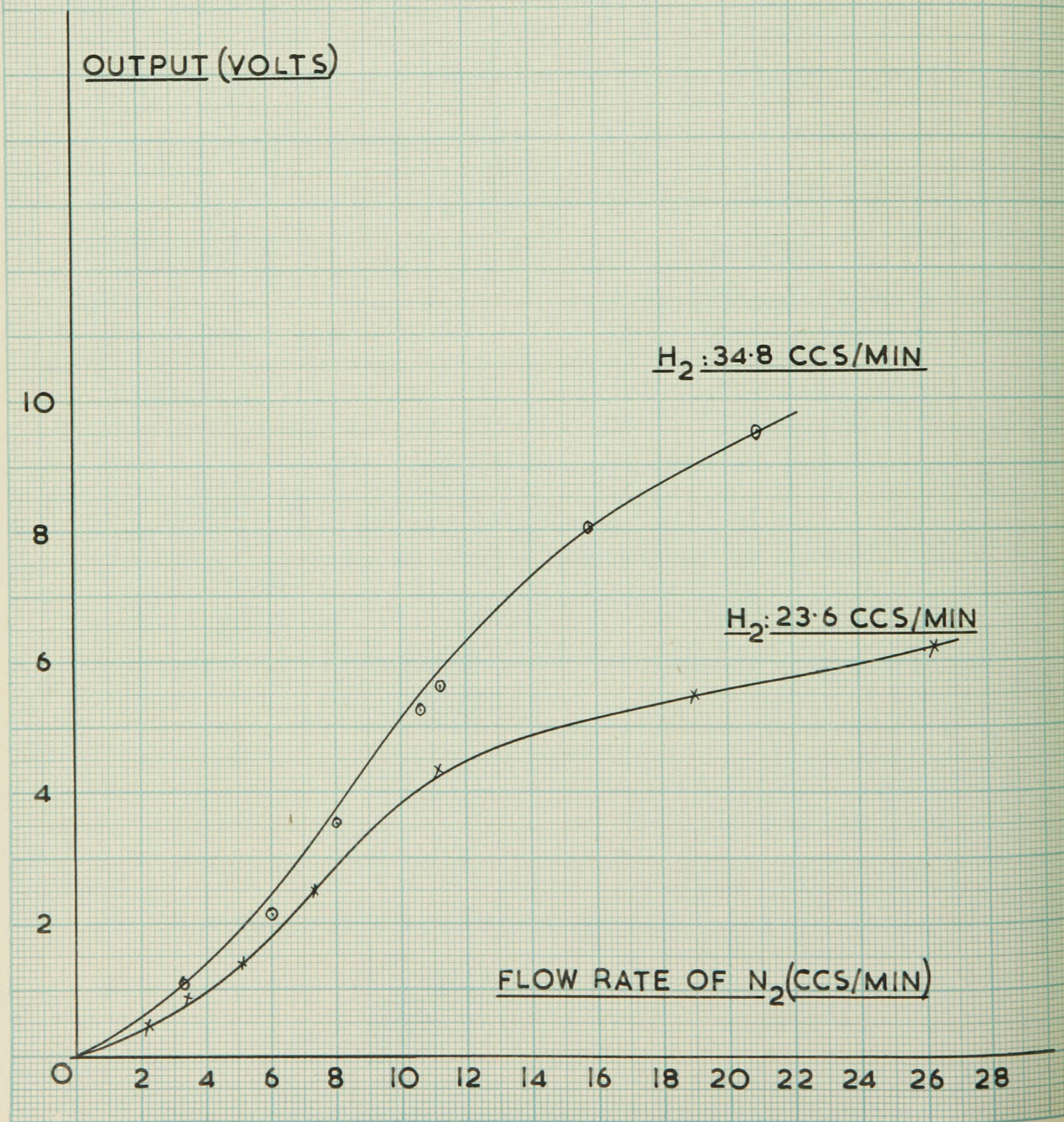


FIG. 27

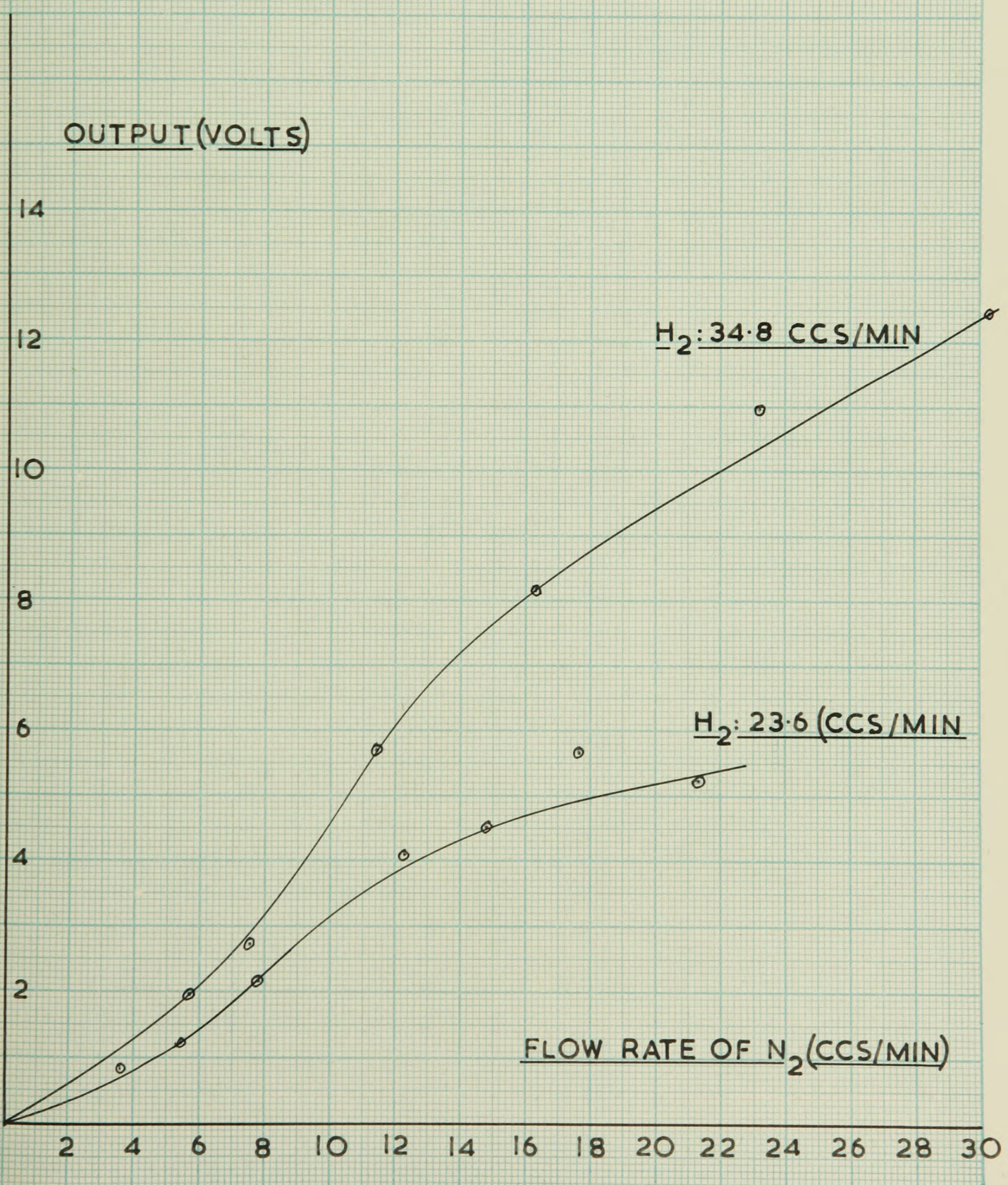

CCl_4 IN SATR. AT 0·3°C.
V.P.: 33 MM. Hg
LARGE DOUBLE JET
JET POSITIVE
OUTPUT (VOLTS)
14
12
10
8
6
4
2
0
H_2: 34·8 CCS/MIN
H_2: 23·6 (CCS/MIN
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
FLOW RATE OF N_2 (CCS/MIN)

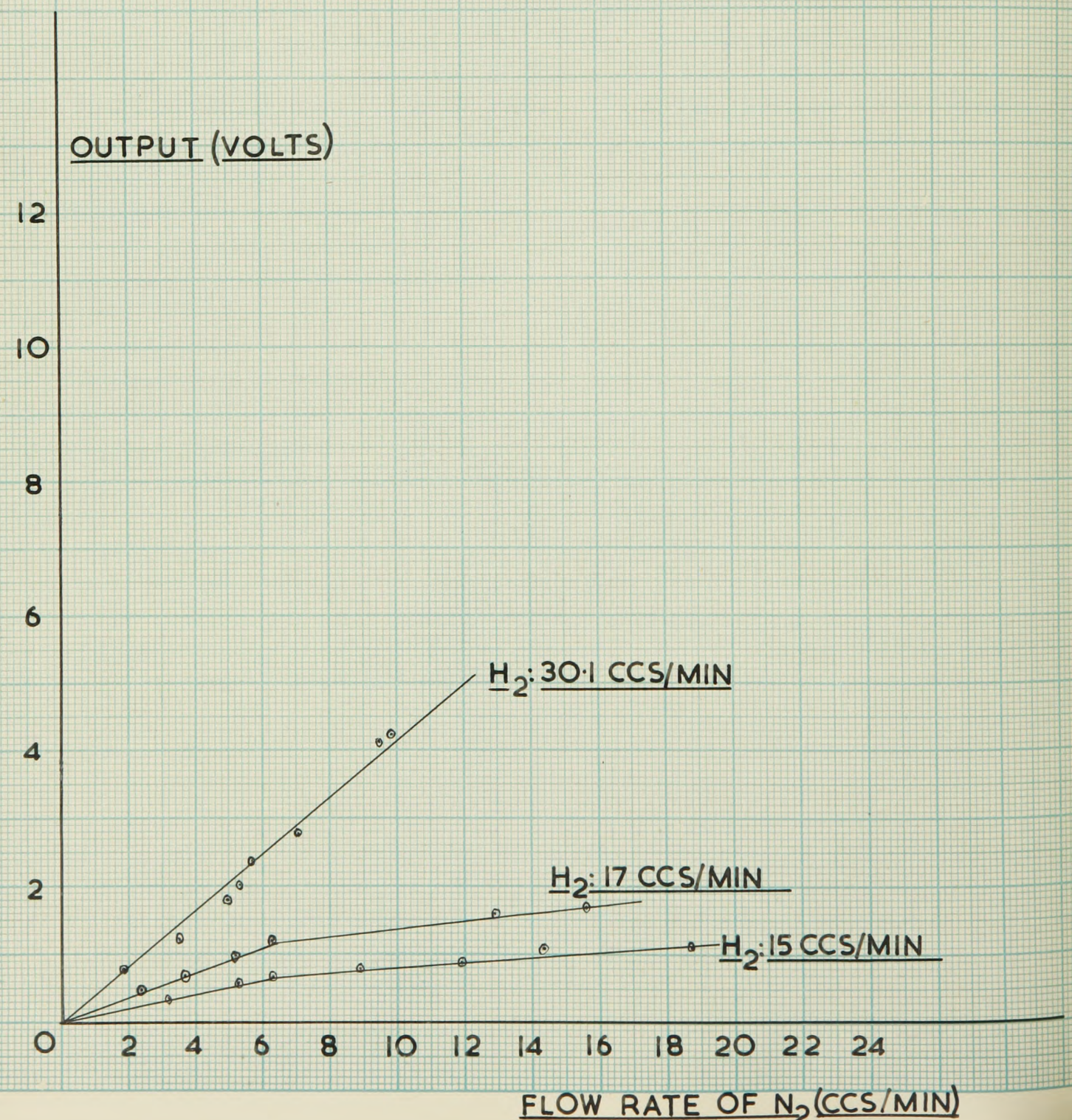
FIG. 28

CCl_4 IN SATR. AT -19°C.

V.P.: 10·5 MM. Hg

SMALL DOUBLE JET

JET POSITIVE



3.6 Response of the Flame Ionisation Detector to Carbon Tetrachloride:

3.6.1 Method:

A saturator was used as the method of injection, and a series of runs at different temperatures were done when the saturator was being evaluated. The detector output was measured either with a pen recorder or a voltmeter. The results are shown as graphs of output voltage against flow rate of nitrogen, repeated for various flow rates of hydrogen.

3.6.2 Results:

If the response of the detector was completely linear, and the saturator was equally efficient at all flow rates, the results would be a series of straight lines. In fact they nearly all show a more or less sharp decrease in gradient as the nitrogen flow passes a certain point. This could be a detector effect: a change in the shape of the flame for example, accompanied by poor mixing of flame and sample, or to the failure of the saturator to saturate the carrier gas fully at the higher flow rates. The latter explanation is made unlikely by the fact that the decrease in gradient does not always occur at the same flow rates and is sometimes missing altogether (as far as the experiments go) at higher flow rates of hydrogen. This last point in particular, makes the effect appear as one for which the detector is responsible.

The graphs in Figs. 26 and 27 show a slight "S-shape". The concavity could be due to the fact that the flame temperature rises as more nitrogen is introduced. (See appendix 5)

FIG. 29

EFFECT OF H_2 FLOW RATE

CCl_4 IN SATR. AT -19°C.

V.P.: 10·5 MM. Hg.

JET POSITIVE

SMALL DOUBLE JET

(FROM FIG. 22)

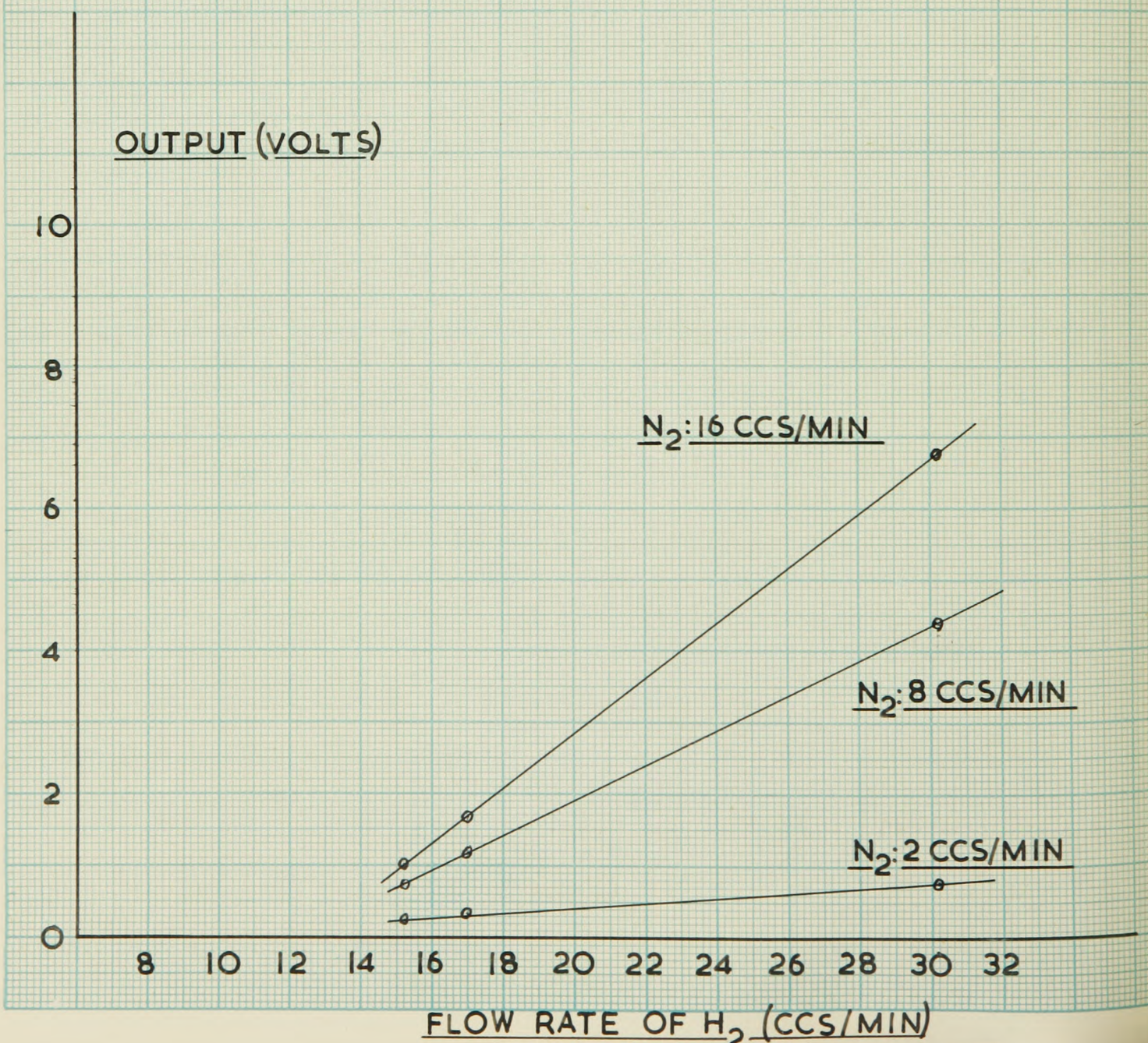


FIG. 30

EFFECT OF H_2 FLOW RATE

CCl_4 IN SATR. AT 0·3° C.

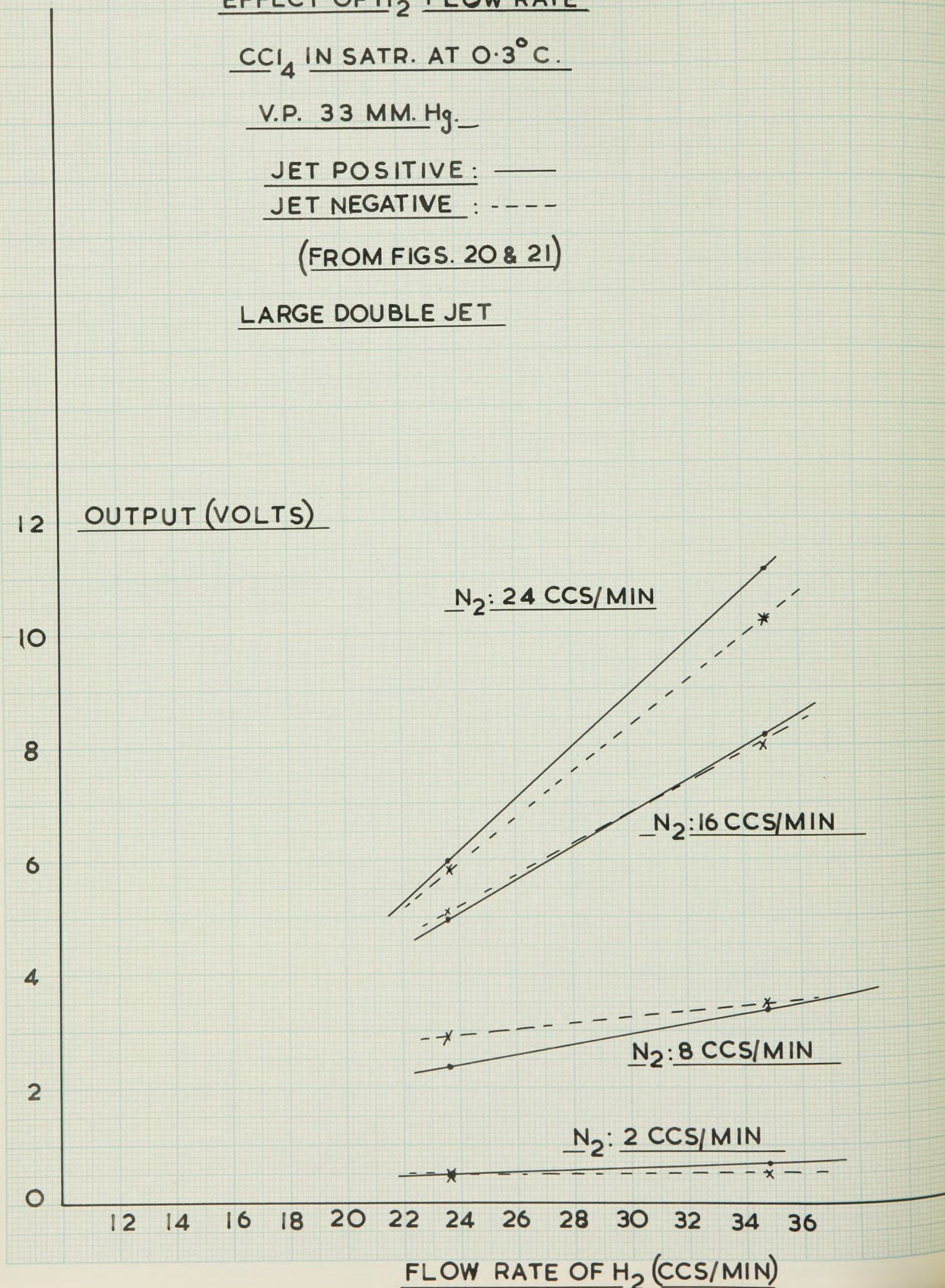
V.P. 33 MM. Hg.

JET POSITIVE: ——

JET NEGATIVE: - - - -

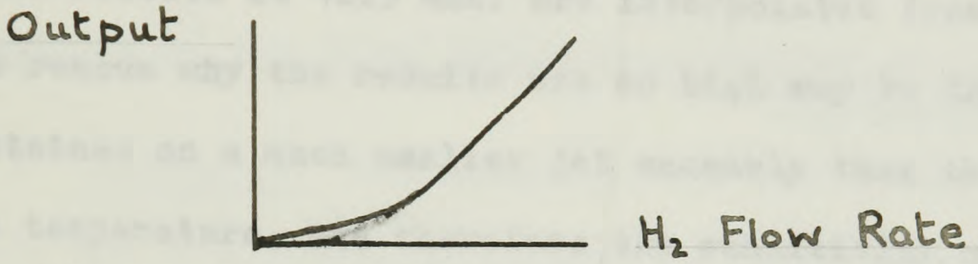
(FROM FIGS. 20 & 21)

LARGE DOUBLE JET

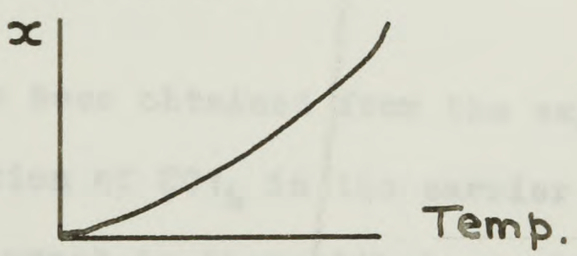


Graphs of output against flow rate of hydrogen, using data from the previous graphs, are shown in Figs. 29 and 30. The output is almost proportional to the hydrogen flow, but the lines, when extrapolated back, do not pass through the origin.

This would indicate that the dependence of output on hydrogen flow was of the form:



The results with thermocouples (Sec. 3.1) which are only approximate, indicate an opposite type of dependence between temperature and flow rate. However, the Saha equation (App. 5) for the variation of degree of ionisation (and therefore output current) with temperature, gives a curve of the required shape:



Comparison of results at different saturator temperatures:

It should be found that under similar conditions of hydrogen and nitrogen flow, the output is proportional to the vapour pressure of the sample. The figures are as follows: (partly from Figs. 27 and 28).

At a H_2 flow rate of 23 cc./min.

N_2 Flow rate = 5 cc./min.		N_2 Flow rate = 20 cc./min.	
V.P.	Output	V.P.	Output
33 mms.	1.4 v.	33 mms.	5.5 v.
83 mms.	5.5 v.	83 mms.	10 v.
10.5 mms.	1.5 v.	10.5 mms.	5.5 v.

The results at 10.5 mms. are interpolated from Fig. 28, and the reason why the results are so high may be that they were obtained on a much smaller jet assembly than the others, and the temperature, and therefore the sensitivity, would be higher. (See Sec. 2.2.5). However the other figures show no proportionality between output and vapour pressure. It would seem that at the high concentrations of vapour involved here, the detector does not remain linear in its response.

Effect of Polarity of Polarising Voltage : See Sec.1.1.5

Sensitivity:

This has been obtained from the experiments with the lowest concentration of CCl_4 in the carrier gas, since these conditions are nearest to those likely to be met in practice.

From graph in Fig. 28.:

At a Flow Rate of Hydrogen of 30.1 cc./min. Flame Temp. $\doteq 1350^{\circ}C$.

Slope of line = $\frac{7.8}{18}$ $\frac{\text{volts}}{\text{cc./min.}}$ = 0.43

Vapour Pressure of CCl_4 = 10.5 mms.

$\therefore$ 1 cc. of carrier gas carries 8.3×10^{-5} gms of CCl_4

$\therefore$ Rate of entry of CCl_4 for a signal of 0.43 volts

$= 8.3 \times 10^{-5}$ gms/min. or

$= 1.4 \times 10^{-6}$ gms./sec.

$\therefore$ for a signal of 1 volt (across 10^9 ohms) i.e. a current of 10^{-9} amps.

Rate of entry $= 3.3 \times 10^{-6}$ gms./sec.

Sensitivity in coulombs/gm. $= 3 \times 10^{-4}$

3.7 Response of the Flame Ionisation Detector to Silicon Tetrachloride:

Method : Saturator: The saturator was filled with $SiCl_4$ (B.D.H.), air being excluded as much as possible. It was cooled in carbon tetrachloride and solid CO_2 in a large Dewar vessel. The cooling bath was stirred efficiently and the temperature read with an alcohol thermometer. The nitrogen carrier gas was dried by passing through a trap filled with glass beads, cooled in liquid oxygen. (For more details of the saturators see App. 1.7).

Results:

Only comparatively few experiments were carried out, the detector proving rather unsuitable for $SiCl_4$.

Saturator Temp.(°C)	-39	-39	-3	-20	+17
Vap.Press.(mms.)	8.5	8.5	65	26.5	138
Flame Temp.(app.) (°C)	1330	1330	1330	1200	1200
Jet Polarity	+	+	+	-	-
N_2 Flow Rate (cc/min)	10.5	24.5	23.5	37	33

Detector current(amps)	4.5×10^{-10}	7.5×10^{-10}	4×10^{-10}	1.2×10^{-10}	1.0×10^{-11}
Rate of entry of $SiCl_4$ (gms/sec.)	1.7×10^{-5}	4.0×10^{-5}	2.6×10^{-4}	2.9×10^{-4}	7.1×10^{-4}
Sensitivity (coul/gm.)	2.6×10^{-5}	1.9×10^{-5}	1.5×10^{-6}	4.1×10^{-7}	1.4×10^{-8}
Sensitivity (gm/sec.for current of 10^{-9} amps)	3.9×10^{-5}	5.3×10^{-5}	6.7×10^{-4}	2.4×10^{-3}	7.1×10^{-2}

Apparatus used:

Detector as in Fig. 4

Jet as in Fig. 6

Cylinder collector as in Fig. 4

Characteristics of the Detector with Silicon Tetrachloride Samples:

1). Sensitivity: This varies with the rate of entry of the sample, being greater for low rates of entry. This means in practice that the peak area obtained from a particular sample size will not be independent of column characteristics and flow rate. A narrow band of $SiCl_4$ emerging from the column would give a lesser peak area than the same sample emerging as a broad band. At low rates of entry the sensitivity is about 1/80 of that to hydrocarbons.
The sensitivity relative to CCl_4, $CCl_4/SiCl_4 \div 10$

2). Polarity: The indications from a few experiments on polarity were that a negative jet gives a higher sensitivity by a factor of about 2 - 3, and also rather less noise.

3). Noise: Very bad. The signal to noise ratio with high rates of entry was sometimes as bad as 1.5 - 2. A typical signal to noise ratio would be 10 - 15. Noise was often fairly regular, and corresponded to small changes in the shape of the flame.

The jet and probe had to be frequently freed from the thick white coating that they acquired. When the saturator was switched into the gas stream, the signal rose to a fairly steady value, then, after about 3 - 4 minutes, fell to a low value. Cleaning the white deposit from the detector restored the signal and the whole process was repeated. The following is a sketch of a typical example.



4). The flame with $SiCl_4$ passing into it was a bright pale blue, which persisted for a while after the saturator had been switched out of circuit.

5). Large amounts of $SiCl_4$ (greater than about 10% by volume of $SiCl_4$ vapour in the nitrogen), tended to extinguish the flame.

This detector does not seem suitable for the detection of $SiCl_4$ in any but the smallest quantities, and then its sensitivity is not sufficiently high to give a good signal. (Condon, Scholly and Averill state that the detector gives "little or no response" to $SiCl_4$) (3) page 13 - table 1)

Note: Subsequent work in this laboratory on silicon chlorides has used the electron capture detector(personal communication) (-for detector -(55)).

