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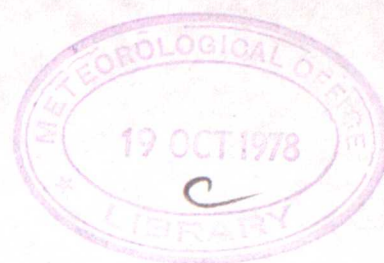
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MET.O.15 INTERNAL REPORT

No. 003

A GAS CHROMATOGRAPH FOR ATMOSPHERIC TRACE GAS ANALYSIS

BY

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DATE : DECEMBER 1976

Cloud Physics Branch (Met.O.15)

A Gas Chromatograph for Atmospheric Trace Gas Analysis

by D J Bamber

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1. Introduction

As a result of the suggested effect on the atmosphere's ozone layer by nitrogen oxides (NO_x) and, more recently, by chlorofluoromethanes from aerosol sprays and refrigerators, it has become necessary to acquire a full understanding of the relevant chemical cycles in the atmosphere. Initially, one aspect of this involves making concentration measurements of a number of chemical species and identifying their sources and sinks.

Halogenated hydrocarbons (eg CFC1_3 , carbon tetrachloride, methyl chloride), substances which are particularly concerned with the catalytic destruction of ozone, lend themselves fairly readily to detection and measurement using a gas chromatograph (GC) equipped with an electron-capture detector (ECD).

Following a design provided by Lovelock a GC-ECD system has been constructed in Met O 15. The principle behind the policy of "home-construction" was, firstly, that the design has been proved by Lovelock to work for the particular analysis required and, secondly, a similar GC-ECD instrument is to be carried on board the M.R.F. C-130 aircraft; there would be a great number of problems involved in, first of all, finding a suitable commercial instrument and, then, most probably, making the necessary modifications to it for aircraft use.

2. Principles of operation

The principle of gas chromatography involves splitting a sample of gas into its component parts and then detecting each component, usually quantitatively. The splitting process is achieved in the gas chromatograph column. This normally consists of a length of tubing (glass, stainless steel, etc) packed with a fine-grained support material (eg crushed firebrick, diatomaceous earth, polymer beads). The support material is coated with a substance (the stationary or liquid phase) specifically chosen to produce the required sample component (solute) separation. A flow of carrier gas (the mobile or gas phase) is maintained at all times and this transports the gas sample through the column to the detector. The separation is achieved by virtue of the fact that the various solutes have different distribution (or partition) coefficients with respect to the liquid phase. There are several physical and chemical interaction forces (i.e. between solutes and stationary phase) which can aid in the separation, the combined effects of which are expressed by the partition coefficient K , where,

$$K = \frac{\text{amount of solute/unit volume of liquid phase}}{\text{amount of solute/unit volume of gas phase.}}$$

The value of K is high when most of a substance is retained in the liquid phase. This means that the substance moves slowly down the column because only a small fraction will be in the carrier gas at any given time. Transport is negligible in the liquid phase, and only that fraction in the gas phase is carried through

the column. Thus, separation between two compounds is possible, if their partition coefficients are dissimilar.

The value of K is temperature dependent, decreasing, in fact, with increasing temperature, i.e. the fraction of the solute in the gas phase will increase and hence the elution time (the time taken for a component to emerge from the column) will decrease. This results in decreased separation since it is the liquid phase which performs the separation.

In practice the choice of column material depends upon the particular molecules it is desired to separate; in general it is easier to separate polar molecules. It is difficult to analyse atmospheric species which are either reactive (such as NO , NO_2 or HNO_3) or have retention times similar to oxygen.

A detector, the type being determined by the physical and/or chemical properties of the compounds, is positioned at the end of the column. When a compound enters the detector a response results which can be calibrated to give a measure of the amount of compound in the original sample.