FIG. 31

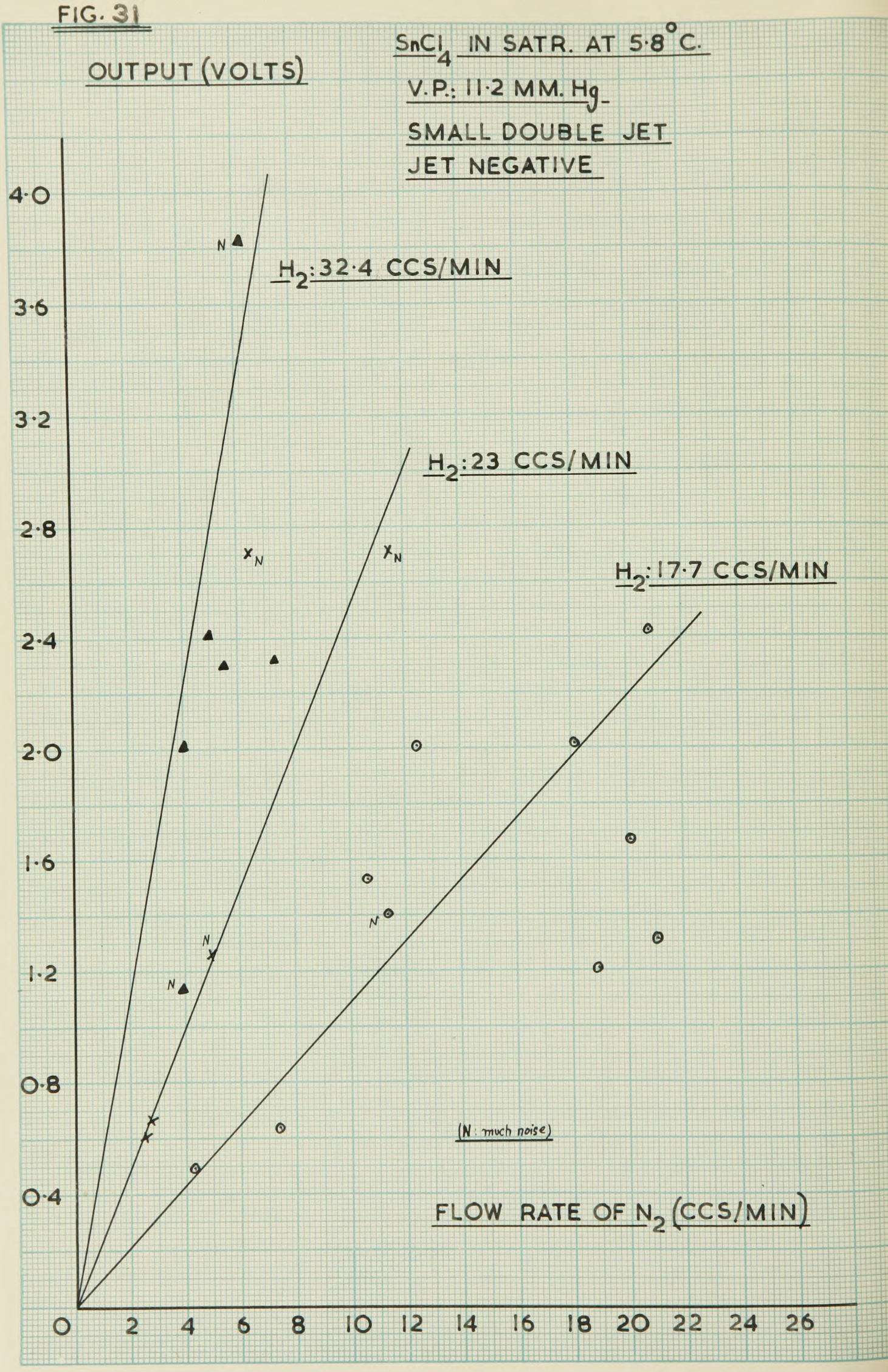

OUTPUT (VOLTS)
SnCl4 IN SATR. AT 5·8°C.
V.P.: 11·2 MM. Hg
SMALL DOUBLE JET
JET NEGATIVE
H2: 32·4 CCS/MIN
H2: 23 CCS/MIN
H2: 17·7 CCS/MIN
(N: much noise)
FLOW RATE OF N2 (CCS/MIN)
4·0
3·6
3·2
2·8
2·4
2·0
1·6
1·2
0·8
0·4
0
2
4
6
8
10
12
14
16
18
20
22
24
26

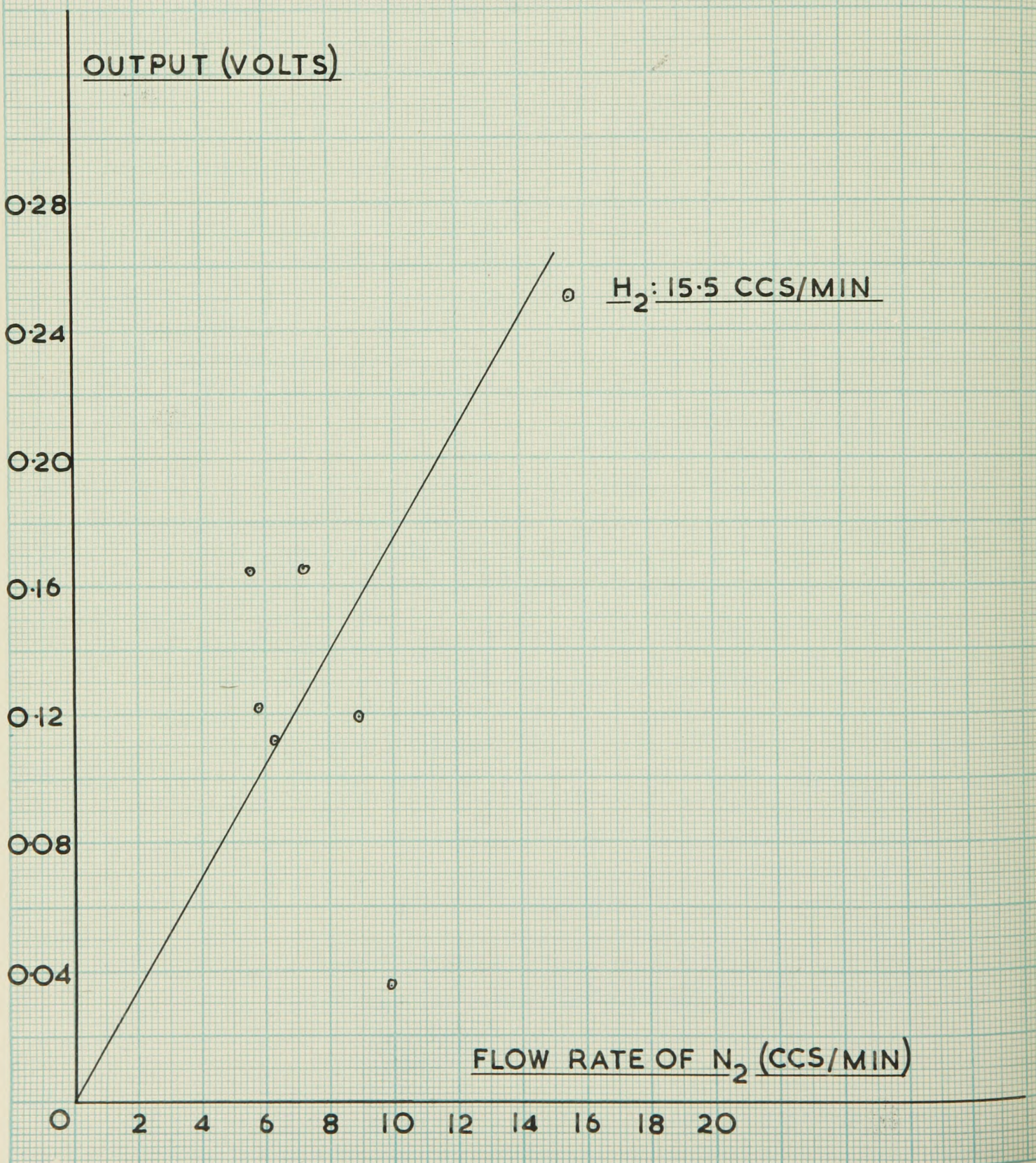
FIG. 32

$SnCl_4$ IN SATR. AT ~5·5° C.

V.P.: 11·2 MM. Hg APPROX.

SMALL DOUBLE JET

JET POSITIVE



3.8 Response of the Flame Ionisation Detector to Stannic Chloride.

Method of Injection: Sealed Tubes, Constant Volume Apparatus, and Saturator (for all these see Appendix 1)

Results: (Detector with cylinder collector (Sec.1.1.4)

Constant Volume Apparatus:

Sensitivity = 6×10^{-3} coulombs/gm. (Jet positive: Flow Rate of H_2 = 45 cc./min).

Saturator Apparatus: (Plotted in Figs. 31 and 32)

Sensitivity (coul./gm.)	Jet Polarity	Flow Rate of H_2 (cc./min.)
6×10^{-6}	+	approx. 15
9×10^{-6}	-	32
5.5×10^{-4}	-	23
2.8×10^{-4} (approx.: much noise)	-	18

Flame Temp. ≑ 1350°C.

The very large discrepancies in these results is probably due in part to the differing concentrations of sample involved, the sensitivity being lower at higher concentrations. A similar phenomenon has been observed with CCl_4 and $SiCl_4$ (see Secs. 3.6.2 and 3.7)

Characteristics of the Flame Ionisation Detector with $SnCl_4$ Samples.

Sensitivity: With the jet positive, the detector is about 40 times less sensitive to $SnCl_4$ than to CCl_4. Polarity has a marked effect on sensitivity, a negative jet giving a greater sensitivity by a factor of 5 - 10.

Noise: Considerable. All the experiments done with $SnCl_4$ showed much "spiky" noise. The average noise level was less with the jet negative by a factor of about 5. Noise varied considerably, but typical figures for signal to noise ratio are:

Jet positive S/N = 10 - 15)
) on peaks.
Jet negative S/N = 15 - 30)

In general, a higher signal was accompanied by a higher noise level.

A persistent type of trouble with the jet positive was the growth of long white filaments (presumably of SnO_2) across from the jet to the collector. When this happened the recorder went immediately off-scale, and the detector had to be cleaned. This could often be done by blowing into it sharply. If it had to be "mechanically" cleaned, there was always a high signal after cleaning, which slowly fell over about 7 minutes.

Conclusions: The flame ionisation detector responds to stannic chloride, the sensitivity (with the jet negative), being about 1/3 that to carbon tetrachloride, and 1/30 that to hydrocarbons.

Sample sizes should be kept small, not greater than about 10^{-4} gms.

Operation with the jet negative gives much higher sensitivity and lower noise level.

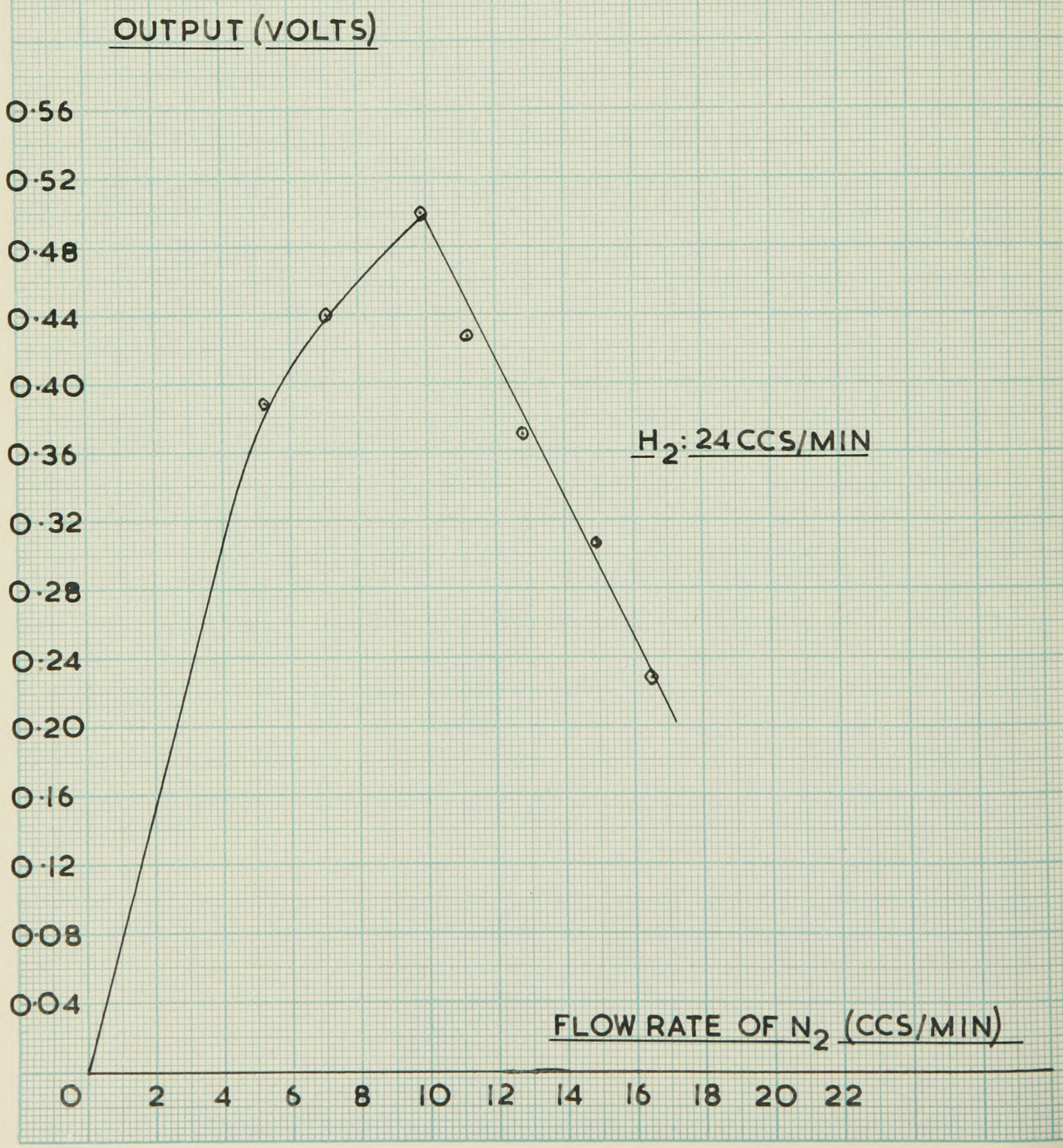
FIG. 33

CHLORINE IN SATR. AT ABT. -85°C.

V.P.: ABT. 42 MM. Hg

SMALL DOUBLE JET

JET POSITIVE



3.9 Response of the Flame Ionisation Detector to the Halogens:

3.9.1 Method: Chlorine (liquid), bromine (liquid) and iodine (solid) were put into the saturator and results obtained in the same way as for CCl_4 etc.

3.9.2 Chlorine: The method of filling the saturator with liquid chlorine is given in Appendix 1. The saturator was cooled in acetone and solid CO_2; temperature assumed to be -85°C. V.P. of chlorine 42 mms.

Results are plotted in Fig. 33. The most striking feature is the maximum in the curve (a similar shape is shown by all the halogens - see below).

A sensitivity for small samples has been calculated from the slope of the first part of the curve (extrapolated back)

Slope = $\frac{0.32}{4.0}$ volts per cc/min. = 0.08

1 cc/min. of carrier gas carries 1.7×10^{-4} gms. of Cl_2

∴ Rate of entry of Cl_2 for a signal of 0.08 volts

$= 1.7 \times 10^{-4}$ gms/min.

or 3×10^{-5} gms/sec.

∴ Rate of entry for a signal of 1 volt (across 10^9 ohms)

= 3.8×10^{-5} gms/sec.

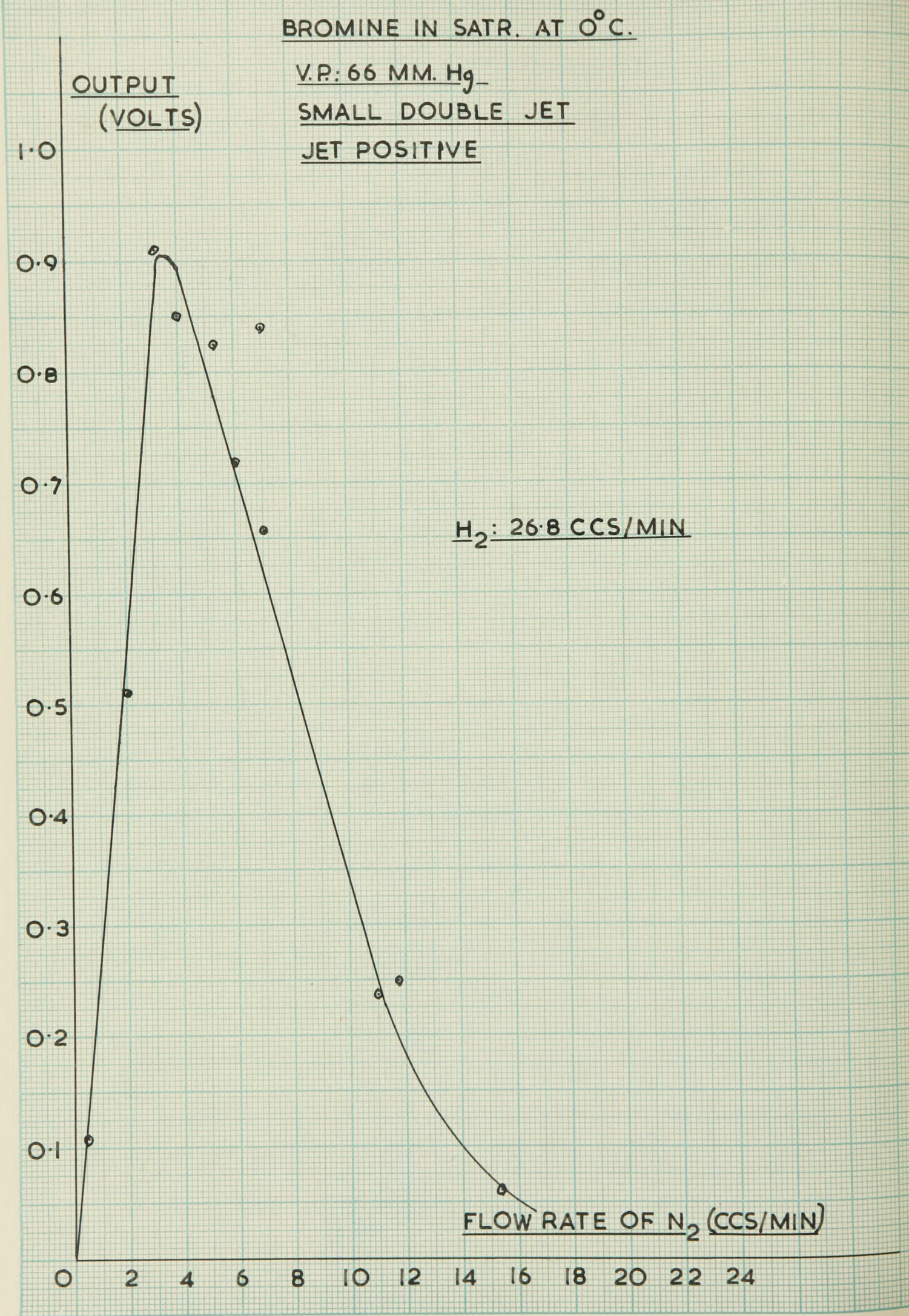
Sensitivity = 2.6×10^{-5} coulombs/gm.

H_2 Flow Rate 24 cc/min. Flame Temperature = 1300° C.

Characteristics of the Detector with Chlorine samples:

There was very little noise, and the detector was not adversely affected.

FIG. 34


BROMINE IN SATR. AT 0°C.
V.P.: 66 MM. Hg
SMALL DOUBLE JET
JET POSITIVE
OUTPUT (VOLTS)
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
H2: 26·8 CCS/MIN
FLOW RATE OF N2 (CCS/MIN)
0
2
4
6
8
10
12
14
16
18
20
22
24

3.9.3 Bromine:

The saturator was cooled in ice and water, Vapour pressure of bromine = 66 mms. Results plotted in Fig. 34.

Sensitivity for small samples:

Slope of first portion of curve = $\frac{0.8}{3.0}$ $\frac{\text{volts}}{\text{cc/min.}}$

= 0.27

1 cc. of carrier gas carries 5.8×10^{-4} gms. of Br_2

∴ Rate of entry of sample for a signal of 0.27 volts

= 5.8×10^{-4} gms/min.

or 9.6×10^{-6} gms/sec.

∴ Rate of entry for a signal of 1 volt (across 10^9 ohms)

= 3.6×10^{-5} gms/sec.

Sensitivity = 2.8×10^{-4} coulombs/gm.

H_2 Flow rate = 27 cc/min. Flame Temp ≑ 1300°C.

Characteristics of the Detector with Bromine samples:

There was more noise than in the experiements with chlorine, the signal to noise ratio being about 50. The detector was not adversely affected by the bromine.

3.9.4 Iodine:

The saturator was placed in a large water-bath maintained at about 90°C. with a thermostat. The tubing connecting the saturator to the detector was electrically heated to prevent condensation of iodine.

The iodine in the saturator was not of course liquid. However, since it is a fairly volatile substance at the temperature of operation, it was felt that the saturator

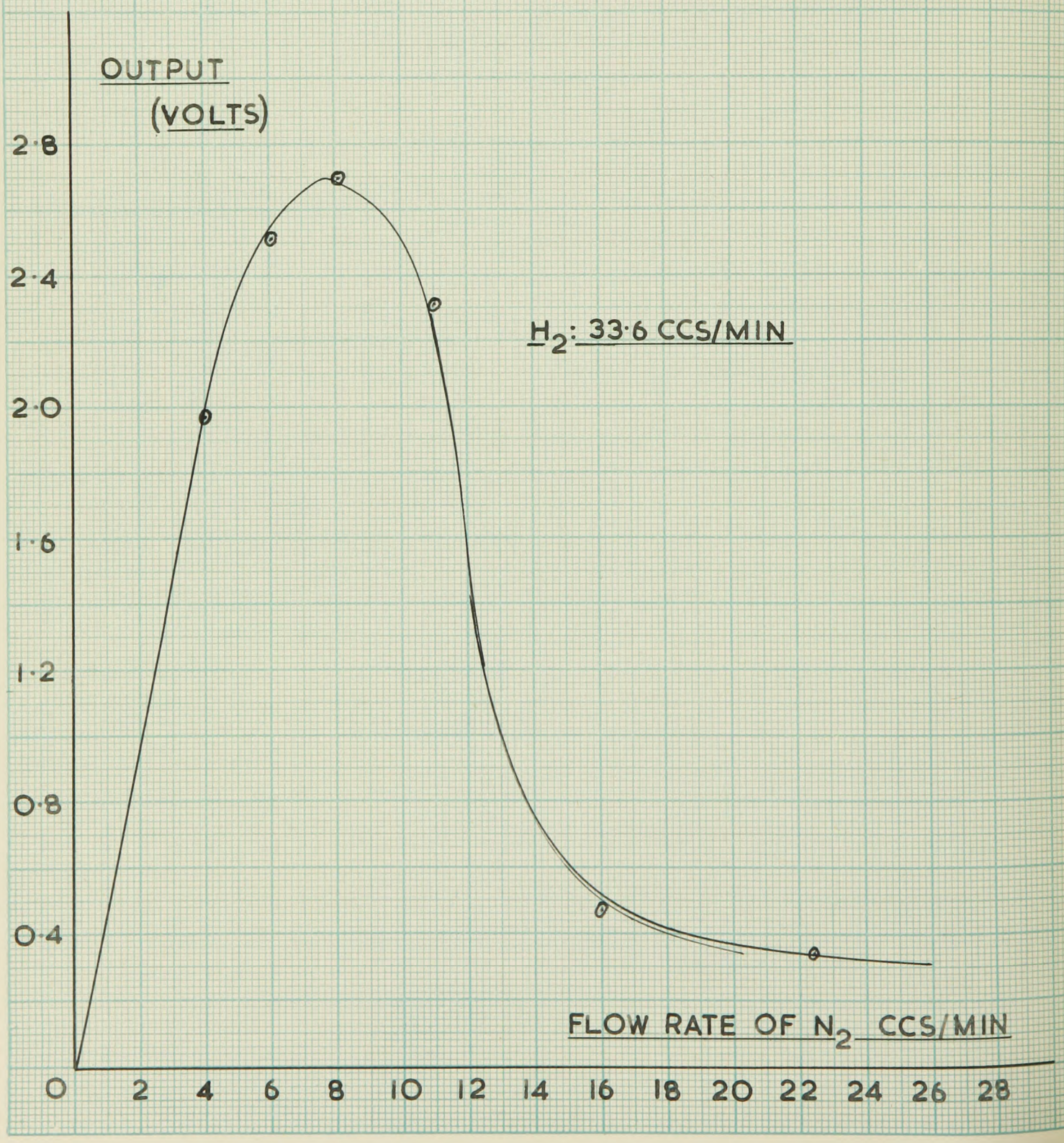
FIG. 35

IODINE IN SATR. AT 91·5°C.

V.P.: 29 MM. Hg.

LARGE DOUBLE JET

JET POSITIVE



would probably work successfully. The only trouble experienced in fact, was when the connecting tubing and the detector were not kept hot enough. Results are plotted in Fig. 35

Sensitivity:

Slope of first part of curve $= \frac{1.6}{3.4}$ $\frac{\text{volts}}{\text{cc/min.}}$

$= 0.47$

1 cc/min. of carrier gas carries 4.1×10^{-4} gms of I_2.

∴ Rate of entry for a signal of 0.47 volts

$= 4.1 \times 10^{-4}$ gms/min.

∴ Rate of entry for a signal of 1 volt (across 10^9 ohms)

$= 8.7 \times 10^{-4}$ gms/min

or 1.5×10^{-5} gms/sec.

Sensitivity = 7×10^{-5} coulombs/gms.

H_2 Flow rate : 33.6 cc/min. Flame Temperature ≑ 1150°C.

Characteristics of the Detector with Iodine Samples:

Noise varied a great deal, being on the whole worse than that with either of the other two halogens. The signal to noise ratio varied from about 8 to about 50. The sample did not appear to damage the detector.

3.9.5 Ionisation Potentials:

Values for the ionisation potentials of the Molecules of chlorine, bromine, and iodine can be calculated from these results, using the Saha equation (App. 6) The figures are as follows:

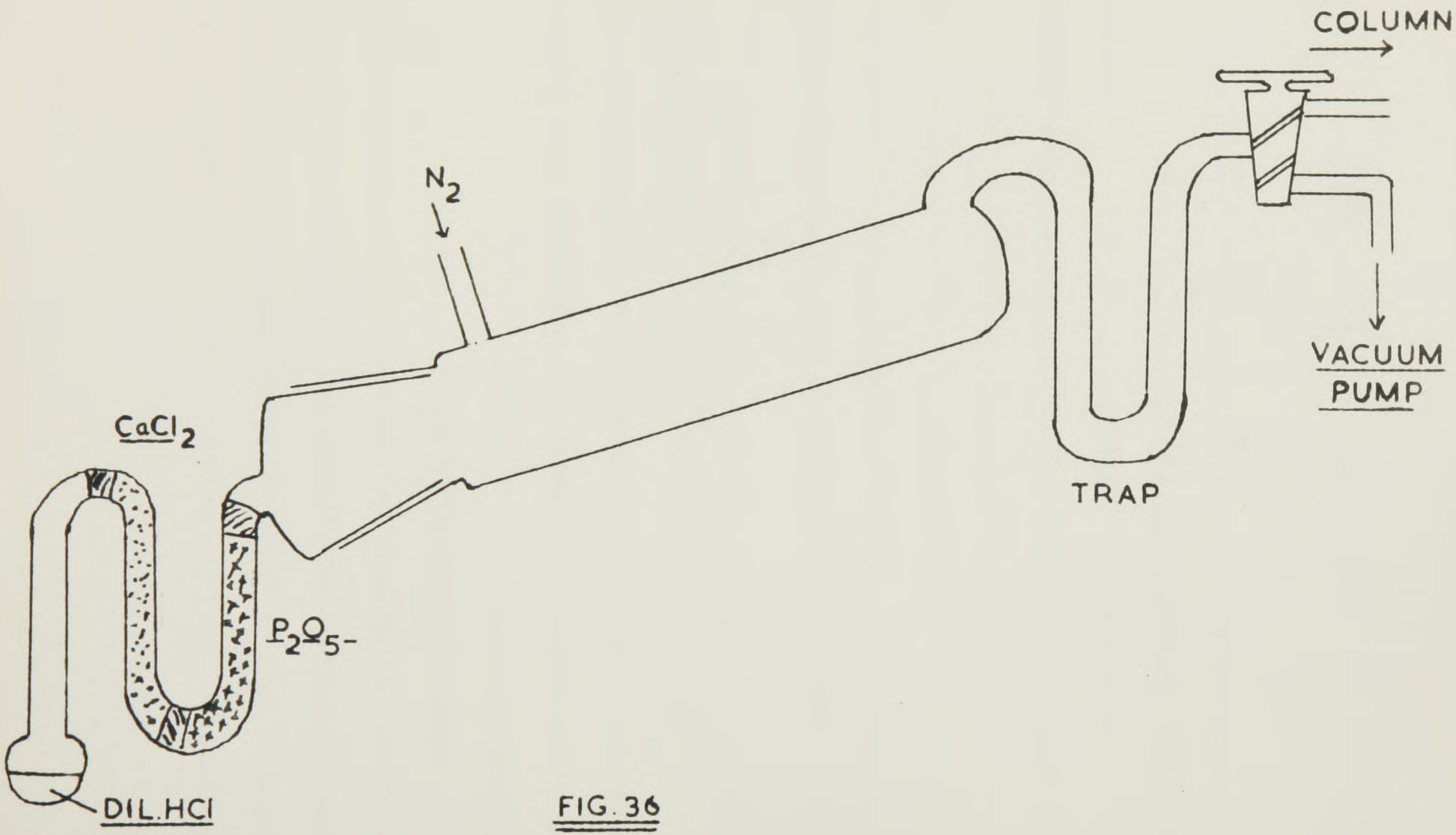


FIG. 36

Cl_2 : 4.7 e.v.

Br_2 ; 4.9 e.v.

I_2 : 4.9 e.v.

(Quoted values: Cl_2 : 8.2) 13.2)
Br_2 : 10.0) (ref. 56) 12.8) (ref. 57))
I_2 : 10.1) 9.7)

3.9.6 Shape of saturator curves:

The shape of the curves may be explicable by the fact that halogens are known to decrease the concentration of free electrons in flames, by combining with them. When the concentration of halogen in the flame ionisation detector rises above certain limits, perhaps the recombination process begins to dominate the ionisation process and the concentration of ions falls.

3.10 Response of the Flame Ionisation Detector to Hydrogen Chloride (approx.)

Method: The apparatus shown in Fig. 36 was attached to the end of the "sealed tube" apparatus (See Appendix 1) as shown in the diagram.

½ cc. of dilute HCl solution had been previously put into the small bulb and the drying tube packed . The solution was then cooled in liquid oxygen and the apparatus evacuated. Then by warming the HCl solution with a hot-air blower the HCl gas was transferred to the cooled injection trap. 5 - 10 minutes were allowed for the transfer. Then nitrogen was admitted and the HCl injected on to the column

by warming the injection trap.

Result: A large peak was obtained - off-scale on the recorder.

Sample Size: ½ cc. of HCl solution (35% solution diluted 180 times) contains approx. 10^{-3} gms. of HCl gas.

Peak Area: more than 7 x 10^{-8} coulombs; say 10^{-7} coulombs.

Sensitivity: at least 10^{-4} coulombs/gm. (Jet positive)

Flame Temperature ≐ 1300°C.

The peak was free from noise.

3.11 Response of Flame Ionisation Detector to Metal Acetylacetonates

$(CH_3.CO.CH_x:C(O^-).CH_3)_nM$ where M is Cu, Al or Be.

Many metal acetylacetone complexes are reasonably volatile, and it was thought that they might be of use in a gas chromatographic technique for the analysis of metals.

Copper Acetylacetonate: (ref. 9; boiling point not quoted).

N/10 copper sulphate solution was shaken with an equal volume of acetylacetone and the complex is extracted into the acetylacetone layer. Samples of this layer were injected.

No peaks apart from the acetylacetone peak were obtained. (Column temperature 156°C.; 1-methyl-naphthalene, b.pt. 240°C. had a retention time of 70 mins.)

Solid copper acetylacetonate was also prepared (8), and injected as a strong solution in acetylacetone or CCl_4. No peaks were obtained apart from the solvent peak.

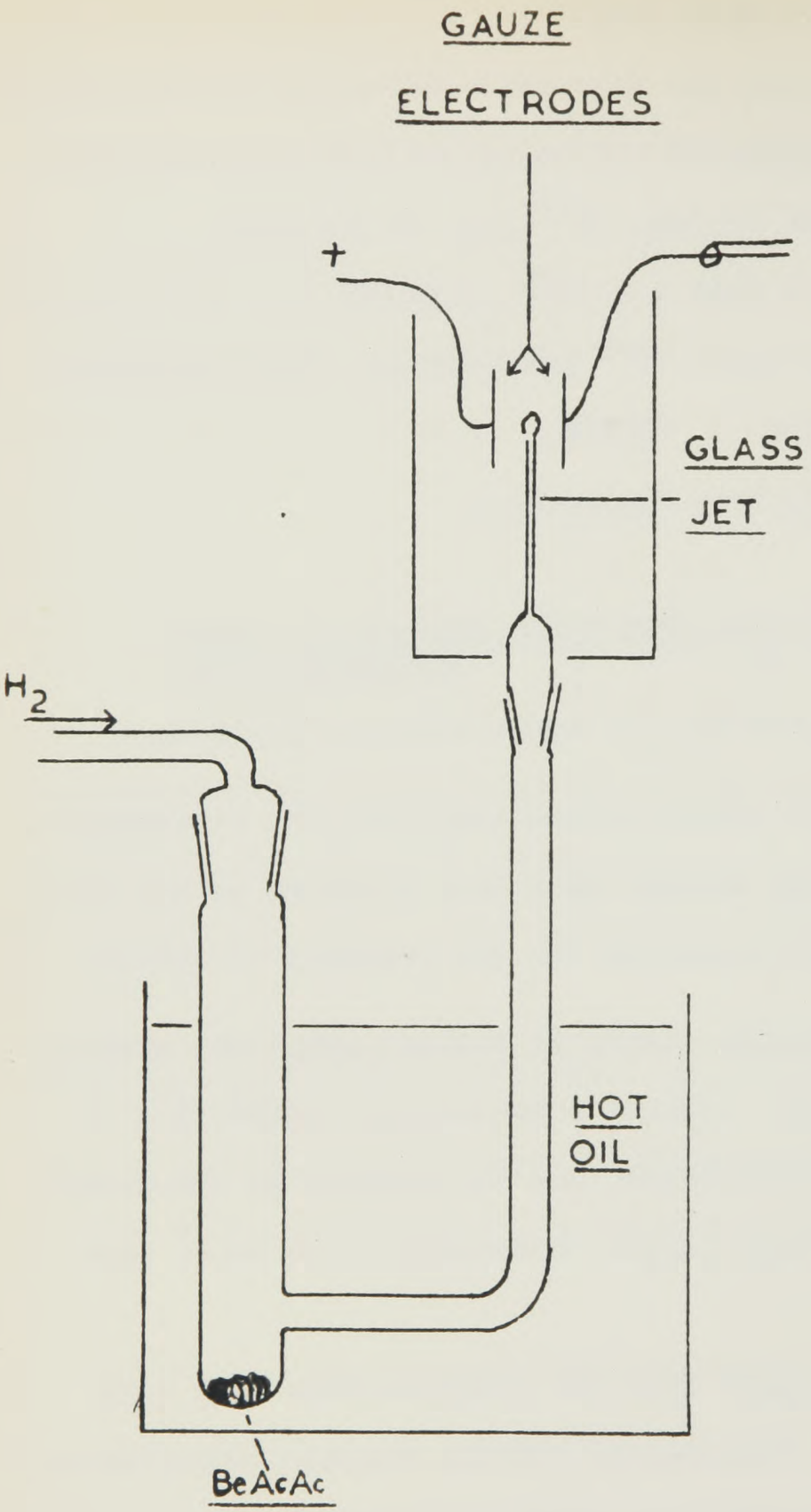


FIG. 37

Beryllium Acetylacetonate: (ref. 8; boiling point 270°C.: the lowest quoted).

Prepared solid and injected as a solution in acetylacetone, benzene or ether.

Result negative.

The boiling point of the compound was determined by the inverted capillary method. The result confirmed exactly the value in the literature.

The apparatus in Fig. 37 was used to pass the vapour of the complex directly into the detector. A small response (0.5v) was obtained with the oil bath at 150° - 200°C.

Aluminium Acetylacetonate: (ref. 8, b.pt.: 314 -315° with decomp.)

Experiments as for the copper compound gave negative results.

Conclusion: These compounds give a very small response if any.

Note: Compounds of this type have since been successfully chromatographed, using a katharometer detector. (Not in this laboratory.)

3.12 Response of the Flame Ionisation Detector to Carbon Disulphide:

1 microlitre samples injected by capillary gave very small peaks. The sensitivity is of the order of 3×10^{-9} coulombs/gm. - approx. 1.5×10^{-6} times the sensitivity to hydrocarbons. A concentration of only one part in a thousand of impurity would have given the observed response.

It has since been stated by several workers that the detector gives "little or no response" to CS_2. (1,3)- p.135, table 1)

Apparatus: detector as in Fig. 4

Polarity : Jet positive.

3.13 Response of the Flame Ionisation Detector to Ammonia:

Method: Ammonia was prepared from '880' ammonia solution, dried and stored in a 2-litre glass bulb. Small sample tubes were evacuated and filled with ammonia from the bulb to a known pressure. (for a diagram of the apparatus see Appendix 2). The method of injection and the type of sample tube used are given in Appendix 1).

Results:

Experiment No.	1	2	3
Pressure of Ammonia (mms. Hg)	228	229	228
Volume of trap (cc.)	3.9	3.9	3.9
Sample Size (gms.)	8.4×10^{-4}	8.5×10^{-4}	8.4×10^{-4}
Peak Area (Coulombs)	7.2×10^{-10}	8.3×10^{-10}	8.3×10^{-10}
Sensitivity (Coul./gm.)	8.6×10^{-7}	9.8×10^{-7}	9.9×10^{-7}
Sensitivity (Gms/sec. for 10^{-9}amps.det.current)	1.2×10^{-3}	1.02×10^{-3}	1.01×10^{-3}

Mean Sensitivity = 9.8×10^{-7} coulombs/gm.

or 1.1×10^{-3} gms/sec. for 10^{-9} amps. detector current.

Conditions for all three experiments:

i) Detector as in Fig. 4, with concentric jet as in Fig. 6.

ii) Jet positive

iii) Flow rates: H_2 : 34.5 cc./min.
N_2 : 8 cc./min.

iv) Flame Temperature about 1300°C.

v) No column.

Characteristics of the flame detector with ammonia as sample:

i) Very low sensitivity - about 1/2000 of that to hydrocarbons. (It has been stated by several workers that the flame ionisation detector gives little or no response to ammonia (1, and 3.) - page 135).

ii) Smooth peaks free from abnormal noise, with a return to the previous baseline after each peak.

3.14 The Application of the Flame Ionisation Detector to the Study of Odours.

3.14.1 Introduction:

This work was done in conjunction with Miss Miriam Rothschild.

The study of odours is one to which gas-liquid chromatography seems well suited. The substances responsible for the odours are naturally more or less volatile, and the amounts given off are generally very small indeed. The technique has been applied by various workers to the smells of paper-making, coffee, fish, meat, onions, natural oils, cigarette smoke etc. (11)

Insects use scents to attract mates, and, it is believed, to discourage predators. Previous attempts to isolate the (attractant) scents of moths have made use of standard macro techniques such as extraction of the abdomen or ovipositor with solvents, and separation of an active principle from the solution. This method has been successful with the female of the gypsy moth - the attractant substance being 10-acetoxy-cis-7-hexadecen-1-ol. (12, also for other similar work: 13) These techniques are slow, require large numbers of insects, and the extracts are likely to contain many substances unconnected with the odour. Using gas-liquid chromatography however, a chromatogram of the minute amounts of volatile substance actually given off by the specimen can be quickly obtained. Identification of the substances involved is not generally possible, though estimates of volatility and probable molecular weight can often be made. Techniques such as mass spectroscopy, infra-red or ultra-violet spectroscophy can sometimes be applied to the trapped-out substances.

This work was undertaken to explore the application of the technique, and in particular the flame ionisation detector, to a particular insect problem. Some much earlier work had been done in this laboratory (partly by the author) on the assembly scent of the oak eggar moth (bombyx mori), and the scent of flowering plants such as rosemary. Quite good chromatograms were obtained from the latter, but the former proved intractable, for two main reasons. The

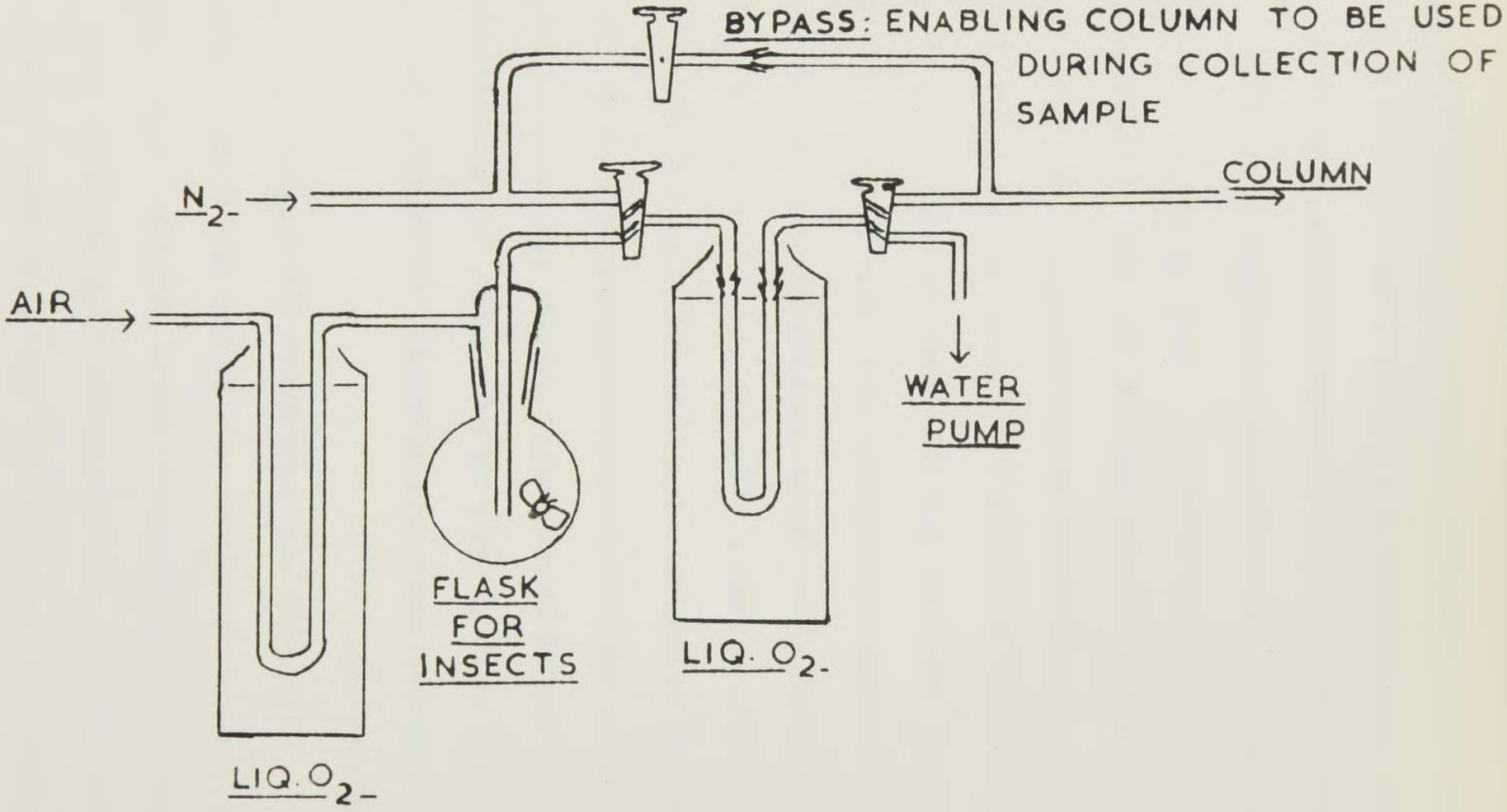

BYPASS: ENABLING COLUMN TO BE USED DURING COLLECTION OF SAMPLE
COLUMN
N_2
AIR
WATER PUMP
FLASK FOR INSECTS
LIQ. O_2
LIQ. O_2

FIG. 38

detectors then in use, katharometers, were not sufficiently sensitive and also the large percentage of water in the sample gave large trailing peaks. The flame ionisation detector is very sensitive to organic compounds and completely insensitive to water.

3.14.2 The Problem:

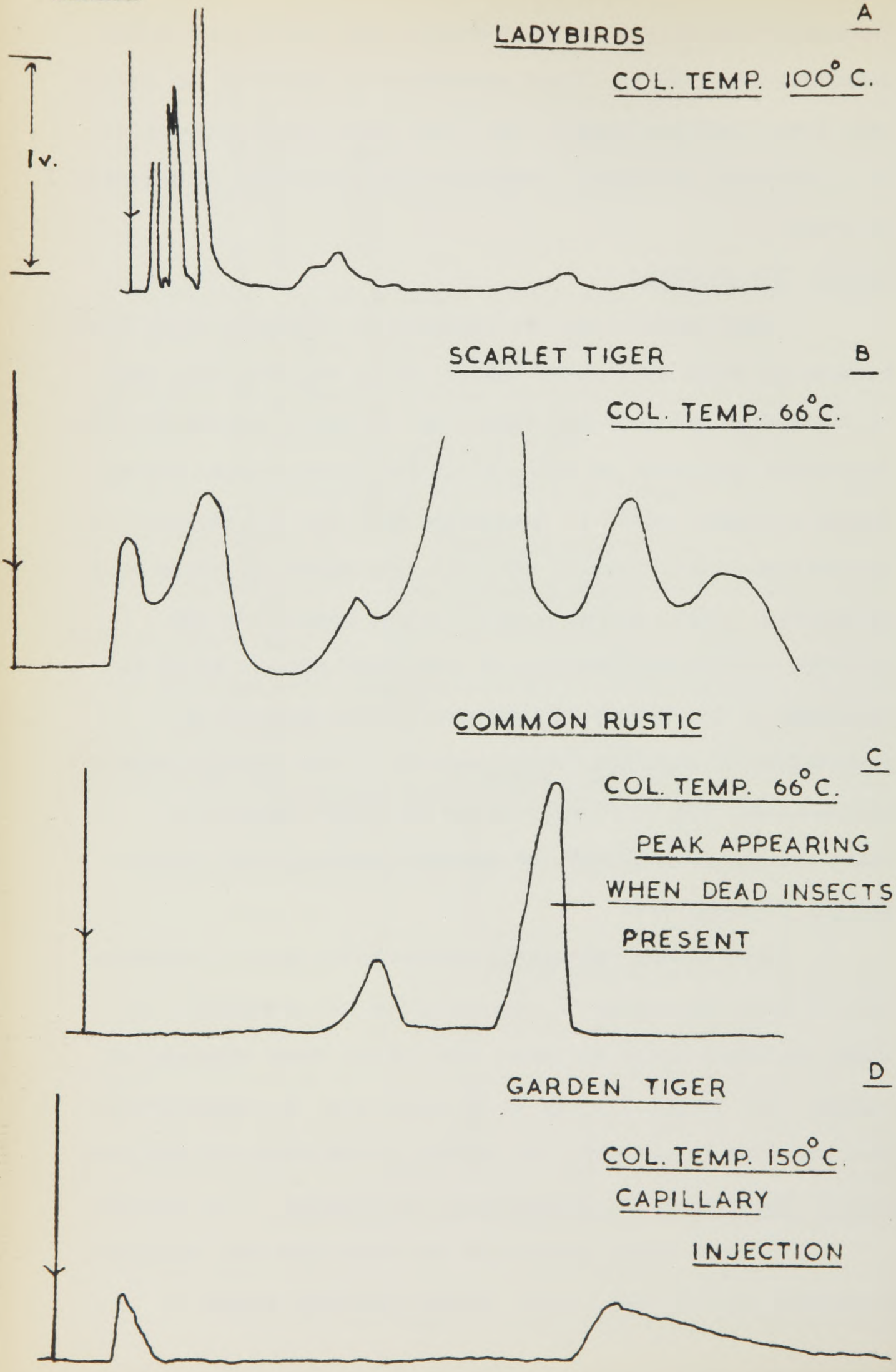
Many insects are not attacked by predators (e.g. birds) because of their unpleasant taste. It is believed that once an individual predator has tasted one of these insects it will shun other specimens of the same insect, being warned off by colour or odour, which it associates with the unpleasant taste. In addition, other species with the same colour or odour will be avoided. (This is known as Müllerian mimicry if the imitator is also unpalatable, and Batesian mimicry if it is palatable.) The object of this work was to explore the possibility of obtaining chromatograms of the volatile substances given off by insects using the flame ionisation detector, and correlating the chromatograms and the acceptability to predators.

Miss Miriam Rothschild claims to be able to distinguish between the smells of insects which are acceptable to birds and those which are not. The latter cause symptoms of asthma. Two common factors in the smells of the unacceptable ones are said to resemble the smells of ladybirds and nettles.

3.14.3 Collection and Injection of the Samples: (see Fig.38)

In most cases samples of the volatiles were obtained by passing air through a trap cooled in liquid oxygen to

FIG. 39


A
LADYBIRDS
COL. TEMP. 100° C.
1v.
SCARLET TIGER
B
COL. TEMP. 66°C.
COMMON RUSTIC
C
COL. TEMP. 66° C.
PEAK APPEARING
WHEN DEAD INSECTS
PRESENT
GARDEN TIGER
D
COL. TEMP. 150° C.
CAPILLARY
INJECTION

remove all condensible material, then through a flask containing the insects, and through a second cooled trap. The sample was usually injected directly from the trap, by passing the carrier gas through it and heating it with a hot-air blower or a pre-heated oil bath.

A few samples of fluid secreted by the insects were injected with an injection capillary and portions of some of the samples collected as above were injected in the same way.

3.14.4 Results:

Insects used were:

Scarlet Tiger	(Panaxia Dominula)	Unacceptable
Garden Tiger	(Arctica Caja)	Unacceptable
Soldier Beetle	(Rhagonycha Fulva)	Unacceptable to most
Ladybird	(Coccinella Septempunctata)	Unacceptable
Small White	(Pieris Rapae)	Unacceptable to many birds.
Common Rustic	(Celaena Secalis)	Unacceptable to some.
Flame Shoulder	(Ochrapleura Plecta)	Acceptable
Noctuella (???)	(? ?)	Acceptable
Yellow Underwing	(Agrotis Pronuba)	Acceptable

Examples of the chromatograms are shown in Fig. 39. For all but one of the unacceptable insects in the above list, and for none of the others, a very early peak was obtained - usually rather small. The amount of sample responsible for this peak was very approximately 1 - 2 micrograms. This peak is marked with an asterisk in Fig. 39. Its retention time corresponds to a boiling point of less than 100°C.

The small white is the exception to the above: and it alone among the unacceptable insects has no red colouring. Miss Rothschild associates the warning smell with a red colouration.

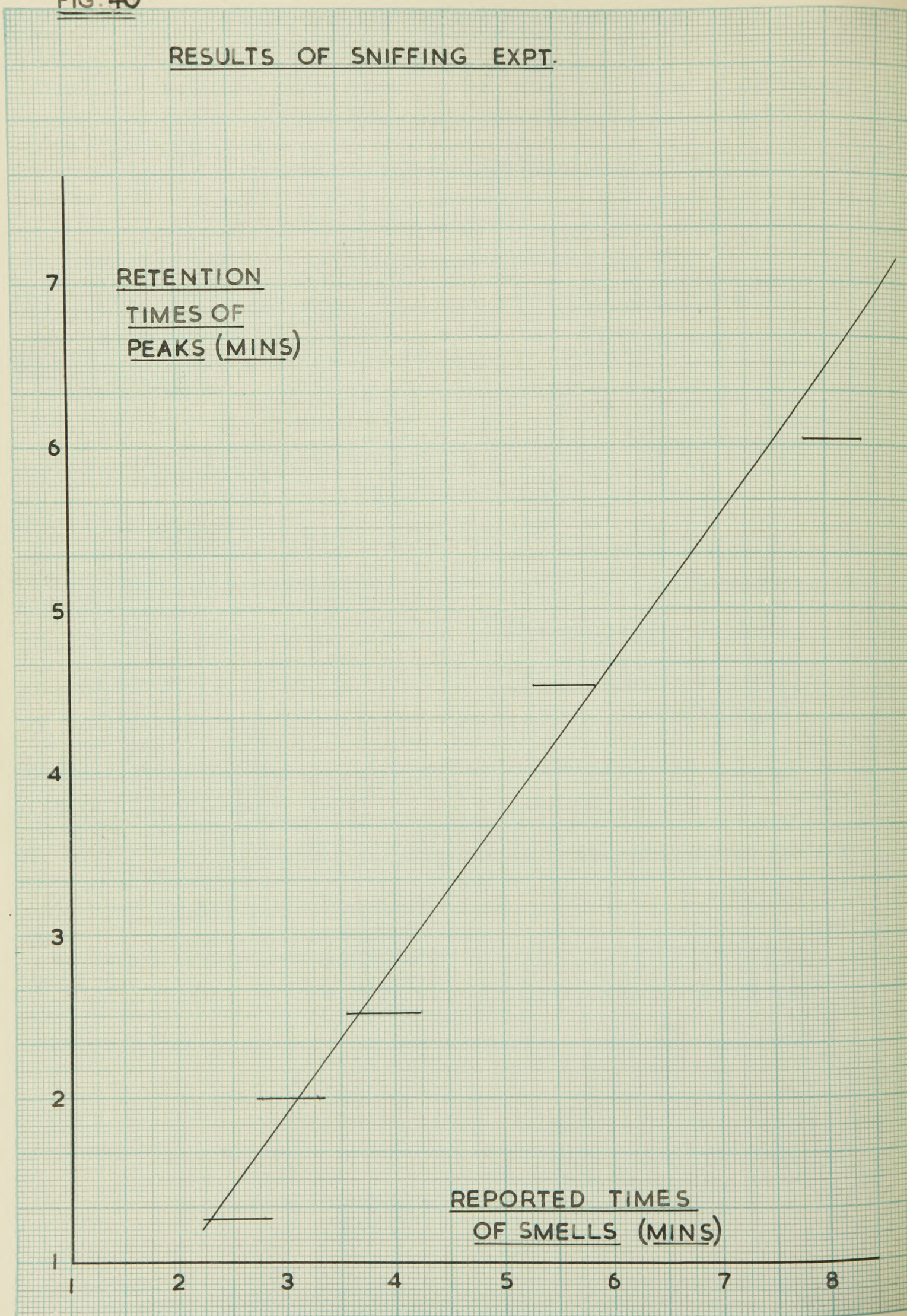
In each of the experiments in which one or more of the insects were found to be dead after collection of the sample, a large peak with a retention time of about 16 minutes was obtained. (Fig. 39c.)

3.14.5 Smells Associated with Different Peaks:

An experiment was carried out to check that the collected material had the smell described by Miss Rothschild and to see if the two common factors in the smell could be correlated with particular peaks.

First a chromatogram was obtained in the usual way from ladybirds, to determine the relative positions of the peaks. Then a second experiment was carried out at the same column temperature (150°C.), with the detector partly dismantled, no flame lit, and Miss Rothschild sniffing the column effluent at half-minute intervals. The flow rate was a little lower than in the calibration experiment, in order to try and separate the peaks further, and also to spread them out and increase the chances of at least part of each peak falling during one of the testing periods.

FIG. 40


RESULTS OF SNIFFING EXPT.
RETENTION TIMES OF PEAKS (MINS)
7
6
5
4
3
2
1
REPORTED TIMES OF SMELLS (MINS)
1
2
3
4
5
6
7
8

Results:

Time from Injection (mins.)	
2.5	Smell: general plant-like
3.0	" " " " ; irritating, slight asthma; sore throat.
3.5	" : acid (like acetic acid); strong
4.0	" : ditto
4.5	" : ditto (faint)
5.0	No smell
5.5	Smell: "maybe the part of the ladybird smell associated with other warningly coloured insects".
6.0	-
6.5	No smell
7.0	" "
7.5	" "
8.0	Maybe faint smell
8.5	-
9.0	No smell
10.0	" "

In the calibration run the retention times of the peaks were:

1.25, 2.0, 2.5, 4.5, 6.0 mins.

The retention times do not correspond directly, due to the difference in flow rate. The results are plotted on Fig. 40, the graph indicating that the flow rates probably differed by a factor of 8/9.

Notes:

1). The smell described as "plant-like" corresponds with the position of the very early peak found in all the unacceptable insects, and this early peak has also been found in a chromatogram of the volatiles from the nettle. (The nettle is known to contain methyl alcohol).

2). The peak corresponding with the description "associated with warning colour", (5.5 mins.) does not seem to be present in the other insect chromatograms. However some chromatograms were obtained in this laboratory by another worker on the burnet moth (zygaena filipendulae). In these the first two peaks have relative retention times which correspond closely with the relative retention times of the peak in question and the first peak in the ladybird chromatograms, (at 1.25 and 2.5 minutes). It is significant that the burnet moth smells very strongly to Miss Rothschild.

3.14.6 Summary:

From a chromatographic point of view these experiments were successful in showing that the high sensitivity of the flame ionisation detector, and its complete insensitivity to water make it a very suitable tool for this type of problem.

The work has been continued in this laboratory by other workers (48, 49, 53). Good correlation has been found between chromatograms and acceptability. It is thought that the chromatograms from insects may be useful in classification.

The detector has been found sufficiently sensitive to enable chromatograms from single insects (e.g. ladybirds) to be obtained (48).

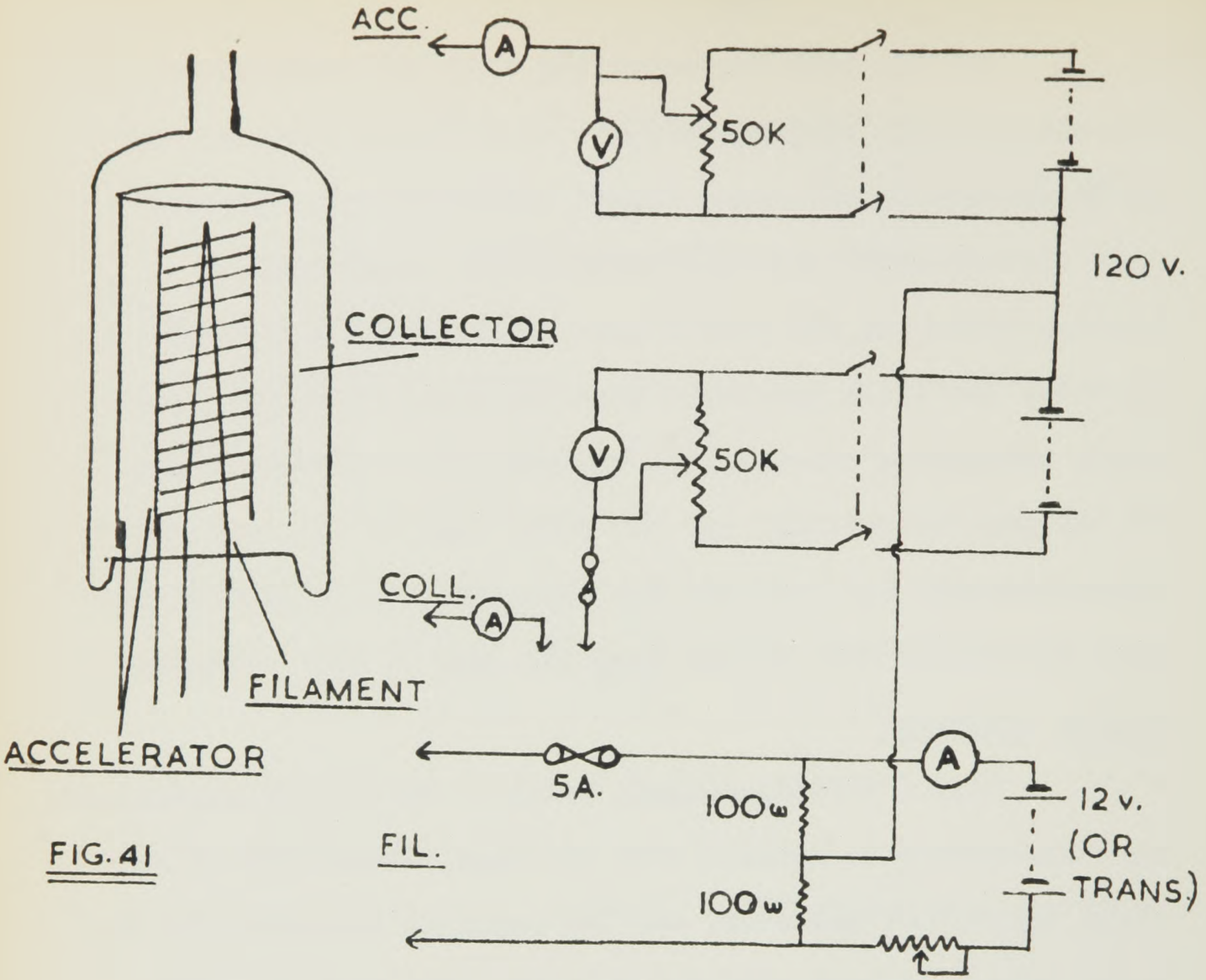


FIG. 41

FIG. 42

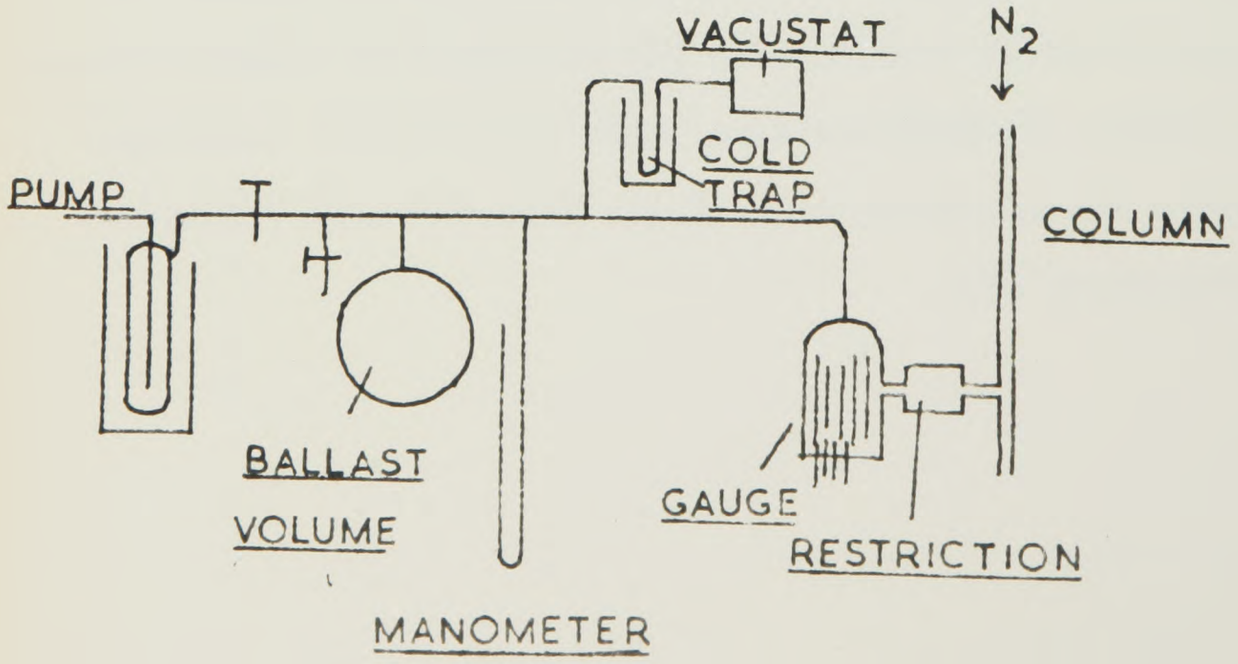


FIG. 43

CHAPTER 4.

The Vacuum Ionisation Gauge Detector

4.1 Principles:

This detector was suggested by Bryce and Ryce (16)

The sensing element is a slightly modified triode ionisation gauge as used for the measurement of very low pressures. The gauge consists of a triode structure (see Fig. 41) in a glass envelope connected to the volume in which the pressure is to be measured. Electrons emitted from the hot filament are accelerated by a positive voltage on the grid ("accelerator") and ionise molecules of gas in the gauge by collision. This only occurs if the energy of the electrons, and therefore the accelerating voltage, is greater than a well-defined maximum. The resulting positive ions are attracted to a negative plate ("collector"). The current in the collector circuit gives a measure of the number of gas molecules in the gauge, and therefore of the pressure. For the electrical circuit see Fig. 42.

As a vapour detector, the gauge is connected as shown in Fig. 43 so that part of the column effluent is drawn into it through a restriction and a connection sealed into the side of the envelope. Most compounds have a lower ionisation potential than the gases used as carriers (e.g. n-butane 10.8 e.v., benzene 9.21 e.v., NH_3 10.25 e.v., SiH_4 12.2 e.v., nitrogen 15.5 e.v.) and the accelerating voltage can be so adjusted that the carrier gas is not ionised, but sample molecules are. A recorder driven by

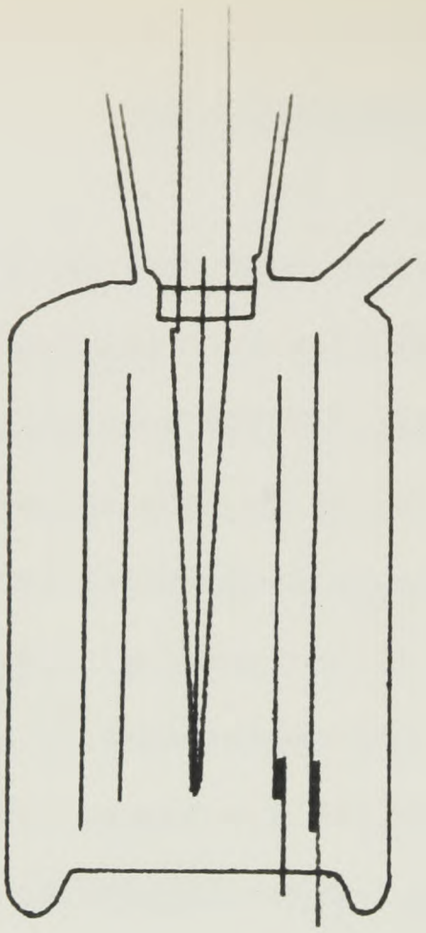


FIG. 44

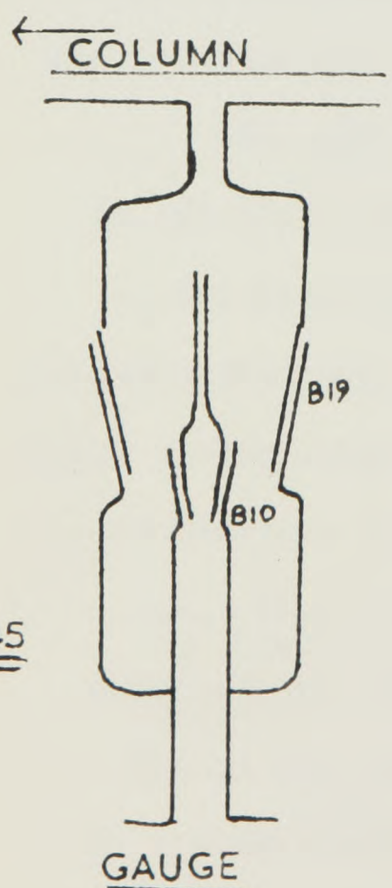


FIG. 45

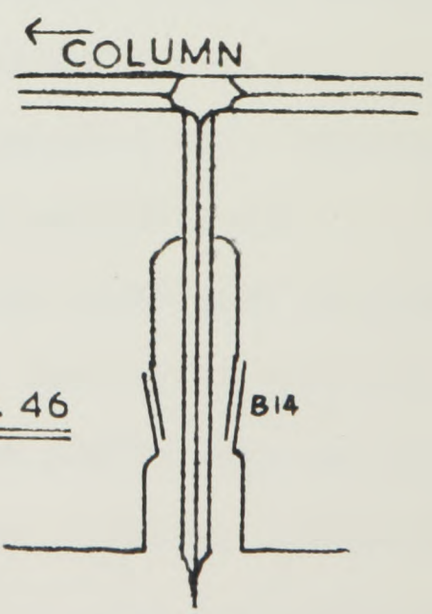


FIG. 46

the collector current will than give a record of the sample leaving the column.