The detector chosen is the electron capture detector (ECD) since it is extremely sensitive to organic and inorganic halogen-containing compounds as well as a number of other types such as anhydrides, peroxides, nitrates, ozone, oxygen and insecticides. The sensitivity for strong electron-attachers such as trichlorofluoromethane (Freon-11) and carbon tetrachloride, both of atmospheric interest, is probably of the order of 5 to 10 pptv (ppt = parts per 10^{12}). Typical atmospheric concentrations, away from industrial areas, are of the order of 100 to 150 pptv. The linear range is low ($c. 10^2$ to 10^3) compared with other types of detector and this can lead to calibration problems if samples containing widely varying concentrations are taken. The ECD used in the Met O 15 instrument is basically an ionisation chamber, the ionising radiation being provided by a $\text{Ni}^{63}\beta$ -source. A baseline current of a few nanoamps results from the carrier gas flow and a pulsed voltage applied to the anode. When an electron-attaching substance passes into the detector, the electron concentration drops, thereby reducing the baseline current, which results in a peak. The detector is designed in such a manner that it operates, at least in theory, coulometrically, i.e. the observed response to a substance is directly related to the amount of that substance. Coulometry is dealt with in more detail in section 4.1. The way in which data are acquired from the chromatograms is detailed in section 5.

One of the limitations of the ECD has already been mentioned; namely its relatively low linear range. This can be improved by one or two orders of magnitude by operating the detector in the constant-current mode. The present detector is supplied with a constant frequency pulse and the variations in current observed. The constant-current mode works by holding the current constant and observing the changes in pulse frequency necessary to produce this. The electronics is necessarily more complex.

The other major problem with the ECD is its susceptibility to contamination and in particular the dependence of its response on the nature of the positive ions formed. A recent paper by Siegel and McKeown (1976) details work done using an atmospheric pressure ionisation mass spectrometer (API-MS). The atmospheric pressure ioniser is essentially an ECD in which positive and negative ion densities are measured instead of electron density. An important feature which has been brought to light is the extent to which the quiescent positive ion spectrum and hence the response is dominated by minute traces of water vapour in the carrier gas. This fact will have to be carefully considered in the work done with the GC-ECD system.

3. Description of instrument

A schematic representation of the gas chromatograph is shown in figure 1.

As the instrument is intended for the detection and measurements of trace substances with mixing ratios of the order of 10^{-11} , the primary design consideration is to maintain cleanliness and avoid contamination as far as possible. To this end, the greater part of the system in contact with the sample and the carrier gas is stainless steel. Small amounts of brass (in the diffusion resistant regulator) and glass (the potassium carbonate drying tube) are used. The use of rubber for 'O' ring seals or diaphragms is not permissible due to the heavy contamination which would occur. The materials used after the detector are not critical provided back-diffusion of contaminants is minimised. Some of the connecting tubing and ferrules in tubing connectors are of PTFE. The effect of this substance on the sample and carrier gas is not certain, although PTFE for most purposes is chemically and physically inert, and it would be preferable to use an all stainless-steel construction. The preferred type of stainless steel is AISI 316 (EN58J) as this has increased corrosion resistance.

For the treatment of stainless steel one good procedure is as follows:

1. Electropolishing
2. Rinsing with increasingly more volatile solvents and finally distilled water.
3. Baking at a suitable temperature in an atmosphere of oxygen to provide an inert oxide layer. (An alternative treatment has been suggested for the treatment of sample bottles which involves filling them with butene and baking at 400°C . This deposits an inert carbon layer on the internal surface).

The technical specification of the Met O 15 gas chromatograph appears in this report as Appendix 1. A detailed description of the construction and operation of the instrument is given below.

The carrier gas is nitrogen and for use with ECDs. must be very pure and, in particular, free from water vapour, oxygen and hydrocarbons. There are two commercially available grades which could be used: B.O.C.'s White Spot grade and Air Product's High Purity grade. The Air Products nitrogen is, in fact, used for reasons of availability. Nitrogen is used since it is not an electron-attacher and is inert towards the sample components of interest.

The pressure regulator is a diffusion-resistant type, i.e. of such a design that diffusion of air into the gas stream is minimised. It is also fitted with a metal diaphragm, rather than the usual rubber diaphragm, to reduce contamination.

A stainless steel cylinder containing molecular sieve type 13X is inserted in the gas line just after the regulator to trap any impurities which may be carried over from the gas cylinder (eg particulates, oil and water vapour). This can be periodically reactivated and cleaned by heating and backflushing with nitrogen.

The regulator gives coarse control of the pressure and flow of the carrier gas; fine control is achieved by use of a needle valve (Hoke Micromite 1600 series).