4.2 Types of Gauge: The gauges used in this work were Edwards High Vacuum Ltd. - type IG - 2AH.

Filaments: the first gauges used had oxide-coated platinum strip filaments. These become"poisoned" very easily by organic vapours (the makers recommend that the gauge be kept under vacuum when not in use). The symptoms are a low accelerator current and failure to respond when samples are passed through the column. The condition could usually be cured by injecting a large (10 - 15 microlitres) amount of ether with a syringe through the rubber connection between column and gauge. This treatment had usually to be repeated each morning.

To try to avoid these troubles, gauges with tungsten wire filaments were obtained, and proved more satisfactory. Their main disadvantage was that the filaments burned out more easily than the platinum strip ones. One of the gauges was therefore modified by the laboratory glass-blower so that the filaments could be replaced, and this was done successfully on several occasions. (see Fig. 44).

Just before the filaments burned out erratic behaviour was often observed, e.g. varying collector and accelerator currents.

4.3 The Restriction between the Column and the Detector:

This should have as small a volumn as possible to avoid an integrating effect. The design shown in Fig. 45

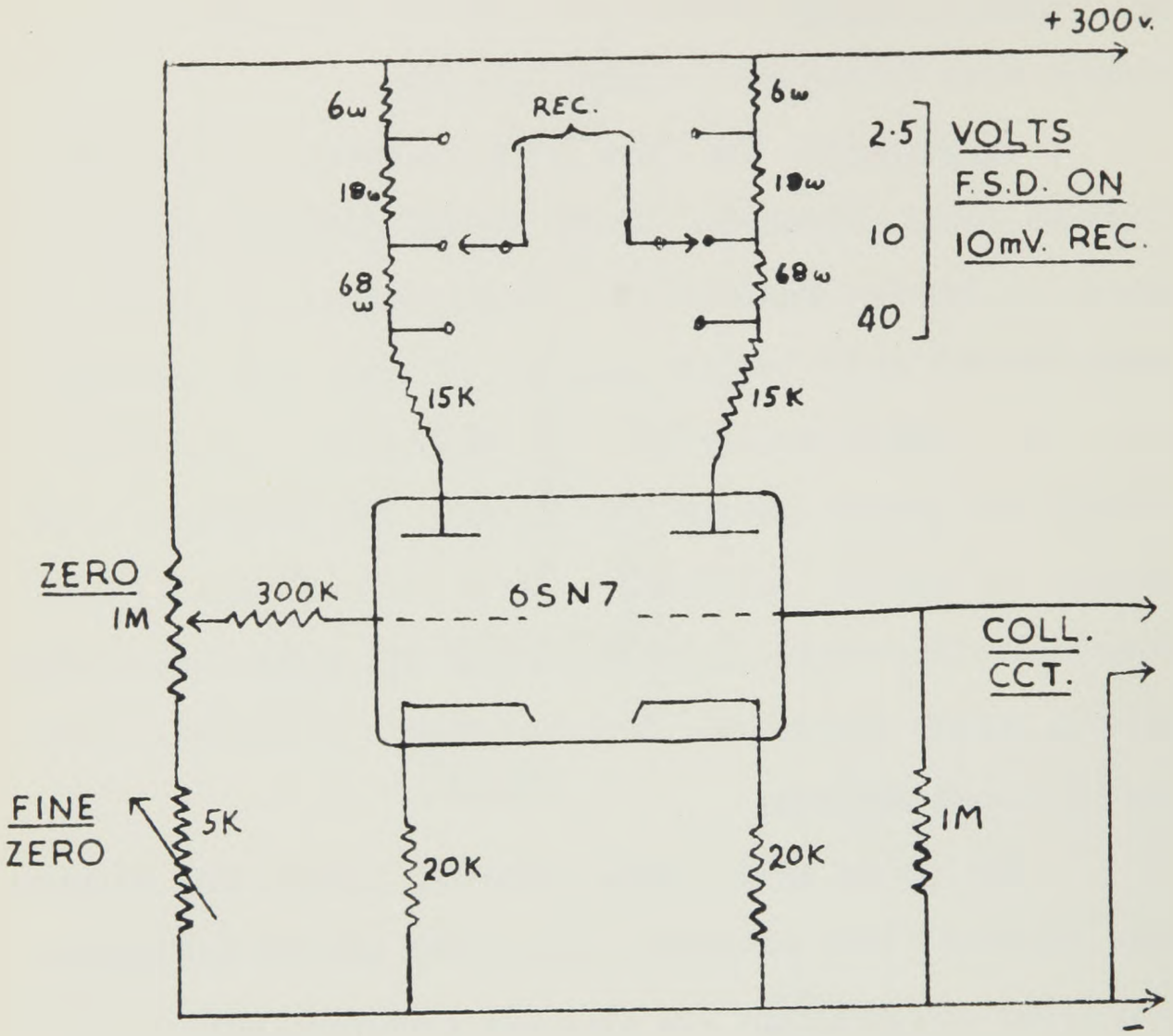

+300v.
6ω
REC.
6ω
18ω
18ω
68ω
68ω
15K
15K
2·5
10
40
VOLTS
F.S.D. ON
10mV. REC.
ZERO
1M
300K
6SN7
COLL.
CCT.
FINE
ZERO
5K
20K
20K
1M
-

FIG. 47

gave a very long, flat peak from a sample that gave two well-shaped and separated peaks on a katharometer connected at the end of the column.

A restriction as in Fig. 46 gave well-shaped peaks.

A variable "Edwards Vacuum Leak" is the most convenient type, having a small volume, and allowing easy adjustment of the pressure in the gauge.

4.4. Pumping Speed:

The tubing connecting the gauge to the vacuum pump must present as little flow resistance as possible. 4 feet of 3/8" glass tubing with sharp bends in it only allowed a flow rate into the gauge of less than 1cc./min. A 1 foot length of wider tubing raised the flow rate to 5 ccs./min. To obtain the flow rates normally employed in gas chromatography (50 - 100 ccs./min.) a very large capacity pump would be necessary, with as little resistance as possible in the pump line and cold trap.

4.5 Recording: The output from the detector is a current of a few microamps, and an impedance convertor circuit was used to feed a recorder. See Fig. 47.

4.6 Typical Operating Conditions:

Filament Current = 2.4 amps. (Pt strip filament)
2.2 amps. (Tungsten filaments)

Accelerator Voltage = 15 - 20 volts.

Accelerator Current = 1.5 - 2 mA.

Collector Voltage = about 50 volts.

Collector Current = about 7 microamps (no sample)

Pressure in gauge = about 0.3 mms. Hg.

The accelerator voltage is adjusted to a value just less than that at which the carrier gas becomes ionised. Ionisation is shown by a sudden large increase in collector current (up to about 150 microamps.) The stability of the base-line is poor if the accelerator voltage is adjusted too close to the ionisation point.

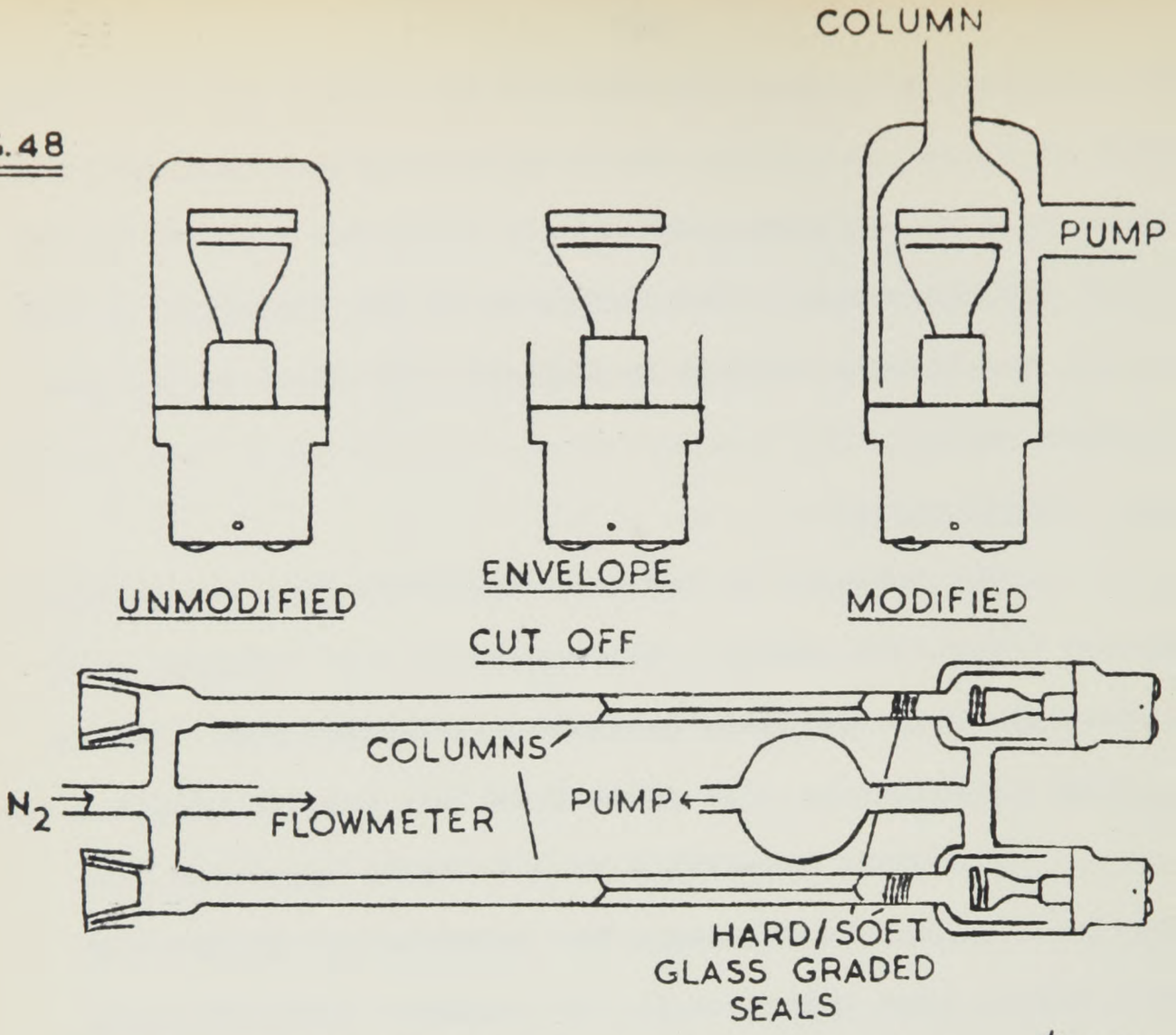
4.7 Conclusions:

The detector is far more sensitive than the katharometer (about 100 times). The apparatus used compared quite favourably with the flame ionisation detectors used later as regards sensitivity. The noise level was greater (about 5 times).

The extra complexity of the vacuum apparatus, the ease with which the filaments are poisoned and their short life (often less than 1 week), are serious drawbacks when compared with the simplicity and robustness of the flame ionisation detector.

The sensitivity of the detector would be very much increased if the whole of the sample from the column passed into it, instead of just a small fraction. The pumping speed would have to be very high to keep the pressure in the gauge low enough (approx. 0.3 mm. Hg).

FIG. 48


COLUMN
PUMP
UNMODIFIED
ENVELOPE
MODIFIED
CUT OFF
COLUMNS
N_2
FLOWMETER
PUMP
HARD/SOFT
GLASS GRADED
SEALS

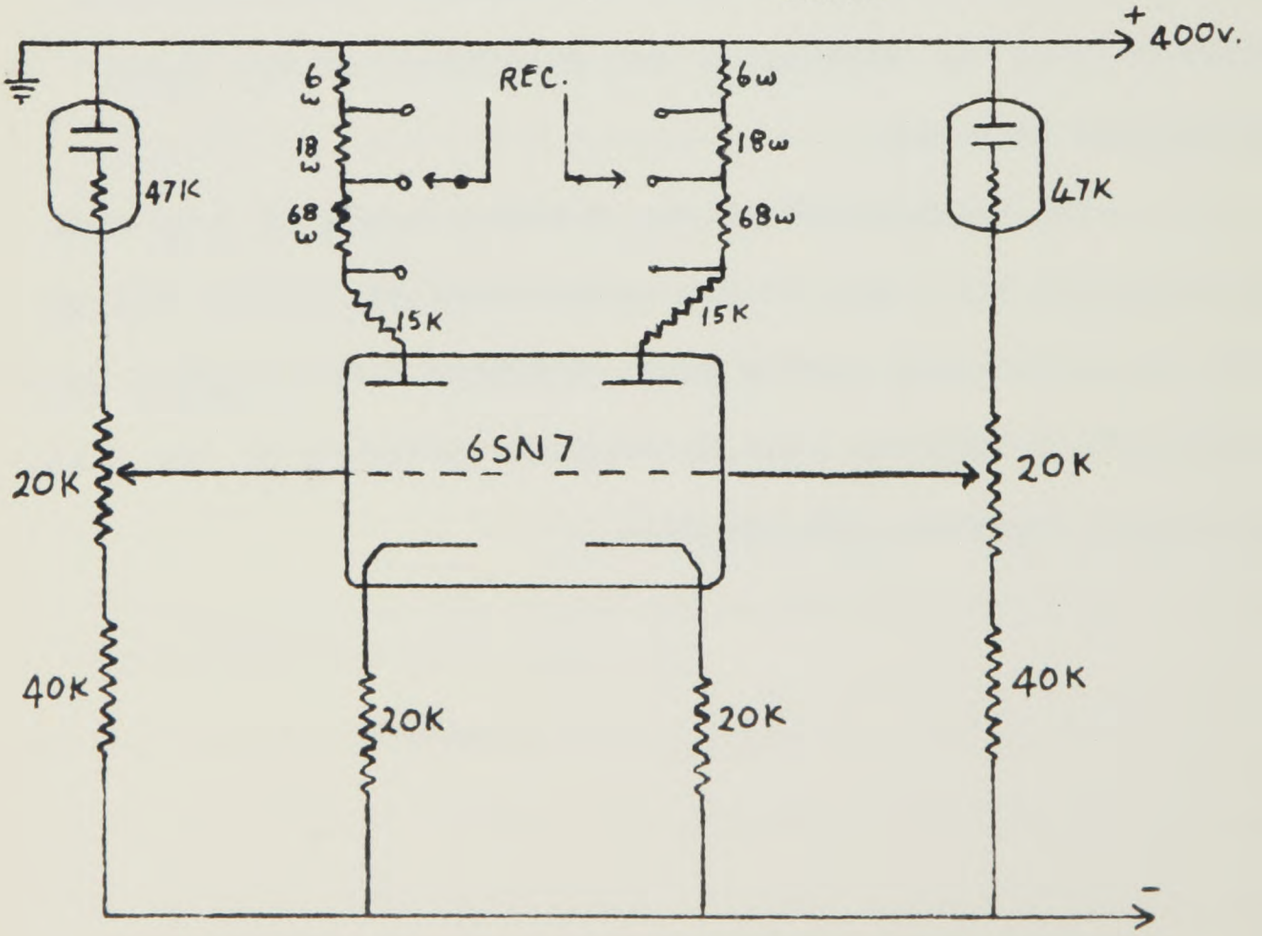

+400v.
47K
6
18
68
REC.
6w
18w
68w
15K
15K
6SN7
20K
20K
40K
20K
20K
40K
-

FIG. 49

CHAPTER 5 The Discharge Tube Detector.

5.1 Principle:

The detector was introduced by Harley and Pretorious (17), see also Basson, de Wet, Nel and Pretorious (18 & 19), and further developed by Pitkethly (20 & 21).

The voltage drop across a low-pressure gaseous discharge is a function of the nature of the gas and is very sensitive to traces of impurities such as organic vapours.

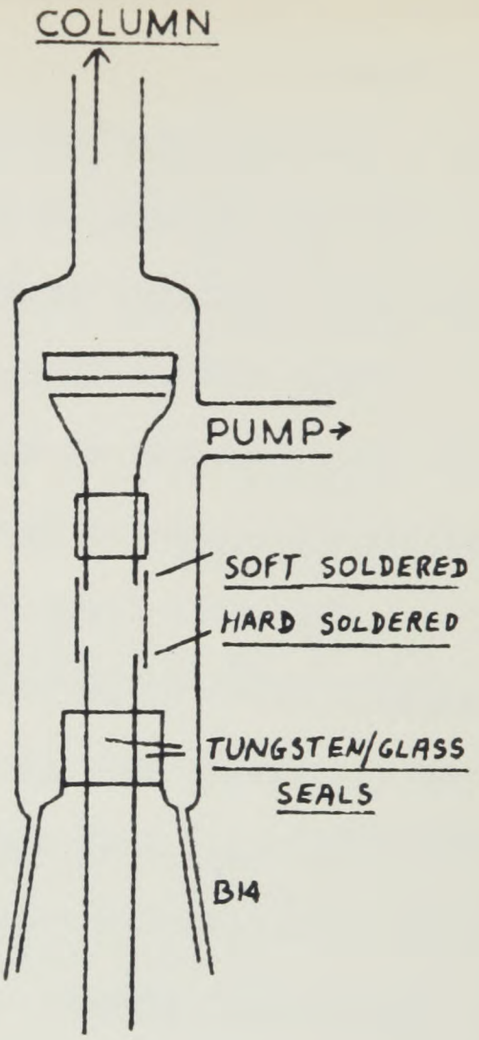
Pitkethly found that the greatest freedom from electrical noise is given by comparatively large closely spaced electrodes made of iron as in Phillips neon bulbs. He modified these bulbs for sample introduction as in Fig. 48, and his apparatus and electronic circuit are shown in Fig. 49.

5.2 Preliminary Work:

Work by another worker in this laboratory, using an apparatus very similar to that of Pitkethly, showed that the detector was capable of great sensitivity, but had a high noise level. For small aliphatic molecules such as pentane his results give a sensitivity of approximately 10^7 mV.cc./mgm., while for a 0.02 mgm. sample of pentane (obtained by flask dilution - see appendix 1), the signal to noise ratio was about 15. The minimum detectable sample would therefore be about 1.5×10^{-6} gms., corresponding to a minimum detectable concentration of 10^{-7} gms./cc. of pentane in nitrogen. The sensitivity was then roughly the same as that of the flame ionisation detector, but the noise level was about 50 times greater.



FIG. 50


COLUMN
PUMP
SOFT SOLDERED
HARD SOLDERED
TUNGSTEN/GLASS SEALS
B14

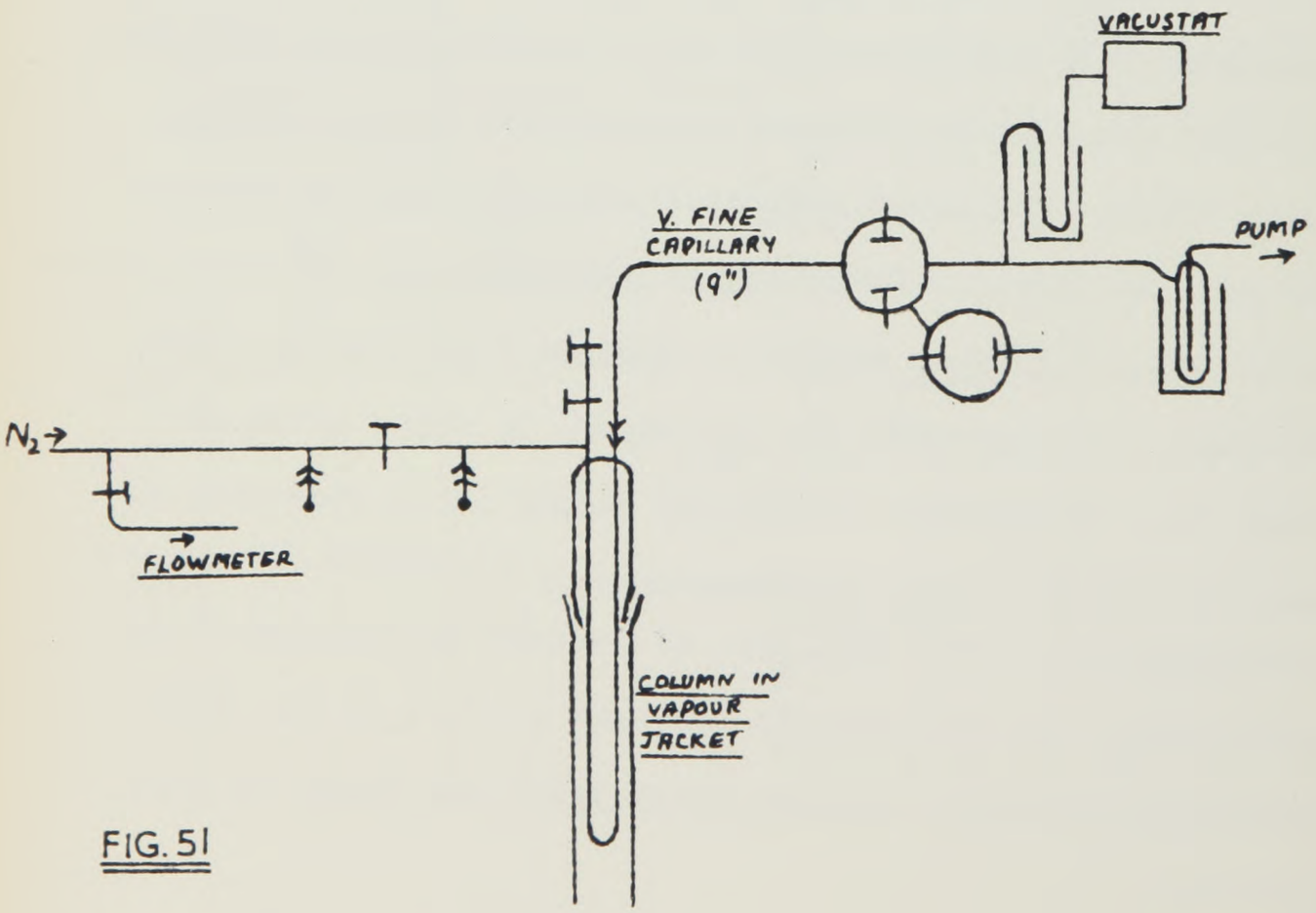

VACUSTAT
V. FINE CAPILLARY (9")
PUMP
N_2
FLOWMETER
COLUMN IN VAPOUR JACKET

FIG. 51

(These figures are only approximate, since the flow rate through the column was not recorded, and has been estimated at 20 - 25 ccs./min.).

When the author took over, a new apparatus had to be built, and three main modifications were made.

5.3 Apparatus:

5.3.1 The Discharge Tubes:

Pitkethly's modified neon bulbs were difficult to make and seal in, particularly since the envelopes were of soft glass, and the electrodes were inaccessible for cleaning, so a different design was used.

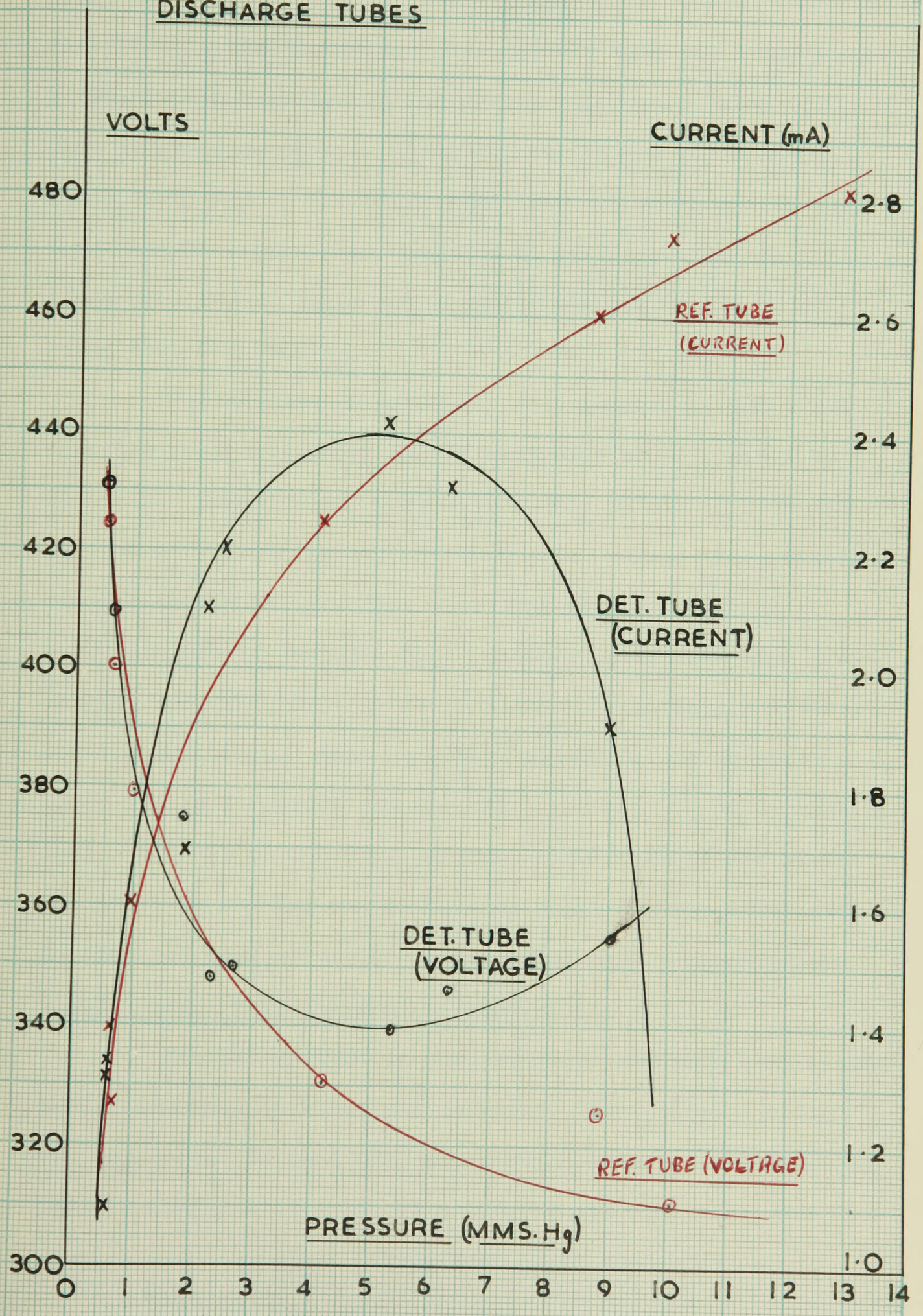
The electrodes were removed from the envelope by carefully breaking it. (Touching the glass with a flame or a hot glass rod usually causes it to break into small pieces.) They were mounted in a hard glass envelope, retaining the original pinch, on a cone and socket joint so that they could be removed for cleaning or replacement. (See Fig. 50).

5.3.2 The Reference Tube:

The purpose of using a balanced arrangement of two discharge tubes and two columns is stated by Pitkethly to be to compensate for fluctuations in pressure and for stationary phase distilling off the columns. Noise due to the latter would not be balanced out, but only the permanent signal. The system used in this work was simpler - only one column was used and the reference tube was connected to the sensing tube by a short wide connection to balance the effects of pressure changes. Any permanent signal was biassed off

FIG. 52

VOLTAGE DROP CURRENT & PRESSURE IN DISCHARGE TUBES



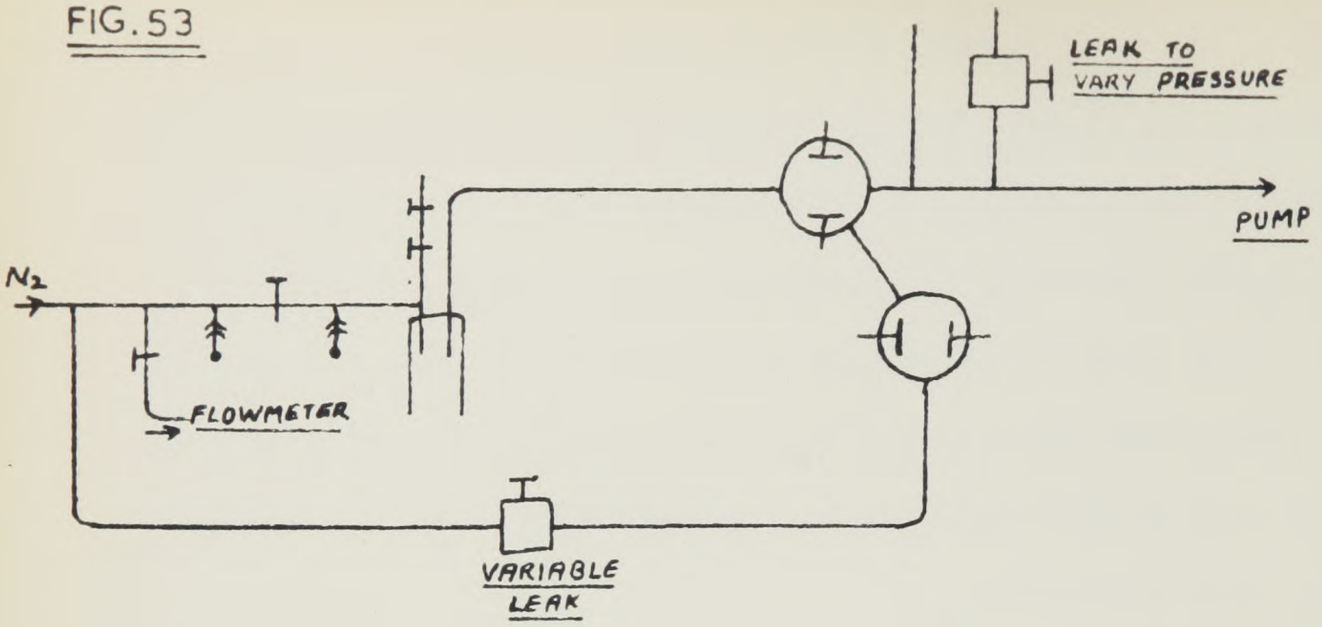
electrically. (See Fig. 51). The reference tube reduced the noise level by a factor of five. This figure was obtained by electrically disconnecting the reference tube and connecting a 178,000 ohm resistor in its place. The noise level with both tubes connected was about 200 mV, period ½-1 minute. Proof that most of the noise came from the tubes is the fact that when they were both replaced by resistors, or by unmodified neon bulbs, there was no noise visible on the recorder. (i.e. less than 10mV.)

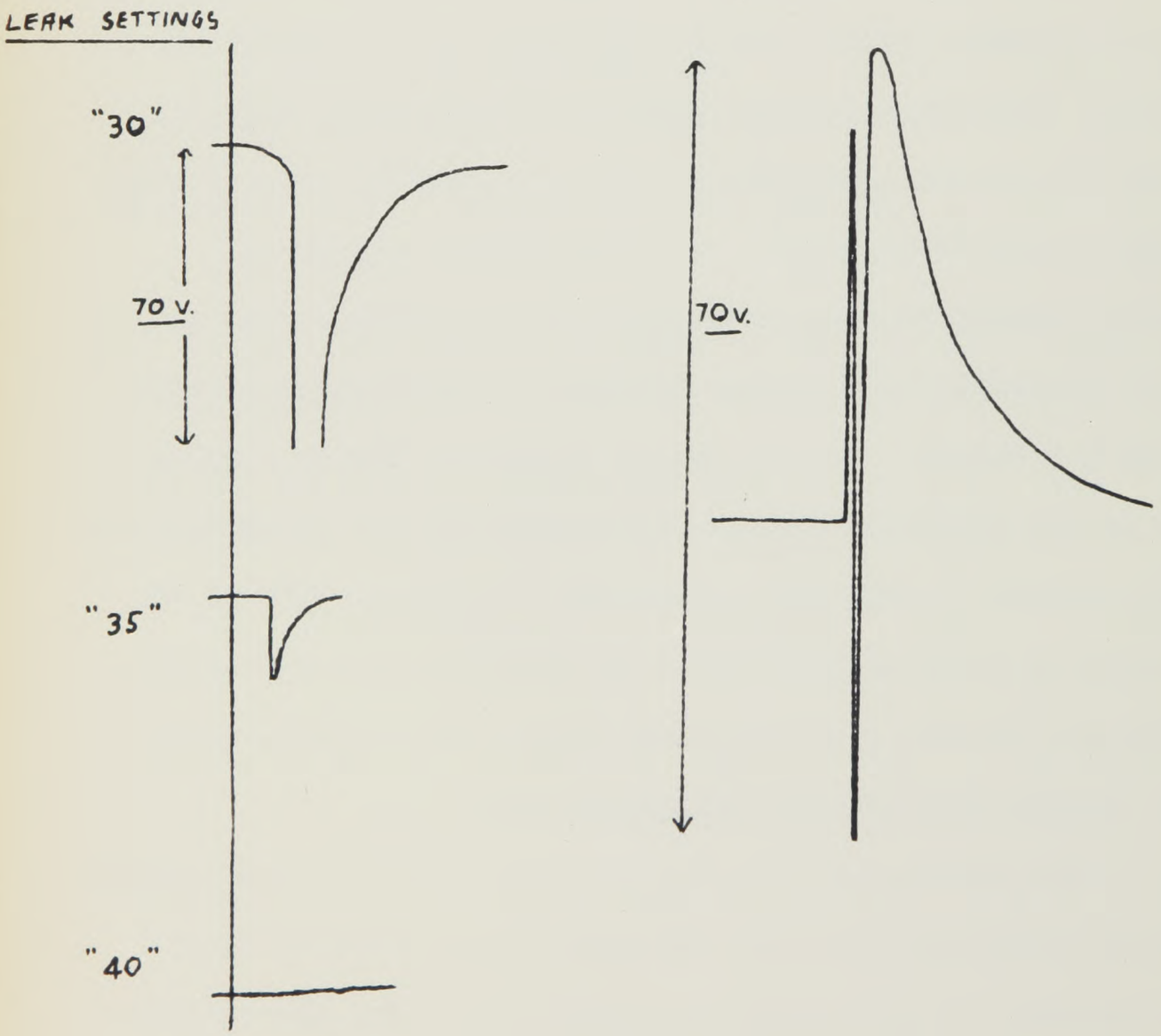
The changes in potential drop across the two tubes when the pressure varies should obviously be as similar as possible. Measurements were made of the potential drop and current at various pressures for the two tubes. (See Fig.52. Similar curves in ref. 19). The most stable region of operation should be that where pressure variations have least effect. However, this region appears at different pressures for the two tubes. This is almost certainly due to differences in the electrode spacing and surfaces. It is worthwhile taking trouble to make the electrical characteristics of the two tubes as similar as possible by adjusting the electrode spacing and keeping their surfaces free from contamination.

3.3.3 Sample Entering the Reference Tube:

The arrangement of the two tubes was such that sample could have been entering the reference tube, thus reducing the response. To find out, the sensing tube was electrically disconnected and replaced by a 178,000 ohm resistor, and samples were injected. "Negative" peaks were obtained,

FIG. 53





SAMPLE: $^1/_2$MGM.
CYCLOPENTANE.

FIG. 54

SAMPLE: 0·1 MGM.
CYCLOPENTANE

FIG. 55

nearly as large as the positive ones obtained with both tubes in circuit.

To stop sample entering the reference tube, the apparatus was modified to allow a slow current of nitrogen to be passed through it in the reverse direction, via an Edwards variable vacuum leak. (Fig. 53). This leak was progressively opened until no peaks were obtained with only the reference tube in circuit. (See Fig. 54). Fig. 55 shows an example of the effect of sample in the reference tube in normal operation.

2.3.4 Electronics:

Pitkethly's circuit has the two tubes and two series resistors in a bridge arrangement. The output from the detector as a whole is the "out-of-balance" voltage of the bridge, after a valve impedance conversion stage.

Treating the circuit as a Wheatstone's bridge, with changes in the resistance of the sensing tube being measured, the sensitivity is a maximum when the series resistors are made equal in value to the resistance of the tubes, i.e. about 178,000 ohms. A value as high as this would, however, necessitate an inconveniently high stabilised supply voltage (800 - 900 volts). (This treatment is in fact an over-simplification, and probably shows no more than that the value of 100,000 ohms in the Pitkethly circuit is below the ideal).

A triode or pentode valve with its grid held at a fixed potential relative to HT negative, and a high value cathode resistor, behaves as a very high resistance as far as

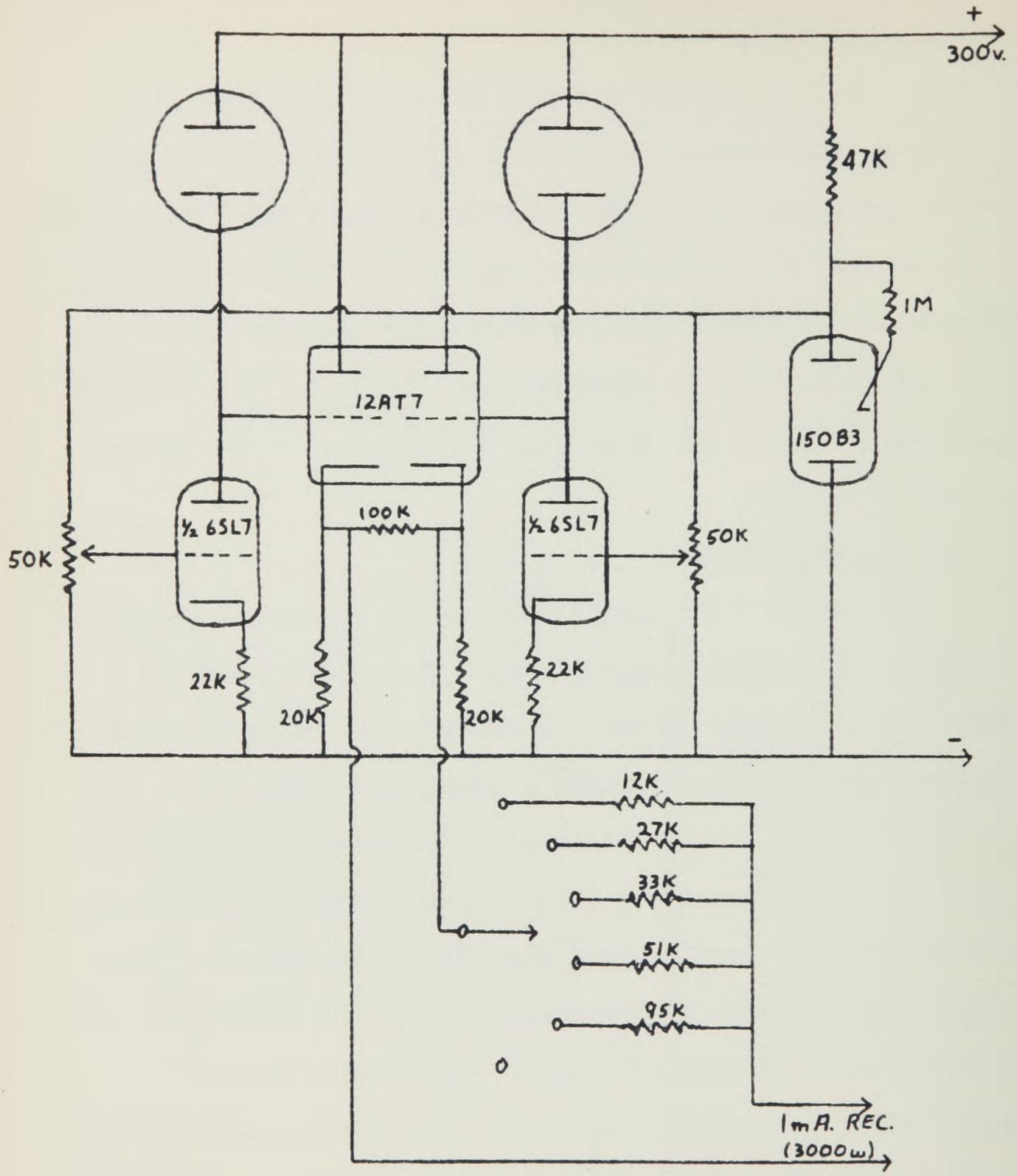

+
300v.
47K
1M
12AT7
150B3
½ 6SL7
½ 6SL7
100K
50K
50K
22K
22K
20K
20K
-
12K
27K
33K
51K
95K
1mA. REC.
(3000ω)

FIG. 56

FIG. 57

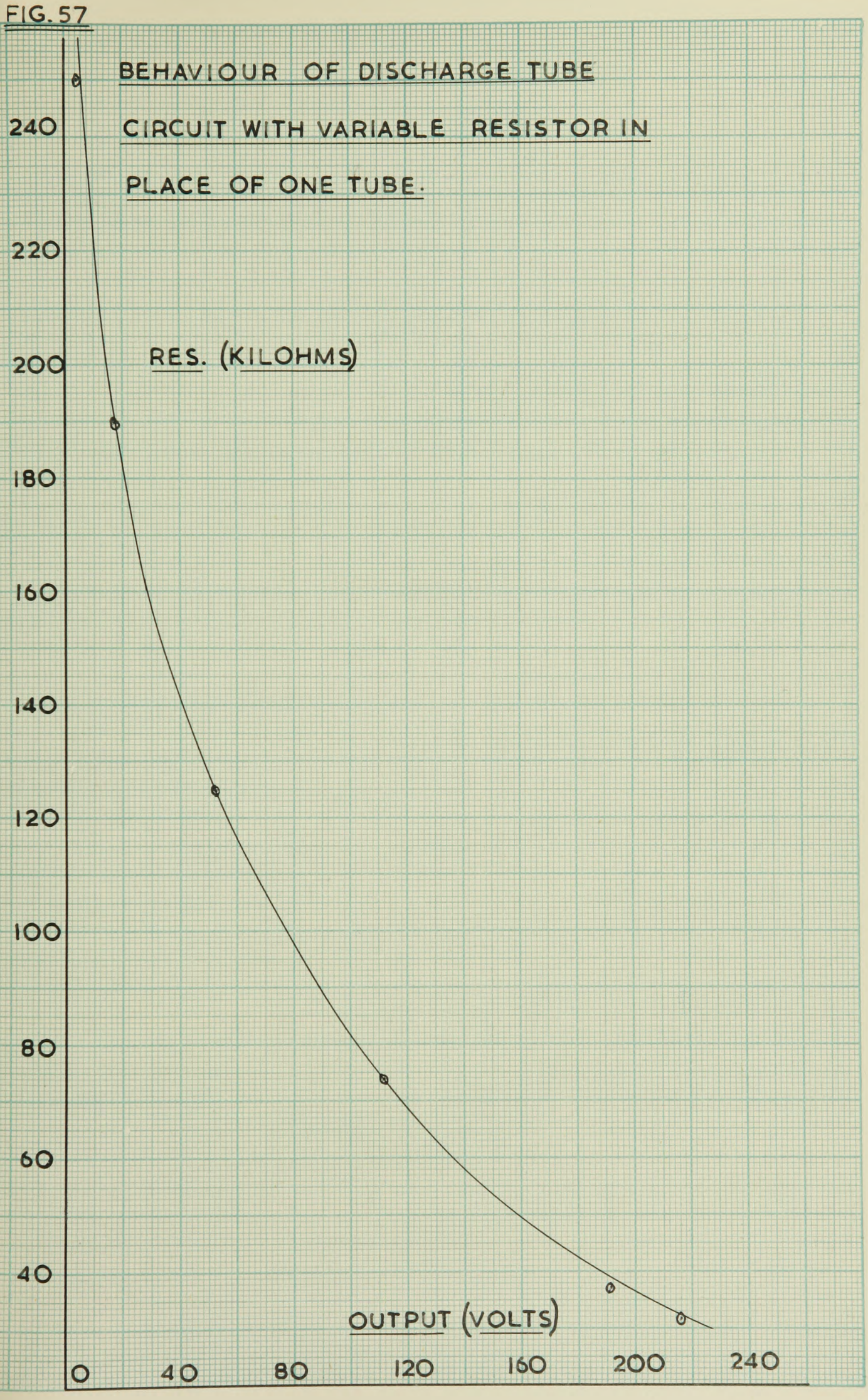

BEHAVIOUR OF DISCHARGE TUBE
CIRCUIT WITH VARIABLE RESISTOR IN
PLACE OF ONE TUBE.
RES. (KILOHMS)
240
220
200
180
160
140
120
100
80
60
40
OUTPUT (VOLTS)
0
40
80
120
160
200
240

FIG. 58

4×10^{-3} MGMS.
BENZENE

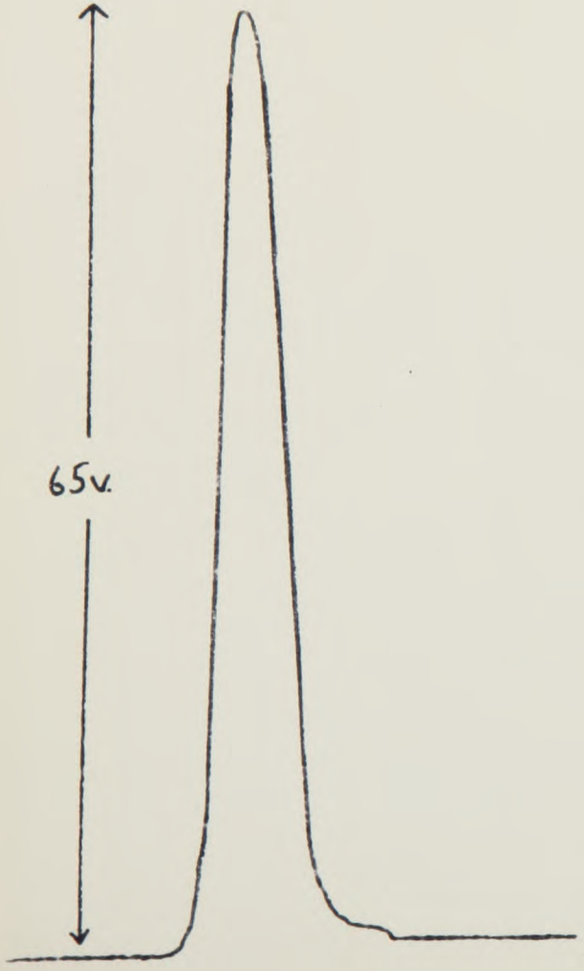


FIG. 59

5×10^{-2} MGMS.
CYCLOPENTANE

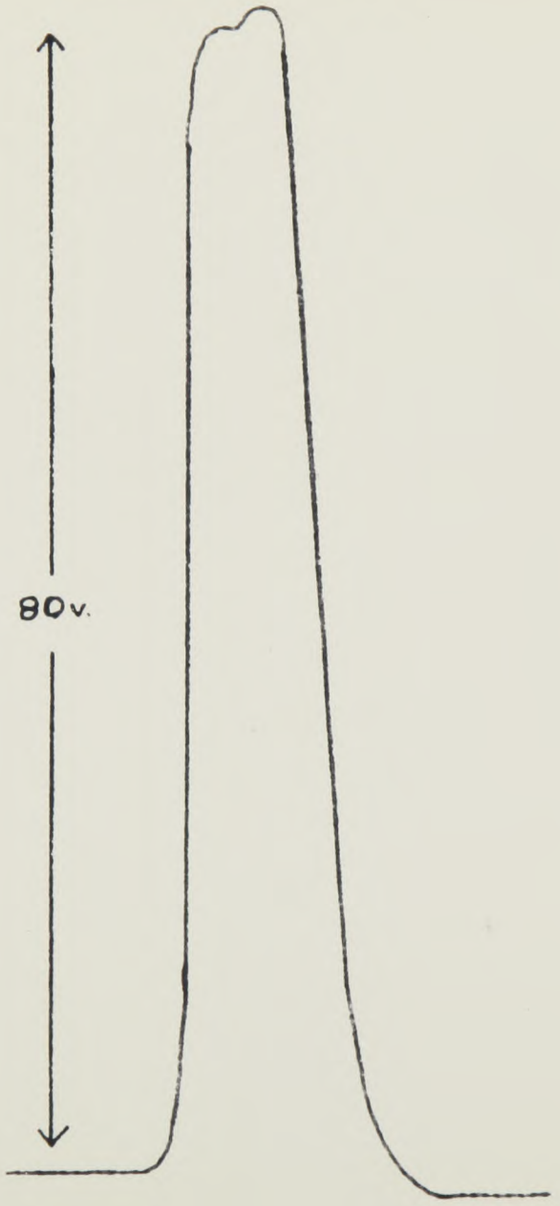
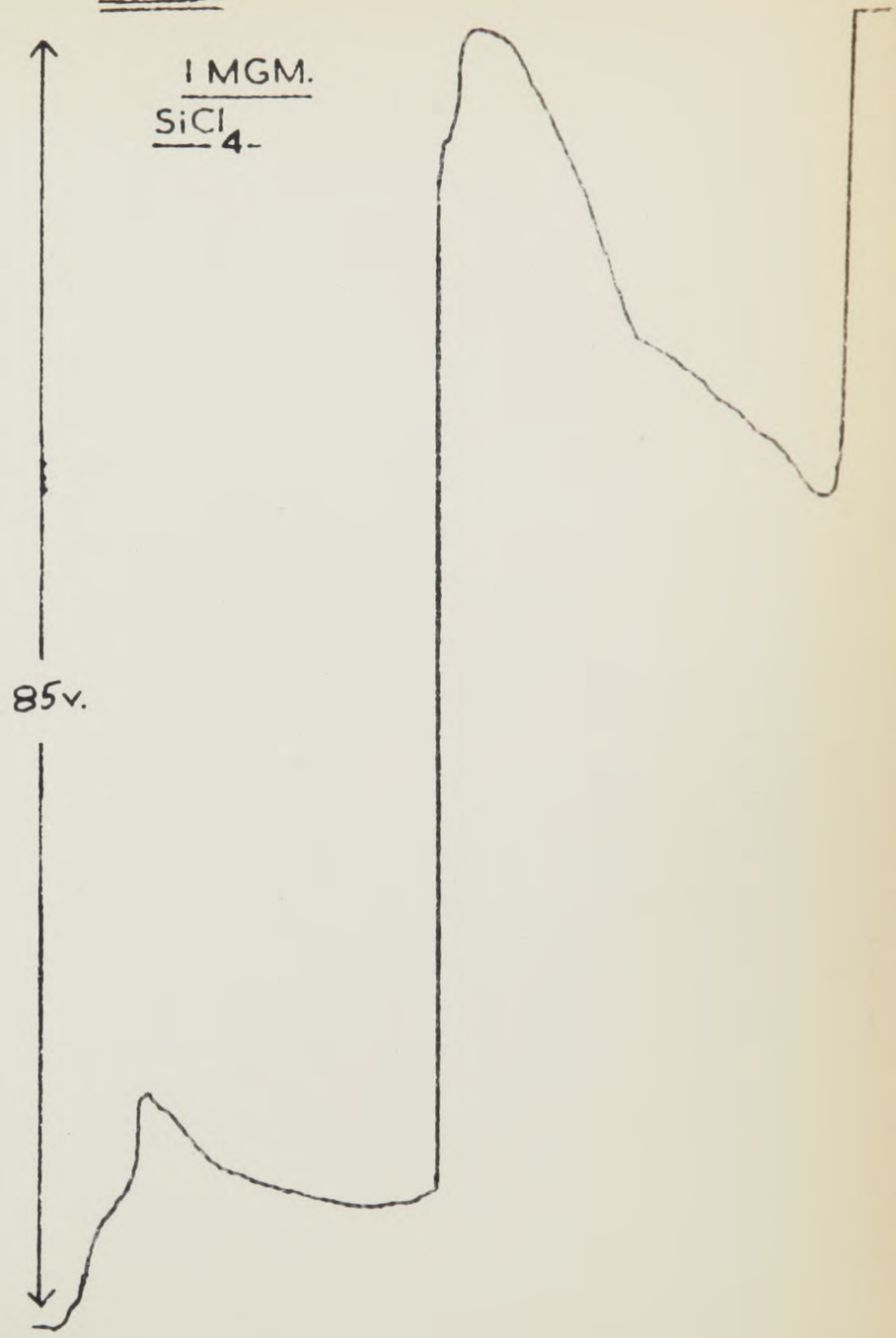


FIG. 60

1 MGM.
$SiCl_4$



variations in its anode potential and anode current are concerned, without the disadvantage of a large potential drop across the valve. (So-called "constant-current" valve.) A circuit embodying this principle was built (to the design of A.E.Thompson), including a low-impedance output stage. See Fig.56. (The characteristics of the circuit are plotted in Fig. 57)

The"effective resistance" of each half of the 6SL7 in this circuit is about 1 megohm. There is a further advantage in the arrangement in that the operating point of the tubes is stabilised by the "constant-current" action of the valves, and the introduction of samples should not have the effect of driving the tubes out of the "stable region of operation". (See above, and refs. 20 and 21).

5.4 Behaviour of the Detector:

Hydrocarbon samples were injected, and with these well-shaped peaks were obtained provided that the sample was small enough (see Fig.58). A sample larger than about 0.05 mgm. of cyclopentane gave a peak with a "rounded-off" top (Fig. 59). 1 mgm of tetralin was enough to extinguish the discharge and to leave the tube in such a condition that it would not relight until a faint black deposit (presumably carbon) had been removed from the electrodes with concentrated nitric acid. After replacing the electrodes the baseline drifted steadily for 1 - 1½ hours before the apparatus was ready for use again. Tetralin was used as a diluent for injecting small quantities of lower boiling compounds, and to prevent the above trouble the discharge was switched off just before the tetralin peak

was due.

The only "non-hydrocarbon" run on the detector was silicon tetrachloride (Fig.60). The base-line did not return to normal after the peak. Injection was by capillary, and the first peak is almost certainly due to HCl

5.5 Sensitivity to Hydrocarbons: (results without the reverse flow into the reference tube - in its final form the apparatus would give sensitivities 2 - 3 times greater than these).

	Sample Size (mgm)	Peak Areas (mV.cc.)	Sensitivity (mV.cc./mgm)	Peak Ht. (volts)	Min.Det. Quant(gms.)
Benzene	4×10^{-3}	1.5	4×10^{8}	60	7×10^{8}
Toluene	4×10^{-3}	1.8	4.5×10^{8}	55	7.3×10^{-8}
o-Xylene	4×10^{-3}	2.1	5×10^{8}	50	8×10^{-8}
Mesitylene	4×10^{-3}	2.5	6×10^{8}	40	10×10^{-8}

Taken from two runs in which the compounds were injected by capillary, diluted with 50 parts of tetralin.

Molar Response

	Sensitivity (mV.ccs./millimole)
Benzene	3.1×10^{6}
Toluene	4.9×10^{6}
o-Xylene	4.7×10^{6}
Mesitylene	5.0×10^{6}

Pitkethly's results show that the molar sensitivity to aliphatic hydrocarbons tends to decrease with increasing molecular wt. (21),as for the first three compounds above.

5.6 Conclusions:

The detector has a very high sensitivity to hydro-

carbons and $SiCl_4$. The absolute sensitivity is about 500 times greater than that of the flame ionisation detectors used in this work. (This high sensitivity is largely due to the use of the "constant-current" valve). The noise level is much higher, however, and the minimum detectable quantity is about the same as that for the flame ionisation detector or a little less. The noise level could certainly be reduced by careful construction of the discharge tubes and attention to the smoothing out of pressure fluctuations.

The detector overloads easily, and cleaning the detector after a large overload is tedious. However, samples can be kept small enough to avoid this trouble without difficulty. For capillary columns, for example, the usual sample size is well below the limit.

The baseline does not always return to its previous position after a peak - probably due to deposits on the electrodes.

FIG. 61

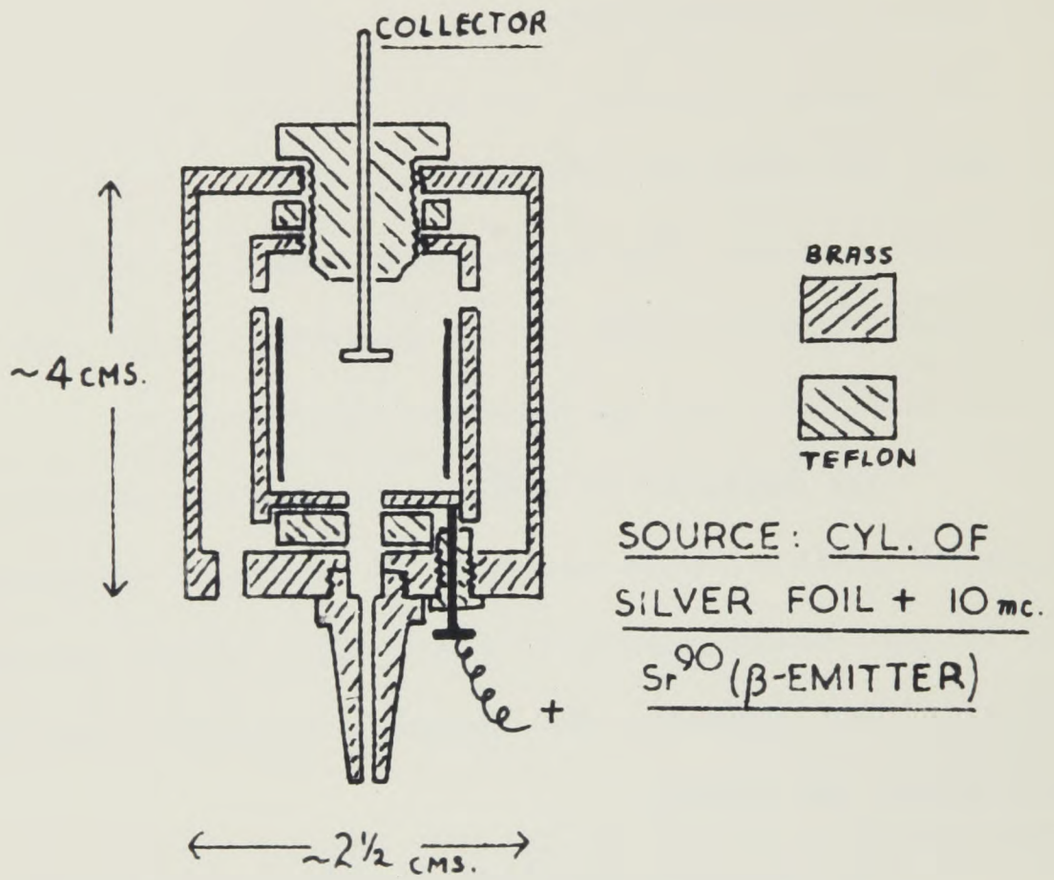
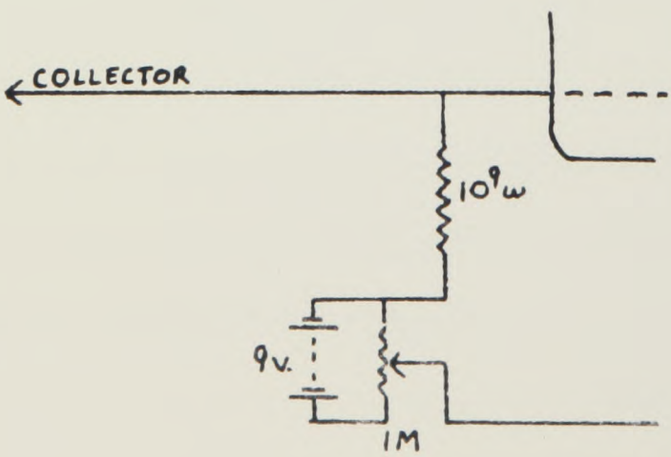

COLLECTOR
~4 CMS.
~2½ CMS.
+
BRASS
TEFLON
SOURCE: CYL. OF SILVER FOIL + 10 mc. Sr^{90} (β-EMITTER)

FIG. 62


COLLECTOR
$10^9 \omega$
9v.
1M

CHAPTER 6 The Argon Detector.

A version of this detector (made by the Perkin Elmer Corp.) was tested with a variety of samples. Measurements of its sensitivity towards tetralin, SiH_4, Si_2H_6, NH_3, H_2S, GeH_4, and PH_3 have been obtained. The effect of hydrogen (and, briefly, CH_4) has also been looked into.

6.1 Principle of the Detector (Introduced by J.E.Lovelock, (23,24,25,26)

The operation of the detector depends on two reactions. First, the excitation of argon atoms to a metastable state (excitation energy 11.7 e.v.) by electron bombardment. The electrons arise from the ionisation of argon atoms by irradiation from an alpha- or beta-emitting radioactive source, and are accelerated by an applied potential of about 1000v. One electron is stated to be capable of producing 10^4 excited argon atoms. The second reaction is the ionisation of foreign molecules by collision with the excited species, which have a lifetime of about 10^{-5} secs. The efficiency of this reaction approaches 100%. (25, 26).

A typical detector consists of a metal chamber, around the inside of which is placed radioactive material (e.g. Sr^{90}, Kr^{85}, H^3 etc.) A high potential is applied between the chamber and an anode, and the current flowing is monitored. The presence of foreign substances in the argon entering the detector causes an increase in this ion current. The detector used in this work is shown in Fig. 61.

(The "typical detector" described above is the type used for "packed" columns, and called by Lovelock the "simple" detector, to distinguish it from the "small" and triode" detectors which have special features making them suitable for use with capillary columns.) (26).

6.2 Associated Apparatus.

The problems are much the same as those already discussed in connection with the flame ionisation detector, and the impedance converter is very similar. A "backing-off" potential was added, since the argon detector has a rather high background current (10^{-8}-10^{-9} amps) See Fig. 62.

The high voltage supply was made up of ten 90 volt miniature H.T. batteries, connected in series with provision for varying the voltage in steps of 90 volts.