The commonest method of injecting samples into a chromatograph is by means of an injection port, the design of which is shown in figure 2. Samples are taken in a hypodermic syringe and then injected through the rubber septum. There are a number of disadvantages in using this method, eg contamination from the septum, the sample is not introduced to the column as a plug, introduction of non-sample air into the chromatograph from the needle. These can be overcome by injecting samples through a special gas-sampling valve, the functional diagram of which appears in figure 1. The sample volume is defined by a length of tubing as shown. This can be switched into the carrier gas flow as a plug simply by operating the valve. The rotary valve shown consists basically of a stainless steel block with six holes and ports and a PTFE based slider with three channels cut into it. In the actual instrument a pneumatically operated slider valve is used, this having four channels in the slider.

The column and detector are contained in a thermostatically controlled oven which, for the particular analysis in question, is maintained at 50°C. A constant temperature is achieved using a proportional control with a thermistor as the heat-sensitive element. Also in the oven, physically attached to the detector body, is the electronic circuitry for the detector. Since the electronics are

particularly susceptible to noise pick-up, this was found to be the best location. The oven is provided with two heater windings; one rated at 60W 30 V for rapid heating or purging and one rated at 30W 30V for temperature control.

Situated in the gas line between the column and the detector is a short length of glass tubing containing anhydrous potassium carbonate. This is for removing water vapour from the column eluent before it enters the detector.

The construction of the electron-capture detector is shown in figure 3.

A flow-meter and flow-controller are situated at the outlet from the detector to respectively monitor the carrier gas flow rate and to help guard against large excursions in flow rate due to external pressure fluctuations. The flow-controller works on the same principle as a conventional gas pressure regulator, i.e with a diaphragm attached to a needle valve.

Apart from the detector circuit the only other electronics in the instrument are the oven power supplies, complete with the temperature control circuit, and the detector power supply. Details of the power supplies are in Appendix 1.

4. Calibration

Under this heading both the quantitative calibration and qualitative identification of peaks will be dealt with.

4.1 Coulometry

The conventional ECD has the form of a cube for its ionisation chamber. Generally speaking the ionisation efficiency for such a construction is somewhat less than 100%. An ionisation efficiency of 100% means that all the substance passing into the detector is removed by ionisation (with one ion being created for each molecule passing through the chamber); the response is then related to the amount of substance by the relation,

$$m = \frac{MA}{F}$$

where m = mass of substance in grams, M = molecular weight of substance, A = peak area in ampere-seconds, F = Faraday's constant (9.65×10^4 coulombs per gram-molecule).

The detector used in the Met O 15 instrument is in the form of a long tube (see figure 3) and effectively consists of a number of "box" detectors in series for gas flow but with their electrical outputs connected in parallel.

As a result the ionisation efficiency of the "tube" detector approaches very close to 100% at least for relatively low flow rates. When coulometric the response of the detector is absolute and independent of the ambient variables of temperature and pressure.

4.2 Quantitative calibration

The only reliable method of establishing the way in which the detector is working is by injection of standard samples. The basic methods of preparing standards involve dynamic or static dilution of more concentrated mixtures or a combination of both. The method which will be used for the Met O 15 instrument consists of three stages of static dilution followed by a continuous flow dilution stage. An all stainless steel construction will be used and the system should yield accurately reproducible standards down to mixing ratios of a few parts per trillion (10^{-12}).

4.3 Qualitative identification of peaks

A typical chromatogram with a number of identified peaks is shown in figure 4. Identification of the peaks can be obtained simply by injecting a sample of air or nitrogen containing a small quantity of the relevant substance. A crude but effective method has been used which really only works for substances which are not normally present in measurable quantities - since the ECD is so sensitive (see section 2) it has been found sufficient to open a bottle or gas cylinder of the substance for a brief period in a closed room and then a short time later inject a sample of the room air into the chromatograph. If it is desired to produce a chromatogram containing peaks only of the substances injected then a more sophisticated technique must be used. This is necessary in the case of substances which are always present in the atmosphere, at least in the location where the peak identification is being carried out. For this purpose an exponential dilution flask is used (figure 5). This consists of a glass bottle fitted with an injection port and a magnetically operated stirrer. A flow of high purity nitrogen is maintained through the bottle. At time zero a quantity of pure substance is injected into the flask. The concentration in the flask then decreases exponentially with time assuming perfect mixing of substance with diluent. In theory this method can be used for quantitative calibration but in practice perfect mixing is impossible to achieve and the actual behaviour of the flask difficult to predict.