A mains power pack was also constructed, using a voltage doubler circuit and a corona stabiliser, but gave an unstable voltage. (Reason unknown)

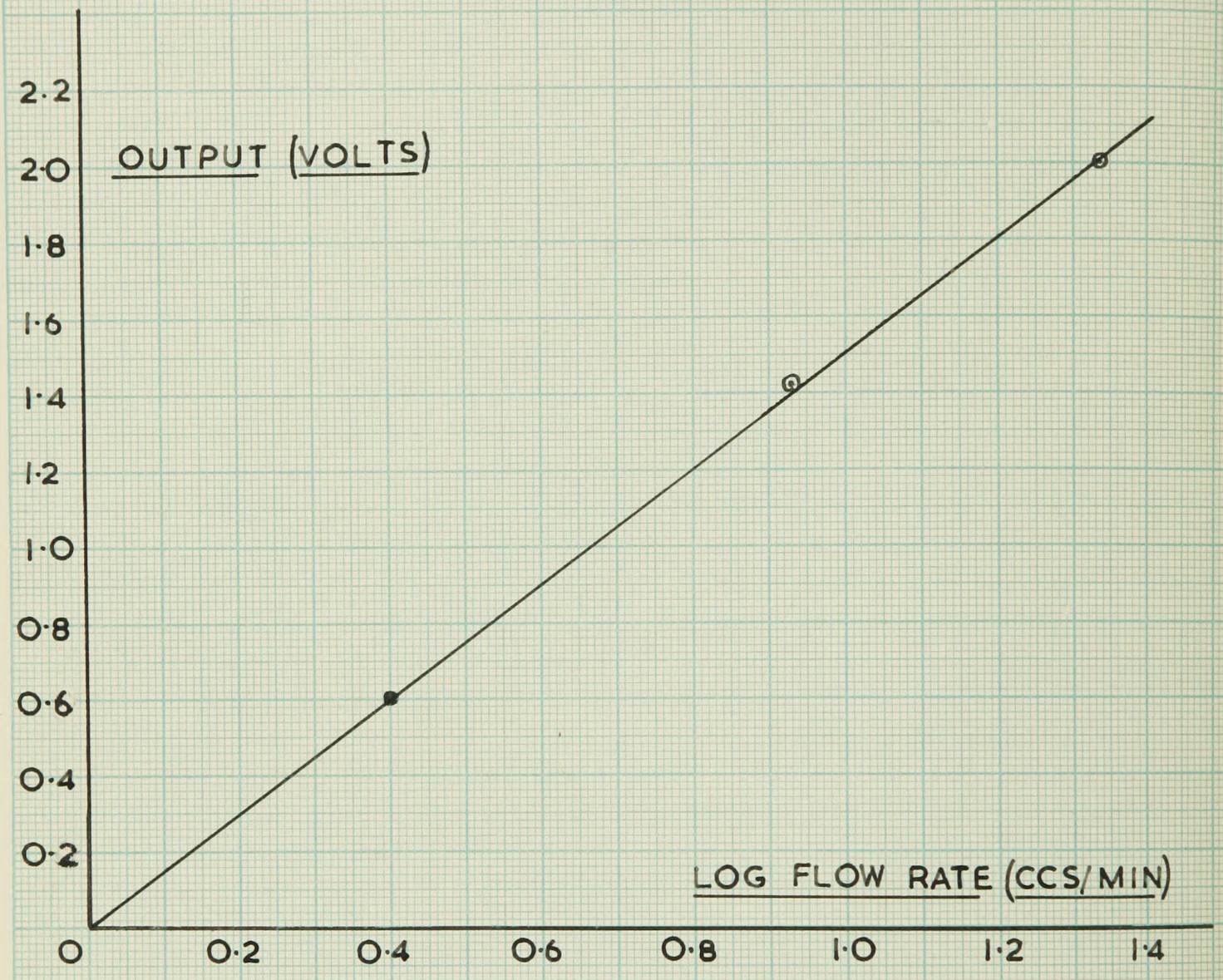
Statements of Sensitivity of the Argon Detector

The cell current in the "simple detector" as used in this work depends on the total mass of sample in the detector at a given instant. For a given detector, therefore, the current depends on the concentration of sample in the carrier gas. (26)

Sensitivities can therefore be expressed as the concentration of sample (gms./cc. of carrier gas), which would give a current of 10^{-9} amps. in excess of the background. Sensitivities in coulombs/gm. can be converted into these

FIG. 63

EFFECT OF FLOW RATE OF ARGON ON RESPONSE.



SAMPLE: TETRALIN 0·04% BY VOLUME.

DET. TEMP.: 40-50°C.

E.H.T.: 900 VOLTS

units as follows:

Let X be the sensitivity in coulombs/gm. at a flow rate of F ccs./min. Then sample entering the detector at a rate of 1 gm./sec. would give a current of X amps. This 1 gm./sec. is in a carrier gas stream of F ccs./min., and therefore its concentration in the detector is 60/F gms./cc. Therefore a current of 10^{-9} amps. would be given by a concentration of $60.10^{-9}/X.F$ gms./cc.

6.3. Effect of Operating Conditions on the Detector:

6.3.1 The effect of Variation of Flow Rate:

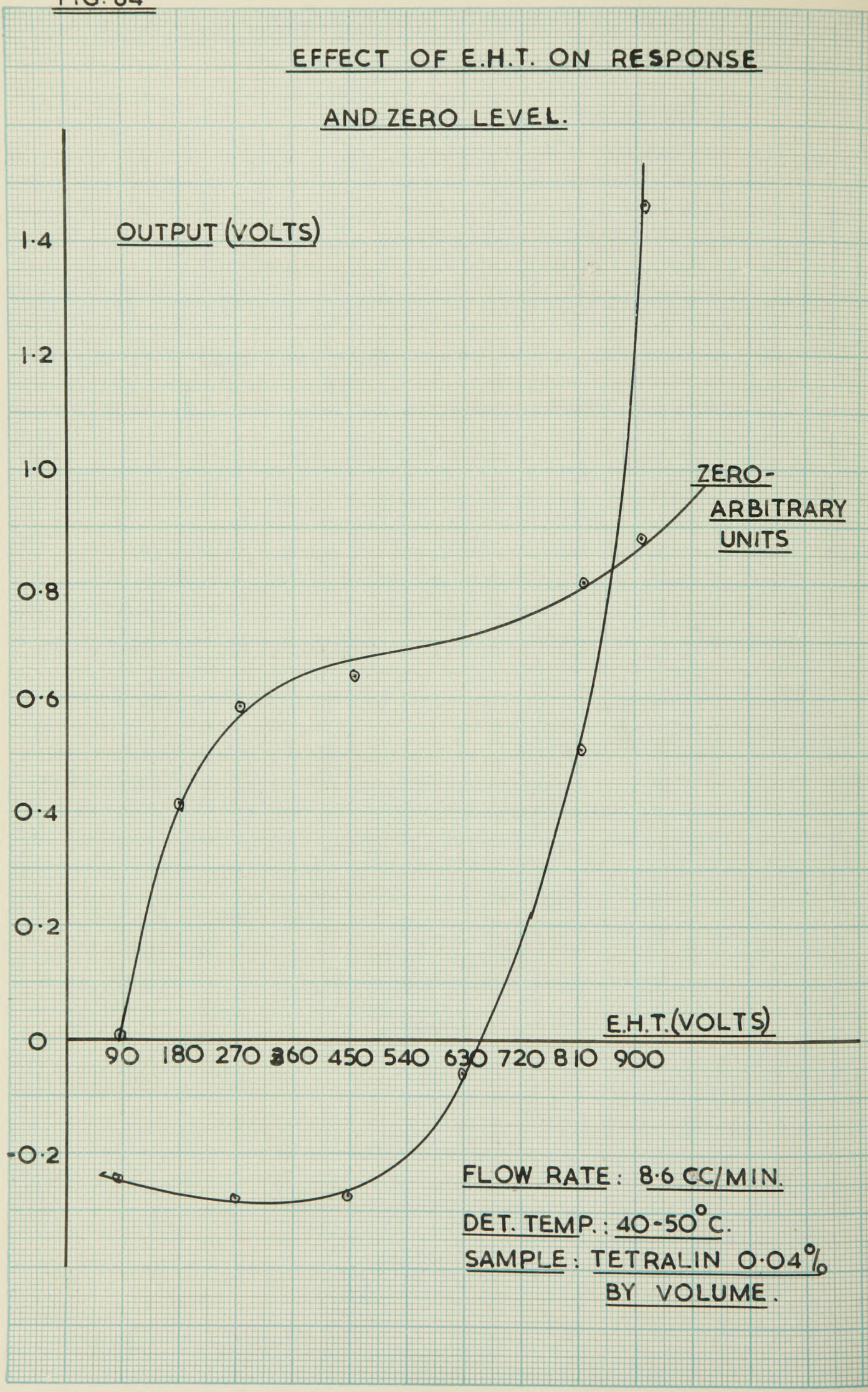
Method: The argon was passed through a saturator kept at a constant temperature in a Dewar of water. The concentration of tetralin in the gas stream entering the detector accordingly remained constant, and the effect of flow rate on the sensitivity could be observed.

Results: E.H.T. = 900 v. Temp. of tetralin = 17.5°C. V.P.=0.29mm.

Flow rate (cc./min)	22	8.6	2.4
Signal (volts)	2.0	1.45	0.61
Log (Flow Rate)	1.34	0.93	0.38

These figures are plotted in Fig. 63. The plot of log (flow rate) against signal gives approximately a straight line. This agrees with Lovelock's statement (26). The effect is stated to be due to the fact that the metastable argon atoms are confined to a region around the anode where the electrons have been accelerated sufficiently to produce them, and that vapour enters this region by diffusion.

FIG. 64


EFFECT OF E.H.T. ON RESPONSE
AND ZERO LEVEL.
OUTPUT (VOLTS)
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
-0·2
ZERO-
ARBITRARY
UNITS
E.H.T.(VOLTS)
90 180 270 360 450 540 630 720 810 900
FLOW RATE: 8·6 CC/MIN.
DET. TEMP.: 40-50°C.
SAMPLE: TETRALIN 0·04%
BY VOLUME.

6.3.2 The Effect of Temperature:

It was observed that raising the temperature of the detector from about 17°C. to about 110°C. increased the signal by a factor of about 5.

When using the detector at room temperature with a saturator containing tetralin, the signal rose very slowly indeed when tetralin was admitted to the gas stream, taking some 20 - 30 minutes to reach equilibrium and vice versa. At about 30°C. a steady signal was reached in about 1/50 of the time. This may be due to the very slow establishment of an absorption film of tetralin on the walls of the detector.

6.3.3 The Effect of Variations in E.H.T.

The concentration of tetralin in the argon entering the detector was kept constant by means of a saturator and the effect of the E.H.T. on the signal is shown in Fig. 64. The variation of zero level (output with no tetralin in the gas stream) is also shown in Fig.64. It can be seen that at lower voltages the signal becomes negative, i.e. the output decreases when tetralin is introduced into the gas stream. The explanation of this latter effect may be as follows. As the E.H.T. is increased the concentration of excited argon atoms (A^*) in the detector rises very much faster than that of the ionised argon (A^+) also present. Therefore at low potentials there will be few A^* and relatively more A^+. (25). The conductivity of the gas will be due to the A^+ ions, and when vapour is introduced there will be insufficient A^* atoms to appreciably ionise it and it will not add to the conductivity.

It probably decreases the number of A^+ ions, perhaps merely by dilution.

(Tetralin is known to capture electrons - this may be an alternative explanation: the detector acting as an electron capture detector at low E.H.T. voltages).

6.4 Sensitivity of the Argon Detector to Various Compounds.

6.4.1 Sensitivity of the Argon Detector to Tetralin:

Method: The argon entering the detector was passed through a saturator containing tetralin, immersed in a Dewar of water at room temperature.

Flow Rate of argon = 8.6 ccs./min.
E.H.T. = 900 volts.
Temperature of detector = 40 - 50°C.
Temperature of tetralin = 17°C.
Vapour Pressure of Tetralin = 0.29 mms.
Signal from detector = 1.45 volts (across 10^9 ohms).
1 cc. of tetralin vapour at 0.29 mms. and 17°C.

$$= 2.1 \times 10^{-6} \text{ gms.}$$

Therefore in one minute $(8.6)(2.1 \times 10^{-6})$

$= 1.8 \times 10^{-5}$ gms. of tetralin enters the detector.

Let this weight of tetralin enter the detector as a band with sharp edges and a constant concentration, length one minute. Then the peak produced would be rectangular, height 1.45 volts and length 1 minute. Area 1.45 volt.mins.

Therefore sensitivity = $\frac{8 \times 10^4}{}$ volt.mins./gm.

Concentration needed to give a detector current of 10^{-9} amps.

$$= 1.45 \times 10^{-6} \text{ gms./cc.}$$

Sensitivity in coulombs/gm.

$$= \frac{4.8 \times 10^{-3}}{}$$

Tetralin caused no increase in noise level. The sensitivity is roughly twice that of the flame ionisation detector to tetralin. At flow rates nearer to those likely to be met with in practice, i.e. about 50 cc./min. the sensitivity would be higher, about 2.4×10^{5} volt.mins./gm. or 1.4×10^{-2} coulombs/gm.

6.4.2 Sensitivity of the Argon Detector to Mono- & Disilane:

Method: A mixture of SiH_4 and Si_2H_6 (made by The Plessey Co. Ltd.) of known composition, was used. A vessel of known volume was filled to a known pressure and the carrier gas stream diverted through it.

Composition of Mixture: The sample available was a mixture of hydrogen, monosilane and disilane. It was cooled in liquid nitrogen and the trap evacuated for some time to remove all the hydrogen and some of the more volatile monosilane. The composition of the resulting mixture was determined by orthodox gas chromatographic methods, using hydrogen as carrier gas and a Pye katharometer as detector. Under these conditions, it can be assumed that the molar response of the katharometer to the two compounds is the same (27). Peak areas were estimated by cutting them out and weighing them. The mean of five experiments (mean deviation = 6.9%), gave the molar proportions as

$$\frac{SiH_4}{Si_2H_6} = 3.8, \text{ or } 79\% \ SiH_4 \text{ and } 21\% \ Si_2H_6$$

Monosilane:

Run No.	403	404	405
FSD of Recorder	10v	27v.	27v.
Chart Speed	30cm/hr.	ditto	ditto
Flow Rate	50cc/min.	ditto	ditto
Total Press. of sample	5.0 mms.	5.5 mms.	7.0mms.
P.Press of SiH_4	3.9 mms.	4.3 mms	5.5mms.
Weight of SiH_4	2.6×10^{-5} gms	2.9×10^{-5}	3.7×10^{-5}
Peak Area (sq. cms.)	1.4	0.54	0.6
" " (volt.mins)	1.1	1.2	1.3
Sensitivity (volt.mins/gm.)	4.2×10^4	4.1×10^4	3.5×10^4

Mean Sensitivity = 4.0×10^4 volt.mins/gm.

Concentration needed to give a detector current of 10^{-9} amps.

= 5.0×10^{-7} gms/cc.

Disilane:

Run No.	403	404	405
Total Press. of Sample(mms)	5.0	5.5	7.0
Part Press of Si_2H_6 (mms.)	1.1	1.2	1.5
Weight of Si_2H_6 (gms.)	1.5×10^{-5}	1.7×10^{-5}	2.1×10^{-5}
Peak Area (sq.cms.)	offscale	0.68	0.68
Peak Area (volt.mins.)	-	1.45	1.45
Sensitivity (volt.mins/gm.)	-	8.8×10^4	7.1×10^4

Mean Sensitivity = 8.0×10^4 volt.mins/gm.

~~4.8×10^{-3}~~ or coulombs/gm.

Concentration required to give a detector current of 10^{-9} amps.

= 2.5×10^{-7} gms/cc.

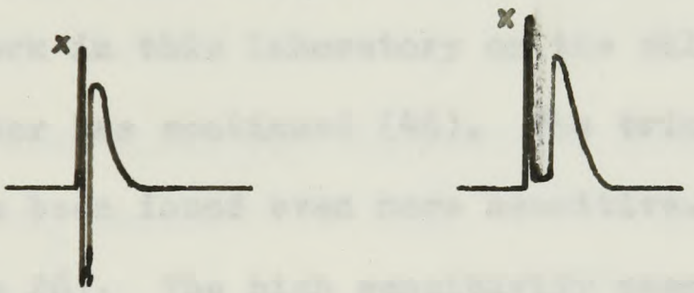
The sensitivity to monosilane is about 1½ times that to tetralin at the same flow rate of argon, and to disilane about 3.3 times that to tetralin.

The sensitivity to disilane is about 20 times that of the flame ionisation detector, (jet negative).

The noise level in a typical experiment was 0.01 volts. The minimum detectable quantity of disilane is therefore about 2×10^{-7} gms. - a least 500 times smaller than the figure for the katharometer.

Peak Reversals with Monosilane:

Samples of monosilane larger than about 2.7×10^{-6} gms. caused "peak reversal", e.g.:



The point 'x' does not appear at the same height above the baseline in all cases.

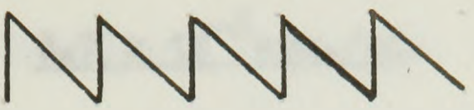
Lovelock states that large samples in general cause non-linearity and "multi-peaking", (presumably as above), due to "reduction of free electron velocity following non-elastic collisions". (25)

No similar effect was observed on the disilane peaks, but the amount of disilane was usually only about 1/10 the amount of monosilane, never more than 1/4. This effect has been observed in later work in this laboratory (46).

Effect of Silanes on the Detector:

When the detector was dismantled, a slight white deposit was noticed on some of the inside surfaces. Trouble was also encountered with oscillation of the recorder pen,

in the form of sawteeth:



or pulses:



This may be due to the deposit acting as a high resistance leakage between the case and the centre electrode, and causing some type of "RC" oscillation.

Work in this laboratory on the silanes using the argon detector has continued (46). The triode form of the detector has been found even more sensitive. (For triode detector see 26). The high sensitivity means that only very small amounts of silane mixtures need be made, with a considerable reduction in the risk of dangerous explosions.

6.4.3 Sensitivity of the Argon Detector to Monogermane.

Method of injection as for silanes.

Volume of trap = 3.8 ccs. Flow Rate = 50 ccs./min. E.H.T. =900v.

	1	2
Pressure of GeH_4 (mms.)	2 mms.	1.6 mms.
Sample Size (gms.)	3.2×10^{-5}	2.6×10^{-5}
Peak Areas (sq.cms.)	3.6	3.3
Peak Areas (volt.mins)	7.8	7.1
Sensitivity (volt.mins./gm.)	2.4×10^{5}	2.2×10^{5}

Mean Sensitivity = 2.3×10^{5} volt.mins./gm. or 1.4×10^{-2} coulombs/gm.

Concentration required for a detector current of 10^{-9} amps.

= $\underline{8.7 \times 10^{-8} \text{ gms./cc.}}$

Sensitivity to Monogermane is about 10 times that to tetralin at the same flow rate, and the argon detector is very suitable for the detection of this compound.

6.4.4 Sensitivity of the Argon Detector to Ammonia:

Method of injection as for the silanes (Sec. 6.4.2), the traps being filled from a large bulb full of ammonia (Appendix 2)

Vol. of trap = 3.9 cc. Flow Rate = 17 cc./min. E.H.T. = 900v.

Pressure of NH_3 (mms.)	230	230	228
Sample Size (gms.)	8.5×10^{-4}	8.5×10^{-4}	8.4×10^{-4}
Peak Area (sq.ins.)	3.2	3.36	3.86
Peak Area (volt.mins.)	39.0	41.0	47.0
Sensitivity (volt.mins./gm.)	4.6×10^{4}	4.8×10^{4}	5.6×10^{4}

Mean Sensitivity = $\underline{5.2 \times 10^{4} \text{ volt.mins./gm.}}$ or

$\underline{3.2 \times 10^{-3} \text{ coulombs/gm.}}$

Concentration required for a Detector current of 10^{-9} amps.

= $\underline{1.2 \times 10^{-6} \text{ gms./cc.}}$

Sensitivity to ammonia is about 2.9 times that to tetralin at the same flow rate.

The peaks due to ammonia were all flat-topped, thus:

6.4.5 Sensitivity of the Argon Detector to Phosphine.

Method of injection as for the silanes (see above)

Results: Vol. of trap = 3.8 ccs. Flow Rate= 50 ccs./min.
E.H.T. = 900 v.

	1	2	3
Pressure of PH_3 (mms.)	4	1	0.2
Sample Size (gms.)	2.9×10^{-5}	7.2×10^{-6}	1.4×10^{-6}
Peak Areas (sq.cms.)	3.5	0.5	0.12
" " (volt.mins.)	7.6	1.1	0.26
Sensitivity (volt.mins./gm)	2.6×10^{5}	1.5×10^{5}	1.9×10^{5}

Mean Sensitivity = $\frac{2.0 \times 10^{5}}{1.2 \times 10^{-2}}$ volt.mins./gm or coulombs/gm.

Concentration required for a detector current of 10^{-9} amps.

= $\frac{1.0 \times 10^{-7}}{}$ gms./cc.

Sensitivity to phosphine is about 7 times that to tetralin at the same flow rate.

6.4.6 Sensitivity of the Argon Detector to Hydrogen Sulphide

Method of injection as for the silanes.

Volume of trap = 3.9 ccs. Flow Rate = 25 ccs./min. E.H.T. = 900v.

Pressure of H_2S (mms.)	204	202	200	190
Sample Size (gms.)	1.6×10^{-4}	1.6×10^{-4}	1.55×10^{-4}	1.5×10^{-4}
Peak Areas (sq.ins)	0.23	0.31	0.29	0.26
" " (volt.mins)	8.1	11.8	10.9	9.9
Sensitivity (volt.mins/gm.)	5.1×10^{4}	7.6×10^{4}	7.0×10^{4}	6.8×10^{4}

Mean Sensitivity = $\frac{6.6 \times 10^{4}}{}$ volt.mins/gm. or $\frac{4.0 \times 10^{-3}}{}$ coulombs/gm.

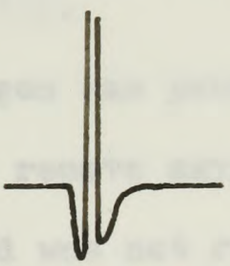
Concentration required for a detector current of 10^{-9} amps.

$$= \frac{6.0 \times 10^{-7}}{} \text{ gms./cc.}$$

Sensitivity to hydrogen sulphide is about 3.3 times that to tetralin at the same flow rate.

6.4.7 Effect of Hydrogen:

Several samples consisting almost entirely of hydrogen, monosilane and disilane were passed through the detector, and the monosilane peaks appeared to be partly standing in a trough:



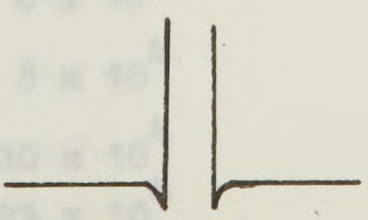
Samples containing no hydrogen did not show this effect. The effect of hydrogen alone was investigated, and it was found that small samples (less than about 4×10^{-6} gm.) gave very small negative peaks (about one third the height of the trough in which the monosilane peaks stood):



a sample of 4.4×10^{-6} gms. gave a peak thus:



and larger samples thus:



One sample of methane was passed through the detector and gave a very similar effect (3.4×10^{-5} gms.):



Lovelock includes hydrogen in a list of substances to which the detector does not respond, and methane among substances to which there is a response 1/10 - 1/100 of the normal (26) - page 10).

The hydrogen was passed through a "Deoxo" on the cylinder outlet to remove oxygen, and the small amount of water so introduced was not removed. Water is known to affect the detector, usually to reduce the response (26) - page 15). However there was no water in the mixture of hydrogen and monosilane.

6.4.8.
Summary of Sensitivities of the Argon Detector to Various Substances.

	Sensitivity at 50 ccs./min. of Argon (volt.mins./gm.)	Ionisation Potentials (e.v.) (Ref.58)
H_2	-	15.44
CH_4	low	13.1 (14.5 Ref.57)
$C_{10}H_{12}$	2×10^4	
SiH_4	4×10^4	12.2
NH_3	6.9×10^4	10.25 (photo)
Si_2H_6	8×10^4	
H_2S	8×10^4	
PH_3	20×10^4	10.0
GeH_4	23×10^4	12.3

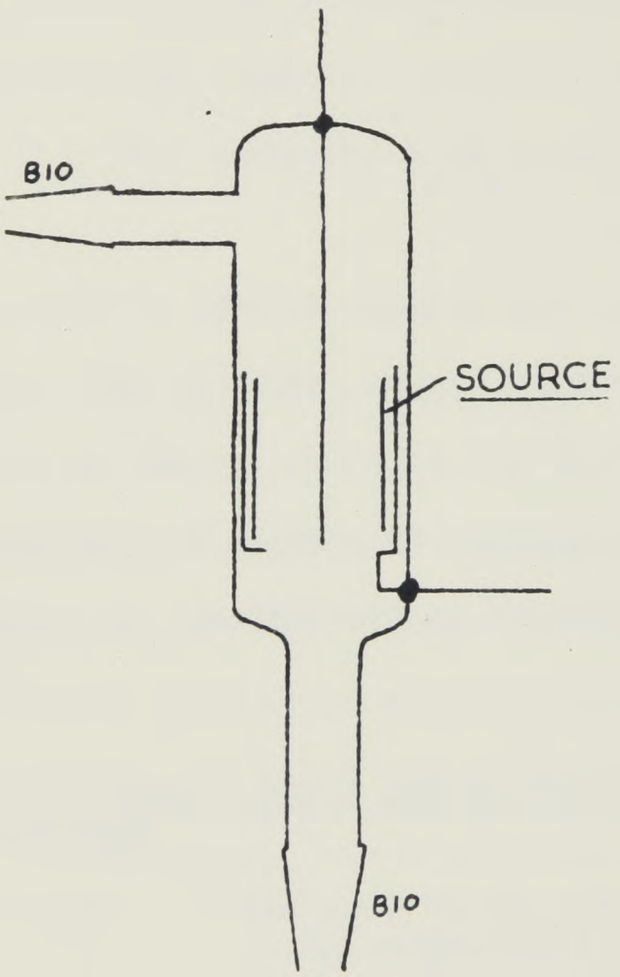
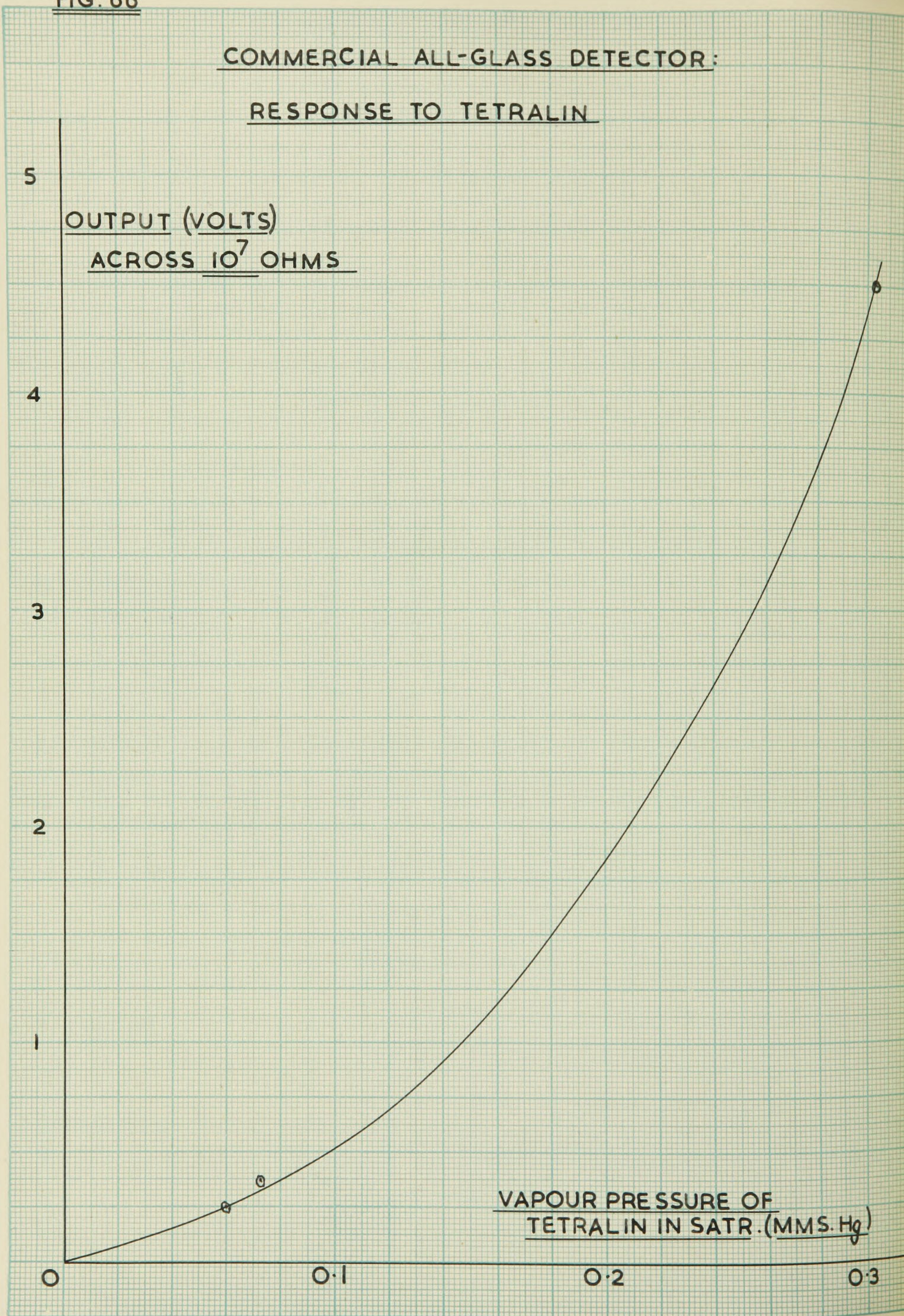


FIG. 65

FIG. 66


COMMERCIAL ALL-GLASS DETECTOR:
RESPONSE TO TETRALIN
OUTPUT (VOLTS)
ACROSS 10^7 OHMS
5
4
3
2
1
0
0·1
0·2
0·3
VAPOUR PRESSURE OF
TETRALIN IN SATR. (MMS. Hg)

Excitation potential of Argon atom = 11.5 e.v.
There is correlation between sensitivities and ionisation potentials, with the exception of monogermane.

6.5 Commercial All-Glass Detector:

Some tests were carried out on a commercial all-glass detector made by Gas Chromatography Ltd. (See Fig. 65)
Results: The standing current (with no sample in the gas stream) was very high. In fact, with the normal 10^9 ohm input resistor in the impedance convertor the voltage developed across the usual 10^9 ohm resistor in the impedance convertor was sufficient to overload the convertor, and a 10^7 ohm resistor had to be used instead, with a consequent 100-fold reduction in sensitivity. (A backing off potential can be added and the 10^9 ohm resistor retained).

Standing current: 1.8 micro-amps.
Even with the polarity of the E.H.T. reversed (probe negative) the standing current was still 0.8 micro-amps., which implies that the insulation is poor.

6.5.1 Sensitivity to Tetralin:

The output was measured at three different concentrations of tetralin in the gas stream - the flow rate being kept constant and the temperature of the saturator varied. The results are plotted in Fig. 66. The response is not linear over the range of concentration, and to work out a comparative sensitivity, the output at a low concentration, (vap. press = 0.1 mm.), has been taken:

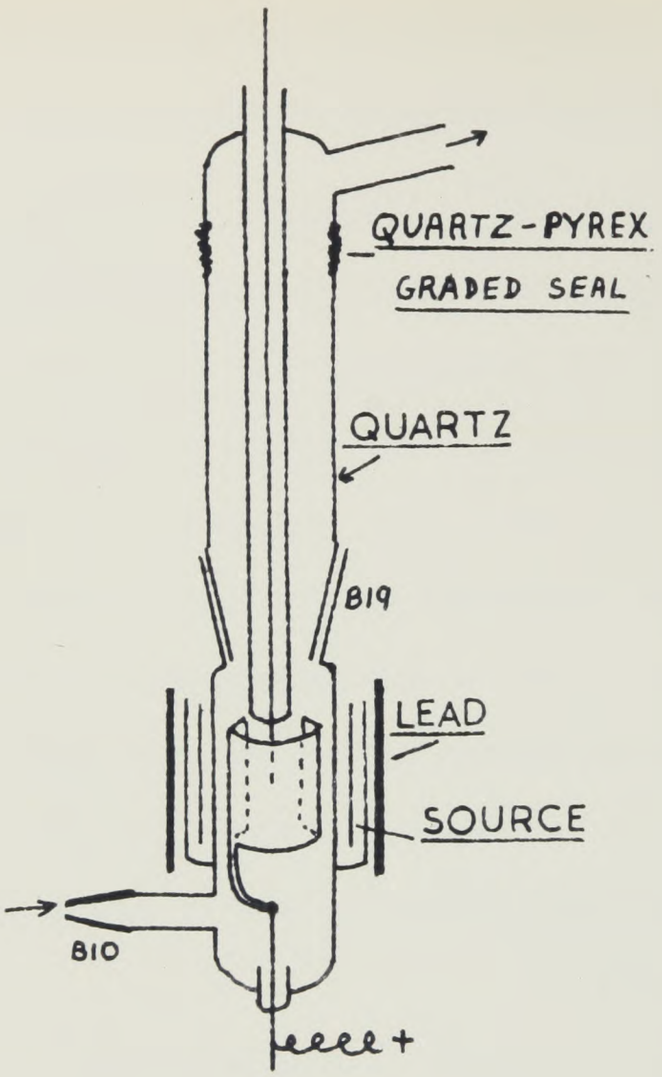


FIG. 67

A vapour pressure of 0.1 mm. corresponds to a concentration of tetralin in the gas stream of 7.7×10^{-7} gms.

Therefore the concentration that would give a signal of 1 volt across 10^9 ohms (assuming linearity)

$$= \frac{7.7 \times 10^{-7}}{0.5} \times \frac{10^{-7}}{10^{-9}}$$

$$= \underline{1.5 \times 10^{-8} \text{ gm./cc}} \quad \text{(At a flow rate of 52.5 cc./min.)}$$

This is higher by a factor of nearly two than the sensitivity of the brass detector at the same flow rate (extrapolated from Fig. 63).

6.6 All-Glass Detector with external source:

With certain corrosive samples there might be some risk of attack on the foil containing the radioactive source with consequent escape of radioactive material into the effluent gas. The makers of the foil, The Radiochemical Centre, Amersham, stated that the strontium 90 was deeply embedded in silver foil, and some 4 - 5 mgm. of silver per sq.cm. would have to be removed to expose it. However it was decided to investigate the possibilities of an all-glass detector with the source outside the ionisation chamber away from all possibility of attack. In view of the poor insulation of the all-glass detector already tested part of the path between the electrodes was made of quartz. The foil was placed in a cup round the ionisation chamber. (The foil was taken temporarily from another detector, being handled with forceps through a small hole in a sheet of $\frac{1}{4}$" Perspex.) See Fig. 67.

Behaviour:

When the gas stream entering the detector was passed through a saturator containing tetralin at room temperature, the detector appeared to give no response at all. The noise level was high.

The tetralin was replaced by liquid chlorine at -95°C., and there was a small response. The concentration necessary to give a signal of 1 volt across 10^9 ohms at an argon flow rate of 18.4 cc./min. would be 2.2×10^{-3} gms./cc.

The high noise level may be due to poor insulation, and the low sensitivity to the fact the electrons from the Sr^{90} must penetrate glass before reaching the argon.

CHAPTER 7

Conclusions

The detectors studied (the flame ionisation, discharge tube, vacuum ionisation gauge, and argon detectors,) are all highly sensitive to organic compounds. The minimum detectable quantities of a typical hydrocarbon (e.g. pentane or benzene,) are equal within the same order of magnitude for all four detectors (10^{-8} - 10^{-7} gms.), although individual sensitivity and noise level figures vary widely. A decrease of about 10 - 100 times in the minimum detectable quantity should be fairly easily realisable in routine use.

The flame ionisation detector has the advantage of being easier and cheaper to construct in a laboratory than the other three. The vacuum ionisation gauge and the discharge tube detectors require glass work and vacuum apparatus, and the argon detector needs careful construction to ensure adequate shielding from radiation. The radioactive source is not easily handled, though this is not often necessary. The electronic apparatus is much the same for three of the detectors, since their output is a small current. A different circuit is used for the discharge tube detector. The argon detector also requires a stable high voltage supply (1000 - 2000 volts.)

The flame ionisation and argon detectors are sensitive to a variety of inorganic compounds. (Flame ionisation: silanes, silicones, stannic chloride, silicon tetrachloride, halogens, hydrogen chloride, Argon: silanes,

monogermane, ammonia, phosphine, hydrogen sulphide). Compounds to which these two detectors are only slightly sensitive or insensitive include:- Flame ionisation: water, carbon disulphide, ammonia, acetylacetone complexes, phosphorus chloronitriles; Argon: methane - at least in small amounts, hydrogen - in amounts less than 4 micrograms). Some compounds give solid, involatile combustion products. The result is a high noise level with the flame ionisation detector, and in larger quantities (greater than about 10^{-4} gms.) the detector may be semi-permanently affected and need cleaning before the noise level returns to normal. The effects can be reduced and the sensitivity to this type of compound increased by reversing the customary polarity of the voltage applied to the detector, (the customary polarity is "jet positive"). There is some evidence that the argon detector is adversely affected by silanes, which may form a deposit on the inner surfaces.

The flame ionisation, argon, and (probably) the vacuum ionisation gauge detectors are not affected by overload (i.e. large samples), but the discharge tube detector is put out of action, until the electrodes are cleaned, by samples larger than about 10^{-4} gms.

The range of sample sizes over which the response remains linear is greater for the flame ionisation detector than for the argon or discharge tube detectors. The behaviour of the argon detector becomes erratic with sample sizes (under typical column conditions,) of the order of 10^{-4} gms., while

the discharge tube detector becomes non-linear at sample sizes of about 5×10^{-5} gms. The linearity of the flame ionisation detector extends to about 4×10^{-3} gms. This figure refers to a hydrogen flow rate of 30 ccs./min., and at lower flow rates the detector becomes non-linear at much lower sample sizes.

The flame ionisation and argon detectors are very suitable for routine gas chromatographic purposes, particularly where high sensitivity is required, (e.g. with types of column restricted to small sample sizes, detection of trace amounts, or work with substances in very small amounts for reasons of danger, or convenience). For a particular problem, apart from the general points of construction made above, the following factors should be considered. The argon detector is sensitive to a greater range of compounds than is the flame ionisation detector; the flame ionisation detector is quite insensitive to water, whereas the response of the argon detector is reduced by it; the range of linear response is some 30 times greater for the flame ionisation detector; the argon detector is non-destructive; the flame ionisation detector is not as suitable as the argon detector for samples which produce solid involatile combustion products.

The discharge tube and ionisation gauge detectors employ more complex means than the other two detectors to attain the same sensitivity, and they are vulnerable respectively to overloading and to failure of

the filaments. Both these detectors seem to be capable of very much higher sensitivity than that obtained in this work although its attainment would be a matter of considerable difficulty and it is doubtful whether it could be exploited in routine use.

Since the completion of this work, both the flame ionisation and argon detectors have been in use in this laboratory for work on some of the types of compound mentioned.

APPENDIX 1 Injection Techniques:

Several ways of introducing samples of known size to the detectors were used. Some samples were stable liquids or solids (e.g. silicones,) other gases (e.g. ammonia, the silanes,) others sensitive to moisture (e.g. stannic chloride,) and each type requires a different technique.

1.1 Flask Dilution: for small samples of volatile stable liquids.

A large flask is fitted with a serum bottle cap and a few Dixon gauze rings put inside. A fairly small amount of the sample is injected into the flask with a micrometer hypodermic syringe and the Dixon rings swirled round to ensure thorough mixing of air and vapour. A known volume of the air plus vapour in the flask is now withdrawn with a syringe (which need not be a micrometer syringe), and injected into the apparatus through a serum bottle cap.

A 2 litre flask was used, with 0.1 ml. of liquid sample added. By extracting 1 ml. of the contents a series of samples equivalent to 0.2 microlitres of liquid could be obtained. Much smaller samples are obtainable by this technique - e.g. 0.001 microlitres.

The method was used with the discharge tube detector (Chapter 5) with pentane samples, and the flame ionisation detector. Both these detectors give a peak corresponding to the air injected. The results are reproducible to about 5%. However the limitation of the method to volatile liquids is a major disadvantage.

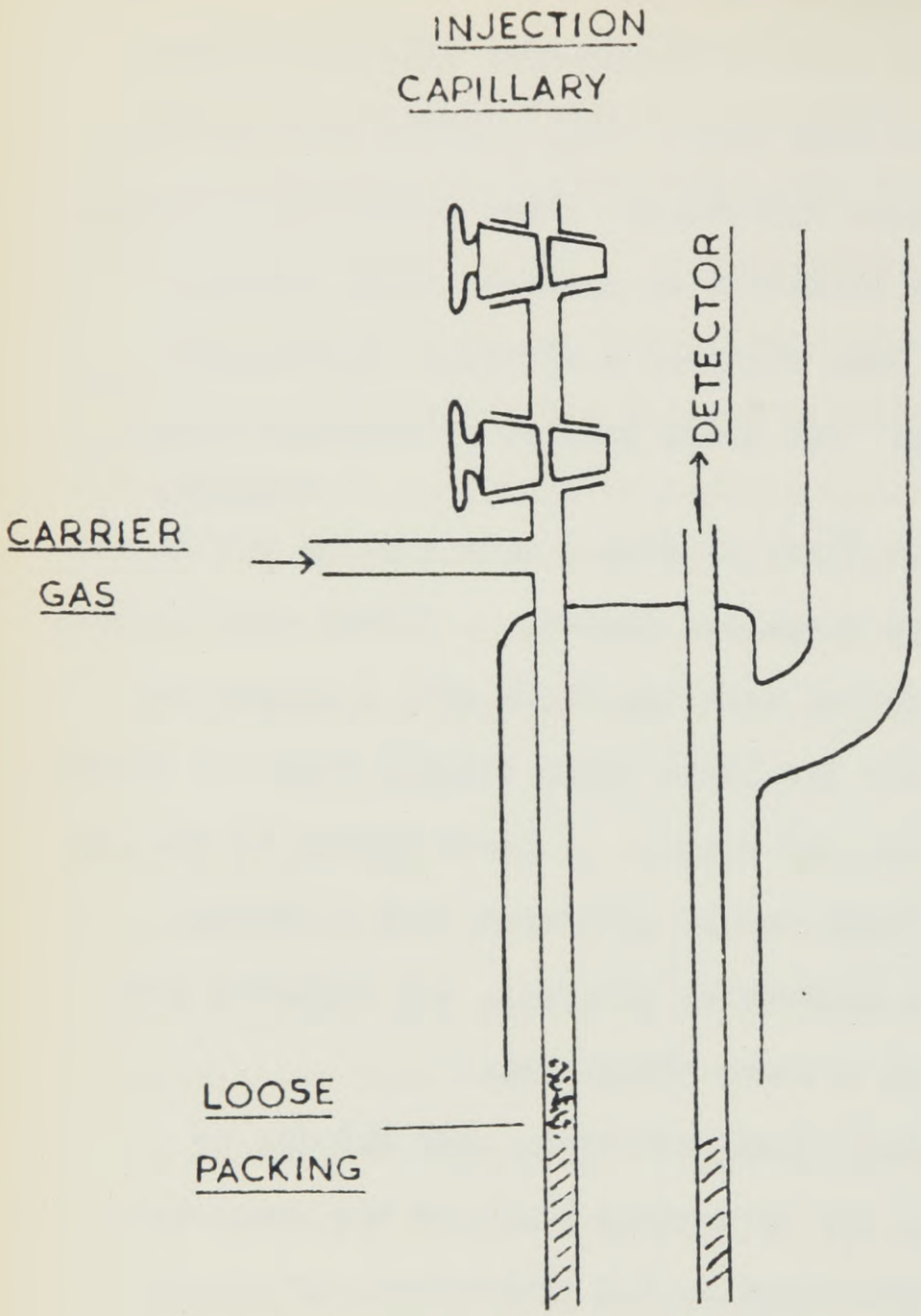


FIG. 68

1.2 Capillary Injection: for fairly small samples of hydrocarbons etc.

A very short length of drawn-out glass tubing is attached to a piece of iron wire about 3 cm. long with "Autostic" cement or "Araldite". A typical capillary would be about 3 mms long and about 0.6 mms. in internal diameter, with a volume of about 1 microlitre. The capillary is filled with sample by dipping its lower end in the liquid, and dropped through two taps (to prevent escape of gas), on to a little loose column packing in the top of the column. (Fig. 68). The capillary is withdrawn with a magnet when required again.

Provided care is taken this method is satisfactorily reproducible. The main sources of error are liquid adhering to the outside of the capillary etc., and failure of the capillary to empty completely. The latter effect was noticed when it was found that a second set of peaks ~~were~~ was obtained when the capillary was withdrawn after an experiment. The capillary could be induced to empty completely by "bouncing" it up and down two or three times with the magnet after putting it in. This failure to empty is surprising since the capillary entered the heated portion of the column, and the effect was often observed with substances whose boiling points were well below the column temperature.

The injection capillaries were calibrated for volume by weighing them several times alternately full of water and empty.

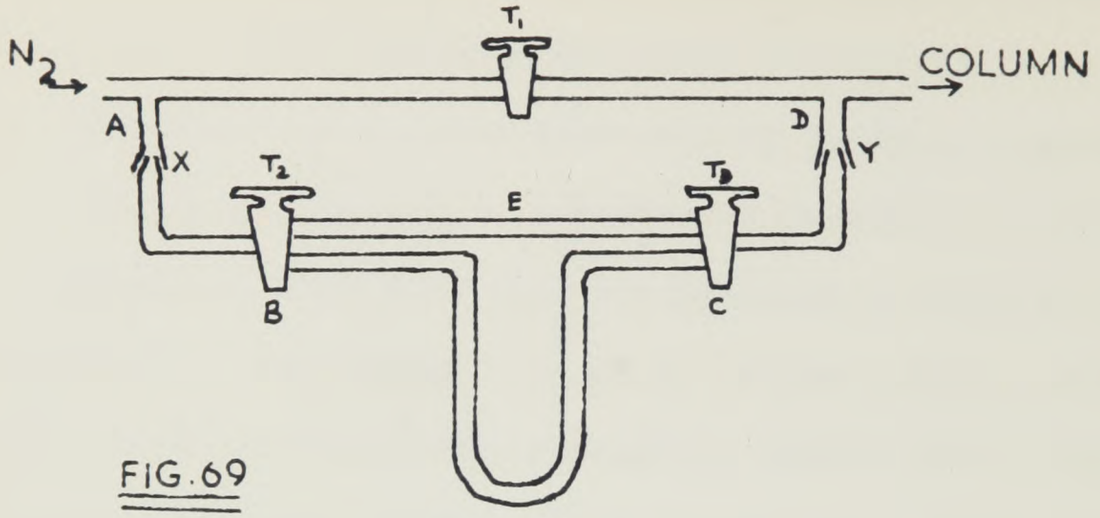


FIG. 69

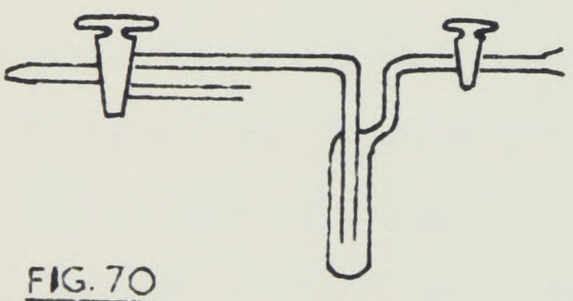


FIG. 70

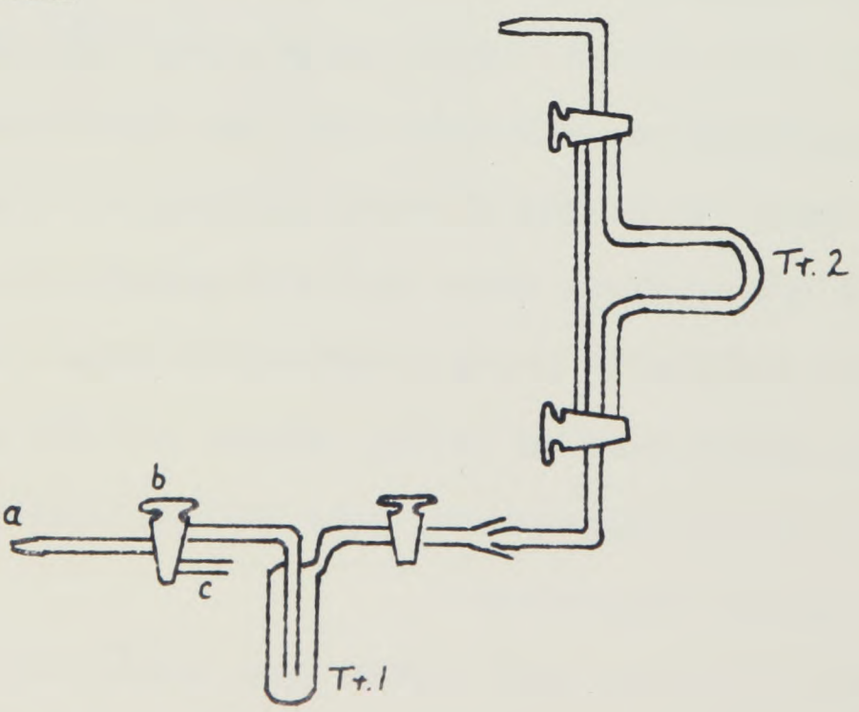


FIG. 71

Smaller and more durable capillaries can be made by using drawn-out semi-capillary instead of ordinary tubing.

1.3 Sample Tubes: used for silanes, ammonia, hydrogen sulphide. (See Fig. 69)

The small U-tube could be filled with sample, attached to the apparatus at X and Y, and the gas flow diverted through it, carrying the sample on to the column. The connecting tubes ABCD were flushed out first by closing T_1 and setting T_2 and T_3 so that gas passed through ABECD.

NH_3 and H_2S: the U-tube was evacuated and then connected to a storage bulb full of gas and allowed to fill at a known pressure. (See Appendix 2)

Silanes (Si_3H_8, Si_2H_6, Si_6H_{14}): were received in a trap as shown in Fig. 70. They were first transferred to the U-tube as follows. (Fig. 71)

H_2 passed through a-b-c (5 mins.) to flush tube a - b.

H_2 " " a, Tr_1 and Tr_2 bypass, with Tr_1 in liq. O_2 (5 mins.) to flush

H_2 " " a, Tr_1 and Tr_2 (5 mins.)

Tr_1 warmed by hot-air blower, with Tr_2 in liq.O_2, to transfer sample.

Tr_2 attached to apparatus, H_2 through by-pass to allow apparatus to settle down.

H_2 diverted through Tr_2, in liq. O_2.

Trap warmed with hot oil at 200°C. to inject sample.

For Si_6H_{14}, the lower vapour pressure and slower rate of

transfer was compensated by running the last stage for some time with the column at room temperature. This gave the silane time to transfer completely, while at this temperature it moves at a negligible rate along the column. The column was then heated and the silane moved through the column, giving a good peak.

1.4 Sample Splitter: Used with cyclopentane on the discharge tube.

The apparatus in Fig. 72 was tested as a means of obtaining very small samples for the discharge tube detector. A sample of about 1 microlitre was injected by means of a capillary on to a short length of loose, uncoated 'Celite'. Carrier gas at about 400 ccs./min. was passed through and a small proportion of this gas stream was led on to the column, most of it going to waste.

Only a small number of experiments were done with this method, and the results were:

Main flow constant at 300 ccs./min:

Peak Areas: 13.6, 21.3, 21.2, 15.5, 22.6

Main flow constant at 400 ccs./min:

Peak Areas: 10.9, 19.2, 6.6, 19.6

The peak areas in each group should, of course, be constant. It is significant that the higher values in each group are in very good agreement, and the low values may well be due to evaporation of the very volatile cyclopentane from the capillary while it was being inserted.

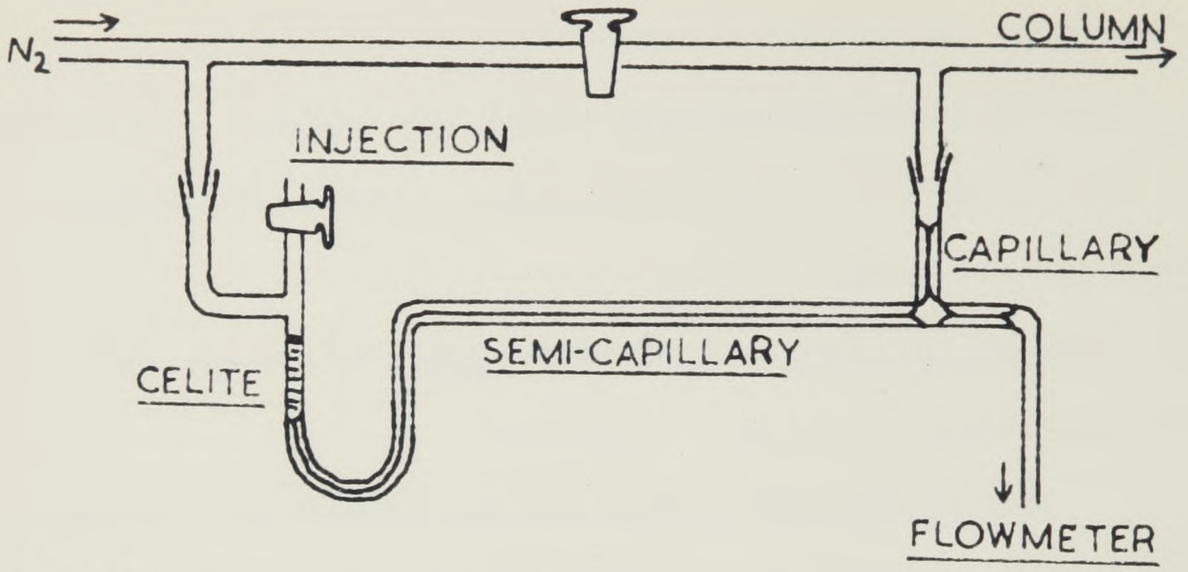

N_2
COLUMN
INJECTION
CAPILLARY
SEMI-CAPILLARY
CELITE
FLOWMETER

FIG. 72

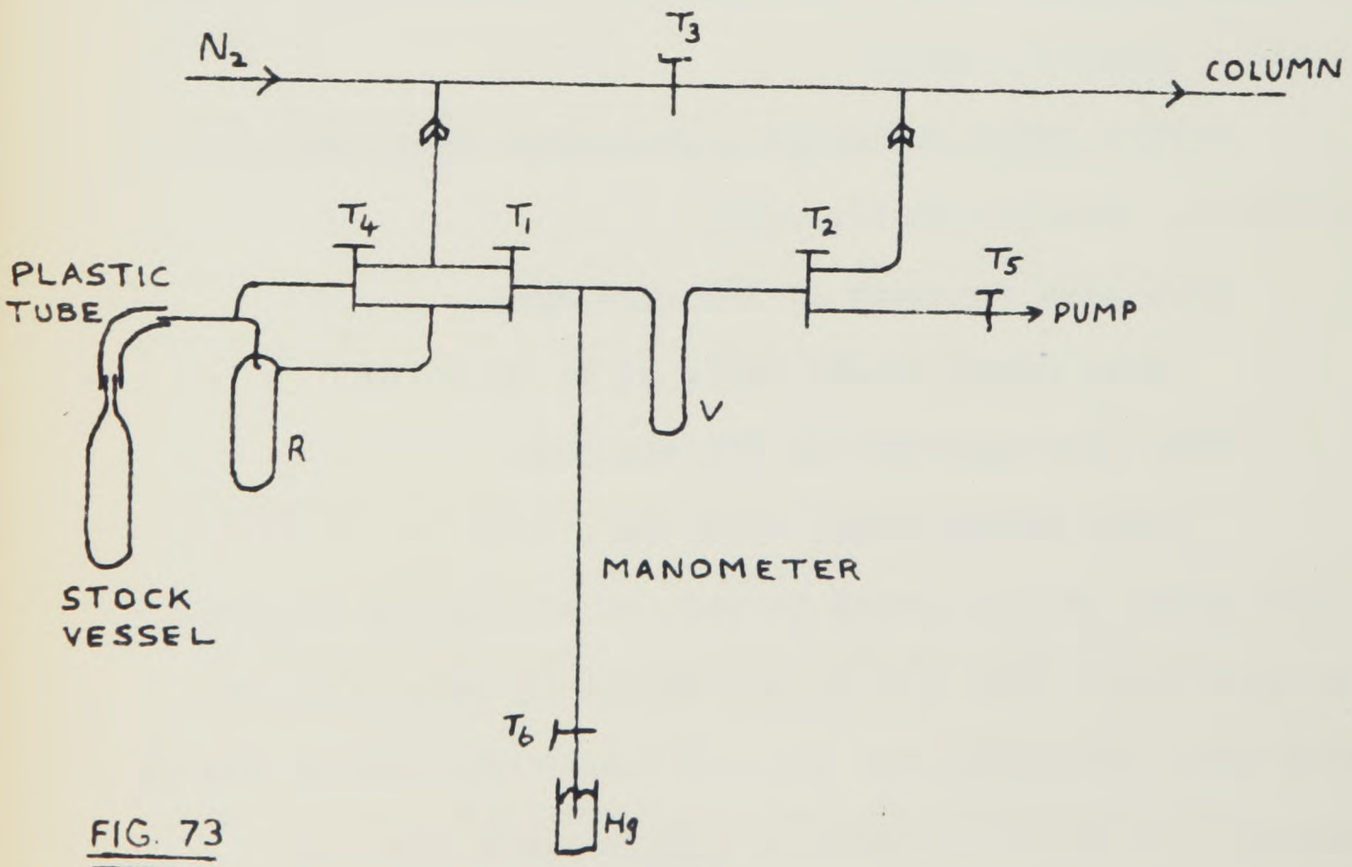

N_2
T_3
COLUMN
T_4
T_1
T_2
T_5
PLASTIC TUBE
PUMP
R
V
MANOMETER
STOCK VESSEL
T_6
Hg

FIG. 73

7.1.5 "Constant Volume" Apparatus: Toluene, Benzene, Stannic Chloride.

Principle: To fill a small trap (V) of known volume with sample vapour at a measured pressure from a reservoir (R) and inject from the trap. See Fig. 73).

Procedure:

1). Evacuate through T_5, T_2 & T_1; "stock vessel" (S) cooled in liq. O_2.

2). Close T_1; allow "stock vessel" to warm up. Pour liquid into Reservoir R. By opening T_4, dry N_2 can be admitted to stop the liquid from S when desired. Clip plastic tube P.

3). Cool R in liq.O_2. Open T_1 and evacuate R. Read pressure (P_1). Close T_2.

4). Warm R by replacing liq. O_2 by cold water. Close T_1 when pressure of vapour has built up to about 15 - 20 mms.

5). Cool V in liq. O_2; evacuate if pressure does not fall to P_1.

6). Warm V with cold water. Read pressure (P_2).

7). Cool V in liq. O_2. Read pressure (P_3). ($P_2 - P_3$) is the value used.

8). Close T_6 to prevent gas blowing out of bottom of manometer. Fill V carefully with N_2 via T_1. Close T_1.

9). Warm V with hot-air blower, close T_3 and open T_2 then T_1 to inject sample.

The apparatus was tested with benzene, and worked satisfactorily. The peak areas obtained were widely scattered, and the input resistor in the impedance convertor

was replaced. Further experiments with stannic chloride gave much better results. Two experiments on benzene with a "Vibron" Electrometer (see end of Ch.1) gave results within 7% of each other.

Results with Stannic Chloride:

In the previous experiments with toluene, the carrier gas had been allowed to pass through the injection trap (cooled in liquid oxygen) for a short time before injection. With $SnCl_4$, it was found that the sample tended to be carried out of the trap under these conditions, and so this was not done.

Seven experiments with a mean deviation of 6.5% for $\frac{\text{Peak Area}}{\text{Pressure of Sample}}$ give a value for the sensitivity of:

Rate of entry of sample for a detector current of 10^{-9} amps. $= \underline{1.7 \times 10^{-7} \text{ gms./sec.}}$

1.6 Sealed Tube injection Method: Toluene, Stannic Chloride

Principle: Sealed tubes of known volume were filled with sample vapour at its own vapour pressure under vacuum. The sealed tube is inserted into the apparatus, and after evacuation the tube is broken and its contents transferred to a cooled trap from which it is injected.

Procedure:

Filling the tubes: see Fig. 74.

Test tubes were drawn down at as near the same place, estimated by eye, as possible. To find their volume they were then filled with carbon tetrachloride from a burette to the narrowest part. The level of liquid was marked on the tube with a wax

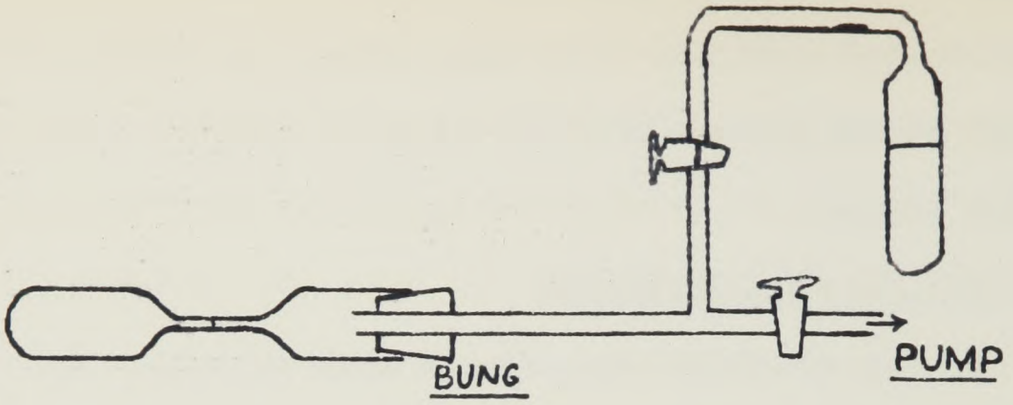

BUNG
PUMP

FIG. 74

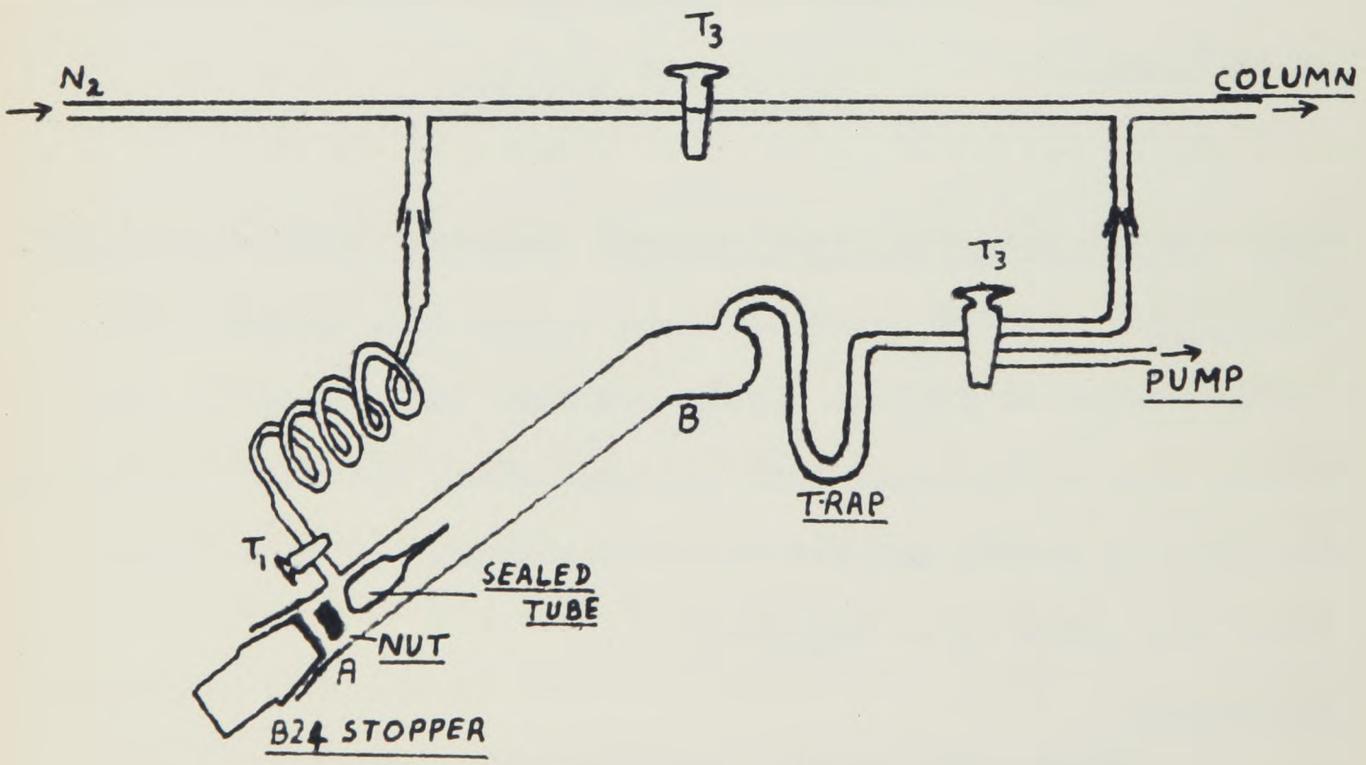

T_3
N_2
COLUMN
T_3
PUMP
B
T-RAP
T_1
SEALED TUBE
NUT
A
B24 STOPPER

FIG. 75

pencil and the volume of CCl_4 recorded together with an identification letter, also marked on the tube. The tubes were emptied and dried for at least an hour in an oven. (CCl_4 was used rather than water because it dried out more easily).

For the actual filling the tube was fitted on to the rubber bung B, and evacuated. The vessel of sample was then evacuated while cooled in liquid oxygen. The apparatus was isolated from the pump, and with the sample vessel surrounded by a bath of water or ice and water, the vessel and tube were connected and the sample allowed to fill the tube at its own vapour pressure. The tube was then sealed off with a very tiny flame at the mark on the neck.

Initially a three-way tap was used. This had a very narrow bore, which easily clogged with grease, so it was replaced by the two two-way taps as shown in Fig. 74.