A useful aid to peak identification is the fact that with an OV-101 coated column (as in the Met O 15 instrument) the various sample components are eluted according to their boiling points - the higher the boiling point the longer is the component retained in the column. A graph of retention time against boiling point is shown in figure 6. Retention time is a linear function of carrier gas flow rate but the form of the boiling point curve is the same for all flow rates used ($10 - 60 \text{ cm}^3/\text{minute}$).

Table 1 lists all the substances so far identified.

5. Analysis of chromatograms

There are a number of methods for obtaining data from chromatograms all of which involve measuring the areas under the peaks. The quickest and most convenient manual method is to use a planimeter as has been used so far in Met O 15. Once the instruments become operational, there will be large volumes of data to be reduced and analysed; this will be particularly true in respect of the aircraft measurements where chromatograms will be produced at a maximum rate of one every five minutes. This will obviously require some form of data handling and reduction system which will give both an instantaneous readout and digitise the data for recording on tape for subsequent analysis using the Met Office computing facility.

Figure 7 shows a number of possible peak configurations and the way in which the peak areas are measured.

The component separation in the column occurs in such a way that the basic peak shape is gaussian. To obtain the peak area it is therefore sufficient to measure the peak height and the width at a fixed height. It can be shown that,

$$A = hw_{\frac{1}{2}} \times 0.96$$

where A is the peak area, h is the peak height and $w_{\frac{1}{2}}$ is the peak width at half height.

6. Problems encountered during operation of instrument

The principal problem during the initial period of operation was baseline drift, the magnitude of which made it difficult to distinguish peaks from drift. The possible causes of this are,

1. Carrier gas leaks
2. Poor carrier gas regulation
3. Oven temperature drift
4. Contamination
5. Column bleeding
6. Defective detector electronics
7. Instrument subjected to excessive drafts or ambient temperature changes.

Of these, the most likely under the prevailing circumstances were gas leaks and contamination. Gas leaks can be more or less eliminated by standardising on the use of "Swagelok" type compression fittings and contamination has been reduced, hopefully, to an acceptable level by the use of more rigorous cleaning techniques (see section 3 for optimum treatment of stainless steel). Column bleed, ie. the carry over of liquid phase to the detector, can be more or less eliminated as a cause of drift since the column temperature is only 50°C. and the liquid phase (OV101 dimethyl silicone fluid) should be stable to 300°C. The other possible

causes have been eliminated or substantially reduced by tests (eg observing drift in the electronics with the detector disconnected) and substitution of components such as valves, lengths of tubing, etc.

Other problems concern the separation of sample components on the column. Referring to figure 6 it can be seen that the low boiling substances are eluted very close together. Since the air samples contain 20% oxygen, which saturates the detector, many of the low boiling substances of interest, eg CF_2Cl_2 , nitrous oxide, methyl chloride, tend to be masked by oxygen. This could be overcome by removing oxygen from the sample prior to injection but is difficult to achieve without affecting the other sample components and linearity of detector response. It can also be seen from figure 6 that high-boiling substances are retained on the column for relatively long periods - this particularly applies to tetrachloroethylene. Two alternatives exist to deal with this,

1. Temperature programming the oven; it has already been mentioned (section 2) that the partition coefficients are very temperature dependent. This means that raising the oven temperature in a fixed manner starting from the time of sample injection would cause the components to be eluted more and more rapidly - in effect, tending to linearise the retention time: boiling point curve. Temperature programming however, requires more complex electronics together with a more powerful heater and a facility for rapidly cooling the oven.

2. Backflushing a precolumn; this technique can be used if the high-boiling substances are of no interest. The main column is simply preceded by a short precolumn. The substances of interest are allowed to elute from this column into the main column and then the precolumn is backflushed with high purity nitrogen via a switching valve.

The backflushing technique is preferred since it can be relatively simply put into operation for the price of a short column and a switching valve. The same oven can be used.

It may also be possible to use an alternative column packing material. This would have to be found by experiment. The first choice for an alternative would be a porous polymer packing (eg Porapak or Porasil). This type of chromatography is known as gas-solid chromatography as opposed to gas-liquid chromatography (ie with a liquid stationary phase) as with the present OV-101 column. Several workers have obtained measurements of nitrous oxide using this technique; Pierotti and Rasmussen (1976), La Hue, Pate and Lodge (1970), Schmeltekopf et al (1975).