Transference from Sealed Tube to Injection Trap: See Fig. 75. The tubes were inserted through A, a large nut put in behind them and the stopper replaced. The apparatus was then evacuated. (T_1 was closed and T_3 open to allow carrier gas to flow on to the column.) Next, T_2 was closed and the U-tube cooled in liquid oxygen. By means of a strong magnet the nut was moved sharply to the right, and the sealed tube was broken when its tip became jammed in the bend B. The construction at this point was such as to stop fragments of glass finding their way into the trap and then blocking tap T_2, as occurred in the first version of this apparatus. After sufficient time for the sample to transfer to the trap, T_3 was closed and

T_1 and T_2 opened to pass carrier gas through the trap. Then the trap was warmed to inject the sample.

Results with Toluene:

Experiments with toluene showed that this method needed care, particularly in keeping the bores of the taps free from grease etc., in keeping the ice and water bath round the sample vessel well stirred, and in sealing off the tubes so that no punctures appeared. It was also found that the tubing carrying sample vapour on to the column had to be electrically heated. The results, eight in number, give a mean value for the ratio

$$\left(\frac{\text{Area in sq.ins.} \times 10^{-2}}{\text{Tube vol.in ccs.}} \right)$$ of 38.4 with a mean deviation of 8.4%

The sensitivity from these figures is 1.5×10^{-7} gms/sec. for a detector current of 10^{-9} amps.

Results with Stannic Chloride:

Values of the ratio $\frac{\text{Peak Area}}{\text{Tube vol.}}$ vary considerably (a factor of 35 between extremes). There is some correlation between particularly large peaks and the fact that a sealed tube had been allowed to stand for more than an hour or two before being used. The retention volumes were identical whether the peak was large or small, thus making decomposition into some product which gave a signal greater than the stannic chloride very unlikely. With the column at room temperature two peaks, differing in area by a factor of 12, had retention volumes of 1040 ccs. and 1067 ccs. (2.6% difference). Both

peaks were well shaped, and it is therefore unlikely that decomposition was occurring on the column (of 'Apiezon L' vacuum grease on 'Celite', about three feet long). The column was removed to check this point, and replaced by a length of capillary tubing which provided roughly the same resistance to gas flow as the column, but peak areas were still widely scattered. The most likely contaminant is water, especially since in a sample that had been left there often appeared tiny white particles adhering to the inside surface of the tube, suggesting a hydrolysis product. However, HCl would be expected to be formed as well, and there was no peak in the place where HCl would be expected, i.e. with a retention volume almost the same as the dead volume of the column. (See Chapter 3 for the response to HCl.)

Cleaning the detector jet, or the taps in the apparatus had no effect on the results.

Results: A rough value for the sensitivity has been worked out from the results.

Ave. flow rate of H_2 = 26 ccs./min.;

Ave. flow rate of N_2 = 23 ccs./min.;

Flame Temp. = approx. 1100 - 1200°C.

Mean Sensitivities:	Large Peaks	Small Peaks
(volt-mins./gm.)	3.13×10^{3}	4.14×10^{2}
Rate of Entry for a signal of 10^{-9} amps. (gms./sec.)	5.4×10^{-6}	4.1×10^{-5}

For a comparison of these results with those from other methods see section 3.8.

1.7 Saturators: (used for toluene, carbon tetrachloride, stannic chloride, silicon tetrachloride, chlorine, bromine, iodine, acetone and tetralin.)

Principle: The carrier gas, before entering the detector, is passed through a device which saturates it with the vapour of the sample. If the flow rate of the gas and the vapour pressure of the sample are known, the rate of entry of sample into the detector can be worked out and the response calculated.

The advantages of the method are:

1). the linearity of the detector can easily be checked, since the signal should be proportional to the flow rate of carrier gas. In all the saturator experiments with the flame ionisation detector, the double jet arrangement was used, and so the flame remains constant, apart from changes in temperature due to the addition of nitrogen, which are fairly small over the range of flow rates used (0 - 30 ccs./min.) (See Chapter 2 and Appendix 5).

2). Any erratic behaviour of the detector can be quickly seen, as variations in the signal. The effect of small modifications can be seen much more easily than when separate injections are being used.

3). Effects of changes in operating conditions on the sensitivity and the noise level can be immediately seen.

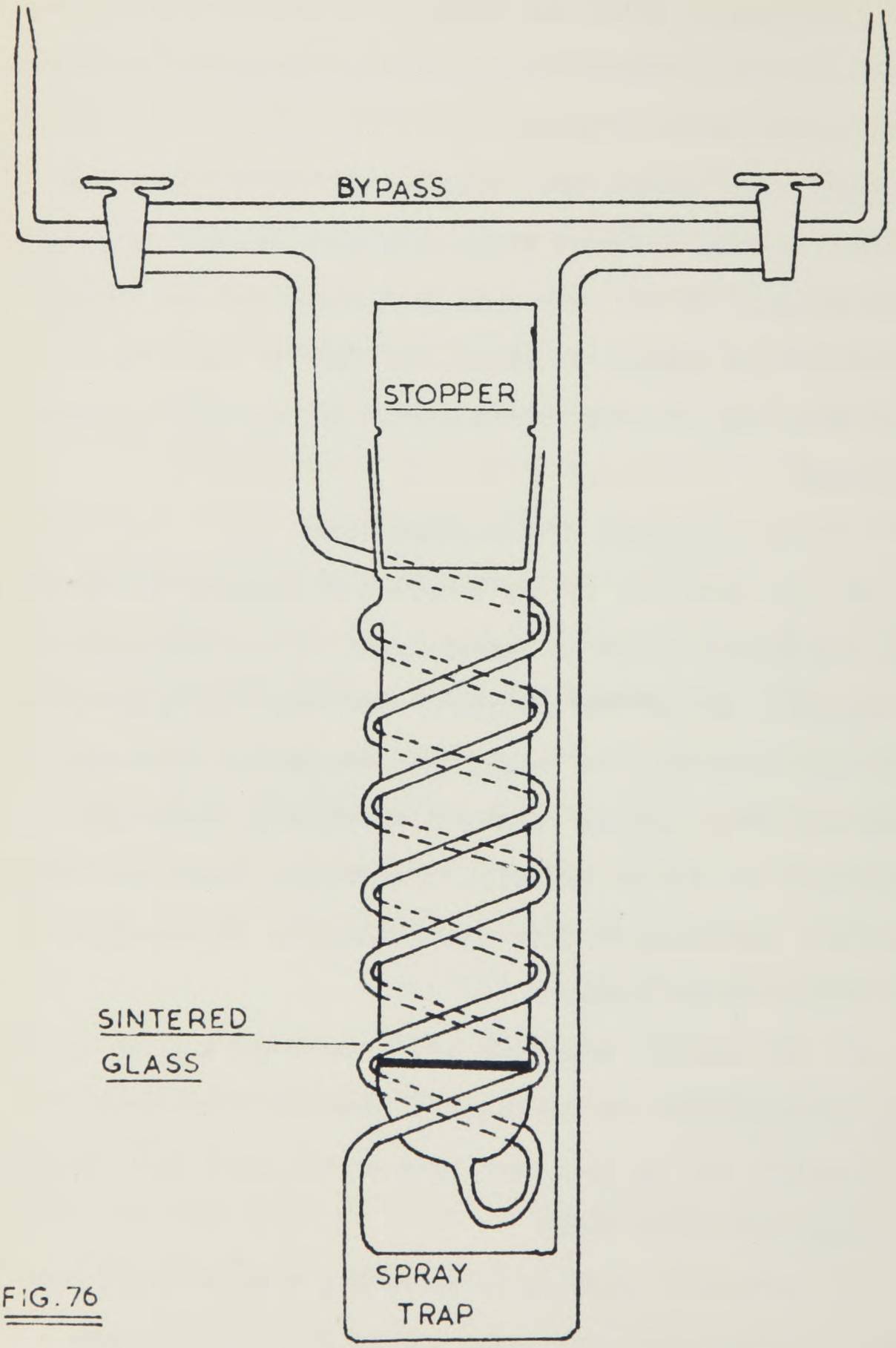


FIG. 76

With a particular sample, the range of vapour concentration is limited, since the sample cannot be used below its freezing point (or above its boiling point, though this is much less important). For low vapour concentrations in these experiments, tetralin was used. Its vapour pressure at room temperature is about 0.3 mms., representing a vapour concentration of 0.04% molar.

Procedure: Saturators had been used previously in this laboratory by a worker studying katharometers, and his design was followed in all essentials. See Fig. 76.

The main features were: The incoming gas was passed through a spiral to give it time to attain the temperature of the bath. It then passed through the liquid, supported on a fine sintered glass disc, as a stream of fine bubbles. The saturatedd gas passed through a further spiral to ensure equilibrium, through a small chamber designed to hold any condensed vapour, and out into the detector. On the one occasion when the saturator was being used above room temperature (with iodine), the tubing connecting it to the detector was electrically heated.

The by-pass enabled the signal produced to be immediately compared with the 'zero' signal produced by pure carrier gas.

Another design had no sintered glass disc, but the body of the saturator, of the same size and shape as the one above, was half-filled with small glass beads. This was effective, the main disadvantage being that the glass beads

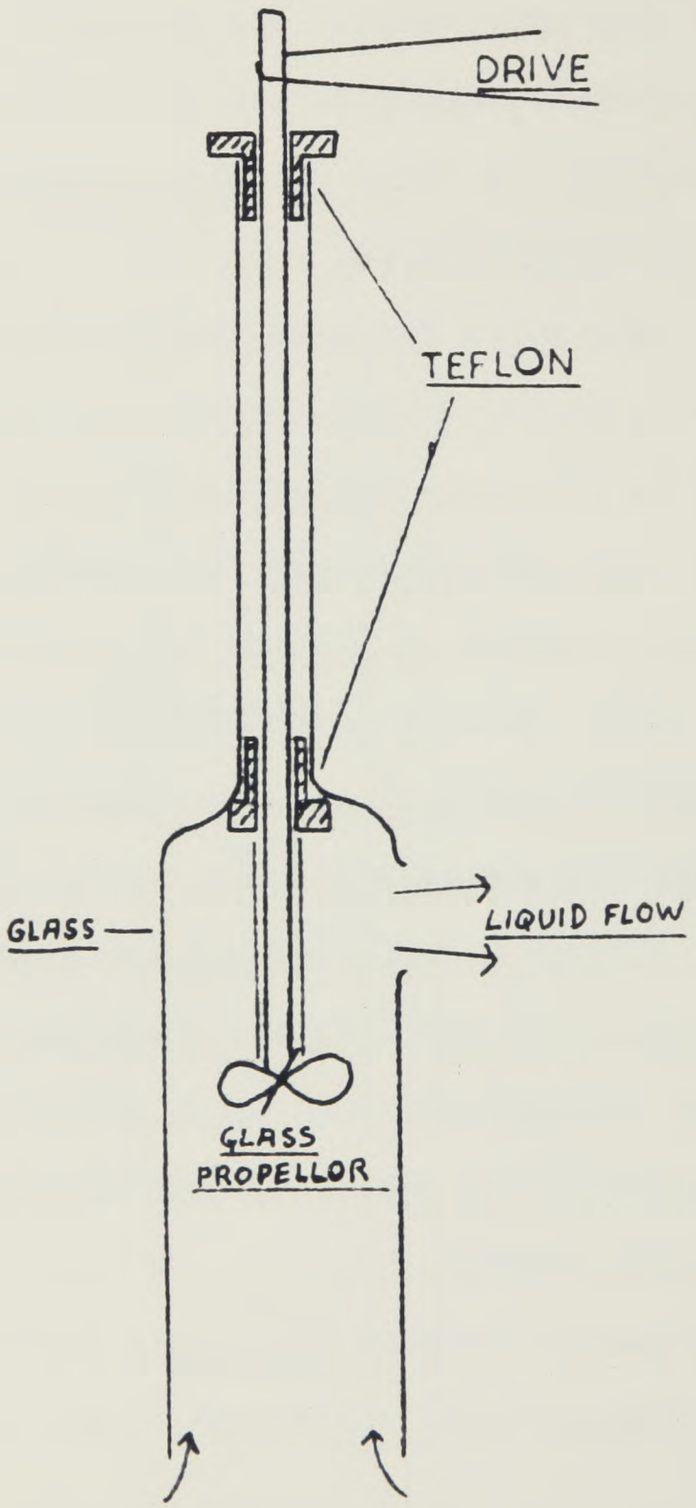


FIG. 77

tended to find their way into the bores of the taps and block them.

To keep the temperature constant, the saturator was immersed in a variety of baths, mostly 'equilibrium baths' of a partly frozen liquid in a wide-mouthed Dewar vessel. The solid-liquid baths were stirred with the device shown in Fig. 77, which was proved very effective.

Cooling of the baths from room temperature was done with solid CO_2, or, since this tended to produce lumps, particularly in the later stages, with liquid oxygen in a test-tube or a closed copper tube about 1" in diameter. The temperatures were measured with an alcohol in glass thermometer.

Filling the Saturator: Some moisture-sensitive samples, e.g. $SiCl_4$ and $SnCl_4$, and liquid chlorine for a different reason, had to be put into the saturator by special methods.

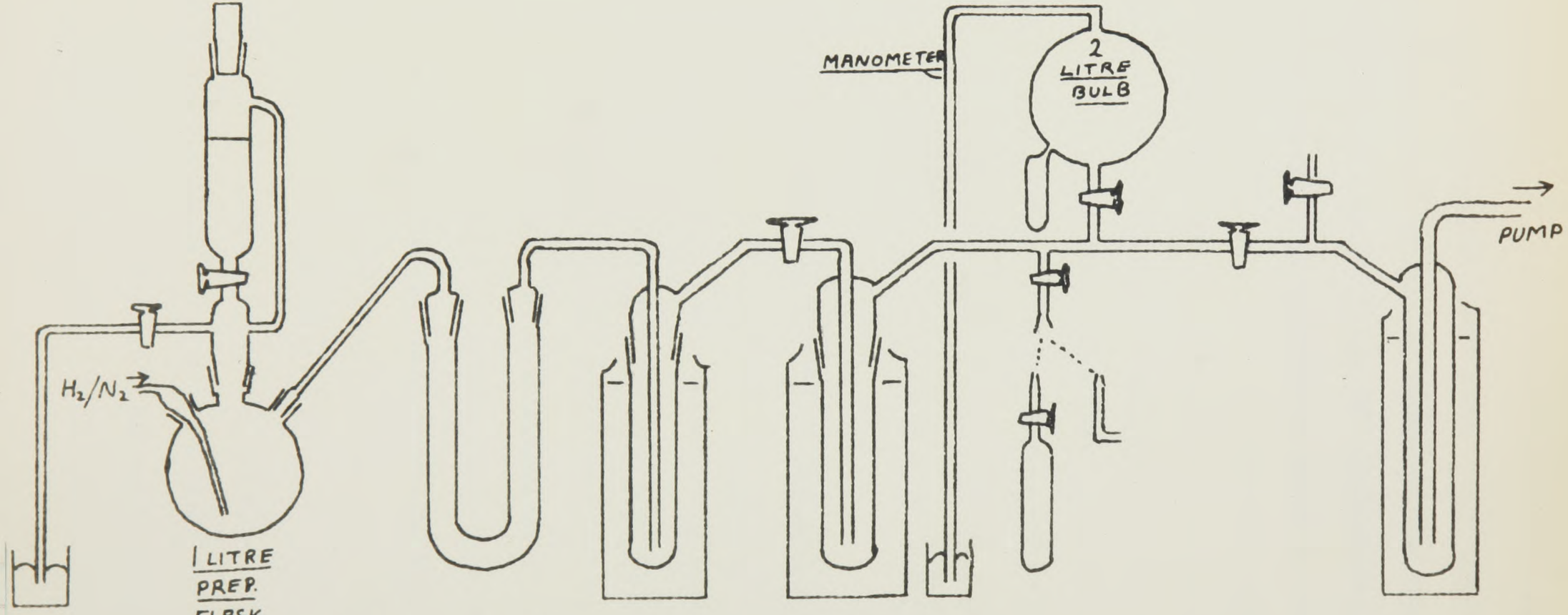
$SiCl_4$ and $SnCl_4$: The saturator was detached from the apparatus and the stopper in it was replaced by a ground-glass joint with a tube attached. The bottle of sample was joined to this with a flexible plastic tube, and the saturator exhausted, through one of the two-way taps, with the plastic tube clipped. Then the tap was closed, the clip opened, and the liquid poured in. With a second clip on the plastic tube the tube could be cut between the clips to remove the sample bottle. The saturator was emptied later by merely evacuating it and allowing the liquid to evaporate into the pump trap (cooled in liquid oxygen), whence it could be

disposed of.

Liquid Cl_2 : The empty saturator was put into liquid oxygen and chlorine passed in from a cylinder until enough had condensed. It had of course to be kept cold continuously to avoid a build-up of pressure and an escape of chlorine.

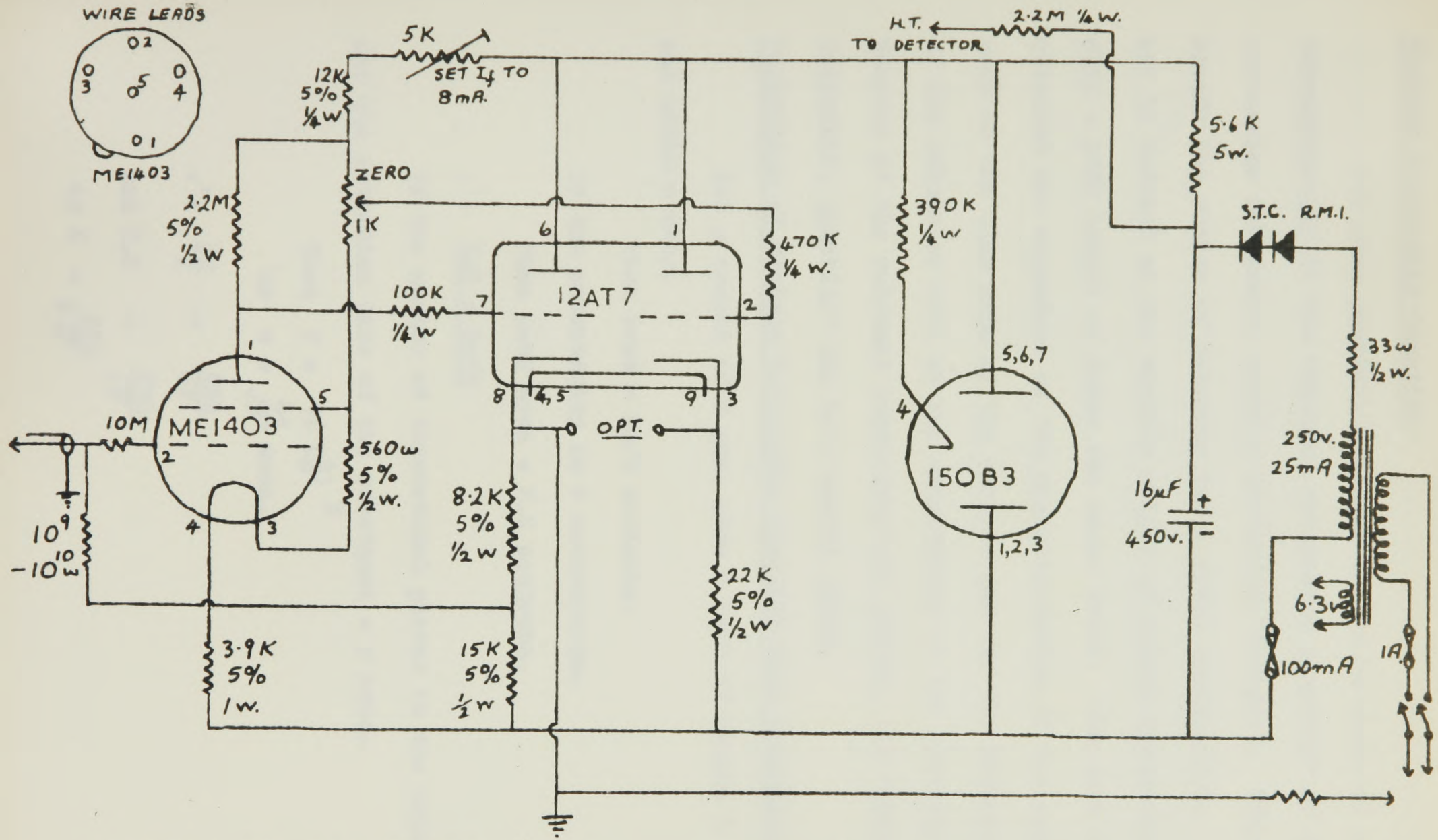
Apparatus for Preparing and Storing GeH_4, PH_3, H_2S, NH_3.

Also for filling Sample tubes to a Known Pressure.



	Funnel	Flask	U-tube	1st trap	2nd trap
GeH_4	3% H_3PO_4	Mg_2Ge	SiO_2 + P_2O_5	ice + water	liq O_2
PH_3	3% H_3PO_4	Ca_3P_2	"	"	"
H_2S	3% H_3PO_4	CaS	"	"	"
NH_3	—	'880' ammonia	"	"	"

APPENDIX 2



IMPEDANCE CONVERTOR (DESIGNED BY A.E. THOMPSON.)

ENCLOSED IN SEALED, DESICCATED METAL BOX.

APPENDIX 3

APPENDIX 4

Minimum Detectable Quantity

For many purposes a useful figure to users of gas chromatography is the "minimum detectable quantity" of a particular substance, using a particular detector. This may decide the choice of detector for a given application. It may be defined as the minimum weight of sample necessary to give a peak height of twice the noise level. The peak heights obtained are dependent on the characteristics of the apparatus, such as the flow rate of the carrier gas and the efficiency of the column as well as the sensitivity of the detector. However if the relevant conditions are stated, the "minimum detectable quantity" can be a useful guide.

Derivation of Minimum Detectable Quantity from Sensitivity.

Let a sample of X gms. give a peak of height h amps. and width w secs.

Then area = hw/2 coulombs.

If the sensitivity is S coulombs/gm.

Then peak area = X.S coulombs.

$\therefore$ $X.S = hw/2$

If the number of theoretical plates in the column = P, and the retention time of the substance = r secs.

$$\text{Then } P = 16 \left(\frac{t}{w}\right)^2$$

$$\text{or } w = \frac{4t}{\sqrt{P}} \text{ secs.}$$

$$\therefore \frac{hw}{2} = \frac{2th}{\sqrt{P}}$$

$$\text{and } X.S = \frac{2th}{\sqrt{P}}$$

$$\text{or } X = \frac{2th}{S\sqrt{P}}$$

Let the series resistor be R ohms, and the gain of the impedance convertor be G, then a detector current of h amps. corresponds to an output from the impedance convertor to the attenuator of hRG = H volts.

$$\text{Then } X = \frac{2tH}{S\sqrt{P}\,RG}$$

If $Q_{min.}$ is the sample (in gms.) required to give a signal of twice the noise level, and the noise level = N volts. (output from the impedance convertor,)

$$\text{Then } Q_{min.} = \frac{4tN}{S\sqrt{P}\,RG}$$

APPENDIX 5

The Effect on the Signal of Small Changes in the Flame Temperature:

Using the Saha equation: (14 & 28)

$$\log_e K = \log_e \frac{x^2}{(1-x^2)} \cdot P = \frac{-U}{4.57\,T} + \frac{5}{2}\log_e T - 6.49 + \log_e \frac{g_{A^+} \cdot g_e}{g_A}$$

where:

A is the species being ionised in the flame

$$A = A^+ + e$$

K is the equilibrium constant for the ionisation

x is the degree of ionisation and also the yield in electrons/mol.

P is the pressure

U is the ionisation energy of A in cals/mole.

T is the absolute temperature

g_{A^+}, g_e and g_A are the statistical weights of the various species.

$$\log_e K = \frac{A}{T} + B \log_e T - 6.49 + C$$

differentiating with respect to T:

$$\frac{d \log_e K}{dT} = \frac{A}{T^2} + \frac{B}{T}$$

$$= \frac{(23000)\ (4)}{(4.57)\ (1600)^2} + \frac{2.5}{1600} \qquad \text{putting } T = 1600^\circ A. \text{ and } U = -4 \text{ electron volts.}$$

$$= 0.0094$$

$$\frac{d \log_e K}{} = \frac{1}{K}\frac{dK}{dT}$$

$$\text{or } \frac{dK}{dT} = K.\frac{d \log_e K}{dT}$$

$$= 0.0094.K$$

$$dK = 0.0094.K dT$$

or applying this to finite differences:

$$\Delta K = 0.0094\, K \Delta T$$

Now $K = \frac{x^2}{(1-x^2)}.P$ = approx. $x^2.P$ since x is very small.

$$\frac{dK}{dx} = 2xP$$

$$dx = \frac{dK}{2xP}$$

$$\frac{dx}{x} = \frac{dK}{2x^2.P} = \frac{dK}{2K}$$

Applying to finite differences:

$$\frac{\Delta x}{x} = \frac{\Delta K}{2K}$$

$$= \frac{0.0094\, K \Delta T}{2K}$$

$$= 0.0047.\Delta T$$

If the flow rate of N_2 changes from 15 - 30 cc./min., then

ΔT = about $30^{\circ}A$.

Therefore $\frac{\Delta x}{x} = 0.0047 \times 30$

$$= \underline{0.141}$$

$$= \underline{14\ \%}$$

APPENDIX 6

Calculation of Ionisation Potentials from the Flame Ionisation Detector Results:

(References 14 & 28)

Saha Equation:

$$\log_e K = \log_e \frac{x^2}{(1-x^2)} \cdot P = \frac{-U}{4.57\,T} + \frac{5}{2}\log_e T - 6.49 + \log_e \frac{g_{A^+} g_e}{g_A}$$

where:

A is the species being ionised in the flame

$$A = A^+ + e$$

K is equilibrium constant for the ionisation

x is the degree of ionisation

P is the pressure

U is the ionisation energy of A in cals./mole.

T is the absolute temperature

g_{A^+}, g_e and g_A are the statistical weights of the various species.

ignoring the last term in the equation:

$$-U = 4.57\,T\,(\log_e K - 5/2 \log_e T + 6.49) \quad \text{- - - - - - - (1)}$$

Now if the rate of entry of the sample to the detector for an output of 1 volt across 10^9 ohms = R gms./sec., or R/M moles/sec. where M is the molecular weight of the sample:

R/M moles/sec. gives a current of 10^{-9} amps.

$= 10^{-9}$ coulombs/sec.

$= 6.3 \times 10^{18} \times 10^{-9}$ electrons/sec.

$= 6.3 \times 10^9$ electrons/sec.

$\therefore$ R/M x 6 x 10^{23} molecules/sec. yields 6.3 x 10^9 electrons/sec.

$\therefore$ Degree of ionisation =

$$\frac{6.3 \times 10^9}{R/M \times 6 \times 10^{23}} = \underline{1.05\ M/R \times 10^{-14}}$$

From this the equilibrium constant can be found and substituted in equation (1).

The ionisation potential in electron volts then equals

$$\frac{U}{23000}$$

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ABSTRACT

Some Studies in Gas Chromatography with Special Reference to Vapour Detectors.

An essential part of a gas chromatographic apparatus is a vapour detector capable of monitoring vapour concentrations in the gas stream emerging from the column. When this work was started (1958), there were three "high-sensitivity" detectors known, (capable of detecting less than 10^{-6} gms.) They were:

1) The flame ionisation detector: Vapour enters a small flame of hydrogen burning in air where it is thermally ionised. A polarising voltage is applied between two electrodes, one of which is usually the metal burner. The ion concentration in the flame allows a current to flow through an external circuit where it is made to drive a recorder.

2) The discharge tube detector: The potential drop across a low pressure gas discharge is very sensitive to small concentrations of impurities. Very small amounts of vapour can therefore be detected by passing the carrier gas into a continuously pumped discharge tube, and using the potential drop across the tube to drive a recorder.

3) The triode ionisation gauge: This piece of apparatus is normally used for low-pressure measurement. Molecules of gas or vapour in the gauge are ionised by electrons from a hot filament, which are accelerated by a positive potential on a suitable electrode. The ions are attracted to a negatively charged collector electrode.

When applied to gas chromatography, part of the carrier gas is fed into a continuously pumped ionisation gauge and the accelerating potential is adjusted so that it is insufficient to ionise the carrier gas molecules, but high enough to ionise molecules of vapour. The ion current constitutes the output from the detector.

Detectors of each of these three types have been built and tested. This was done with the object of assessing their relative merits in various applications, in this laboratory and elsewhere, for which less sensitive detectors had been found inadequate. The parameters compared include simplicity of construction and operation, reliability under operating conditions, noise levels with, and suitability for, various types of sample, and sensitivities, both of one detector to a range of compounds,,and of different detectors to the same compound.

The flame ionisation detector has the merits of simple and rugged construction (although for the highest sensitivity the detector and the electronic "impedance convertor" must be carefully made.) It is highly sensitive, particularly to hydrocarbons, and has a low (potentially very low) noise level. Various detectors were built, differing in details of construction, and the merits of the different arrangements compared. The final form adopted incorporated a "concentric double burner," in which the sample in a stream of nitrogen was fed directly into the flame by a narrow tube inside the actual burner. This was to avoid the possibility of reaction between hydrogen and some of the samples, which might have occurred if the

nitrogen and hydrogen were mixed before the flame, as is the usual practice. The use of separate gas flows for flame and carrier allows them to be adjusted independently.

With certain samples, in particular those, such as compounds of tin and silicon, which give involatile oxides on combustion or pyrolysis, there was considerable noise of a "spiky" kind. This could largely be eliminated by reversing the customary polarity of the high polarising voltage (the usual polarity is 'jet negative,') and by using an unusual type of electrode - a wire ring or metal foil cylinder.

This detector is not damaged by overload, and is completely insensitive to water: two properties which make it very suitable for biological problems. This has been shown by some work on the scents of moths; the compounds of interest being present in trace amounts in excess of water.

The response of the flame ionisation detector to the following compounds has been checked, and in most cases values for the sensitivity have been obtained: hydrocarbons, carbon tetrachloride, and many other organic compounds, mono-, di-, tri-, and hexa-silanes, silicones, phosphorus chloronitriles, silicon tetrachloride, stannic chloride, chlorine, bromine, iodine, hydrogen chloride, metal acetylacetonates, carbon disulphide, ammonia.

For theoretical work on the flame ionisation detector a knowledge of the flame temperature under various conditions is needed. Measurements were made on the detector used in the rest of this work,

by the sodium line reversal method, and by small thermocouples. The value obtained was about 1380°C. at a large burner and about 1700°C. at a small one. (H_2 flow rate: 50 cc./min.)

The triode ionisation gauge is potentially very sensitive indeed to organic compounds and the noise level is low. However the filaments are very susceptible to "poisoning," and the requirements in vacuum apparatus are exacting.

The discharge tube detector is very sensitive, but the noise level is high. The minimum detectable sample is roughly the same as that for the flame ionisation detector, though the absolute sensitivity is much greater. The detector overloads easily and the electrodes become contaminated and the discharge is extinguished, but samples smaller than 10^{-4} gms. have no adverse effect.

After the work had begun a fourth high sensitivity detector was announced, the argon ionisation detector. Here vapour molecules carried in a stream of argon are ionised by collision with excited argon atoms. The excited argon atoms are produced by bombardment with electrons, accelerated by a potential of 1000 - 2000 volts. Radiation from a radioactive source within the detector provides the electrons by ionisation of argon atoms. The ion current is monitored.

Some work was done on this detector, and it was seen to be capable of very high sensitivity along with a very low noise level, but to be liable to erratic behaviour if the samples were too large. It is the only one of the four detectors which is non-destructive (although the triode ionisation gauge usually takes only

a portion of the sample.)

The approximate response of the detector to some organic and inorganic compounds has been determined. They include mono- and di-silane, monogermane, ammonia, phosphine and hydrogen sulphide.

Two variant forms of this detector were also briefly investigated: a commercial all-glass detector, and an all-glass detector with the source of radiation outside the ionisation chamber, both of which may be useful for corrosive samples.

Various methods of injection of known amounts of sample have been used: a capillary of known volume filled with sample, injection of vapour from a trap of known volume at a known pressure, injection from sample tubes filled with vapour at a known temperature and pressure and sealed, and continuous saturation of the gas stream with vapour from a sample at a known temperature. The last method was the most satisfactory where it was applicable.