7. Applications

So far, only one instrument has been built, this being situated in the laboratory at Bracknell. It has been used primarily for design and development with a view to installing a similar instrument on board the MRF C-130. This will have the major benefit of providing real-time trace gas concentration measurements which should enable one to locate sources and sinks of these substances. For this type of work it is important to have a rapid analysis time; preferably of the order of a few minutes. It has been found by experiment (see Appendix 2) that the optimum practical gas velocity is 3.5 cm/sec (ie equivalent to a carrier gas flow rate of 60 cm³/min). At this flow rate the retention time of the last component of interest is about 15 minutes. It has been decided to provide the aircraft instrument with three columns and three detectors which means that an air sample can be analysed every five minutes.

Two substances of interest - methyl chloride and nitrous oxide - have not yet been satisfactorily separated from the oxygen peak and detected. Methyl chloride requires a modified detector; one with a body heated to 270°C to encourage the reaction of methyl chloride with free electrons. The detection of nitrous oxide probably requires an alternative column (see section 6).

It is quite likely that in the near future, time series for trace gases will be started, at least in Bracknell. There should soon be facilities (i.e. cleaning, vacuum, and calibration systems) for the preparation of stainless steel cylinders for atmospheric sampling from the C-130 and the subsequent analysis of their contents.

The potential exists for the gas chromatograph on board the aircraft as an air-mass tracer (eg in Met O 14's studies of SO₂ transport). The ECD is particularly sensitive to sulphur hexafluoride (SF₆) which is a very common tracer gas. The present air sampling rate is about one per five minutes which, in an aircraft, is too slow for plume profile measurements. Thomsen and Lovelock (1976) have recently described a method where the ECD can be used in a continuous mode for hydrogen-free molecules. This offers considerable possibilities for air-mass tracing.

Thought is being given at the present to methods whereby grab samples can be taken by balloon-borne equipment. It is possible that this could be done on a routine basis using standard radio-sonde balloons.

The two basic problems concerned with any type of air sampling are firstly, ensuring that the sampling cylinders and associated equipment are free from contamination and secondly, sample handling and introduction into the chromatograph when the original sample is effectively at sub-ambient pressure (ie less

than the GC column inlet pressure). Much of the present development effort is being directed towards these two problems, together with the construction of the version for the C-130.

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- Schmeltekopf et al (1975) Geophysical Research Letters,
Vol. 2, No. 9, p. 393.
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Technical specification of Met O 15 GC-ECD instrument

Column: 8' x $\frac{1}{4}$ " O/D stainless steel packed with 12% OV 101 (dimethylsilicone fluid) on 100-120 mesh Chromosorb W-HP.

Detector: Electron-capture (Lovelock coulometric design).
 β -source = 15 mCi Ni⁶³ (giving 63 keV electrons).
Mode of operation: pulsed, constant frequency.

Carrier gas: Nitrogen (Air Products high-purity grade, i.e. 99.999% N₂, 2-4 ppm. O₂).
Flow rate: 10-60 cm³/min.

Column and detector temperature: 50°C \pm 0.2°C.

Power: Supplies; Detector \pm 15V. (40 mA per rail max).
Oven controller 30 V @ 30 W
Oven warm up 30 V @ 60 W

Total requirements; on rapid warm-up approximately
90W @ 240 V 50 Hz

normal operation approximately
20W @ 240 V 50 Hz

Determination of optimum practical gas velocity (OPGV)

A number of processes contribute towards band spreading in a GC column. If the variances due to each of the processes are $\sigma_1^2, \sigma_2^2, \dots, \sigma_n^2$. Then the total variance of the band (or peak) is $\sum \sigma_n^2$. The total variance is not such a useful measure of column performance as the variance per unit length, h , ie,

$$h = \frac{\sum \sigma_n^2}{l}$$

where l is the column length. Column efficiency, N , is defined as,

$$N = \frac{l^2}{\sum \sigma_n^2}$$

Thus, $h = \frac{l}{N}$.

Van Deemter et al have developed an equation for the variance per unit length, or height equivalent to the theoretical plate (HETP) as it is more commonly known,

$$h = A + B/u + (C + D)u.$$

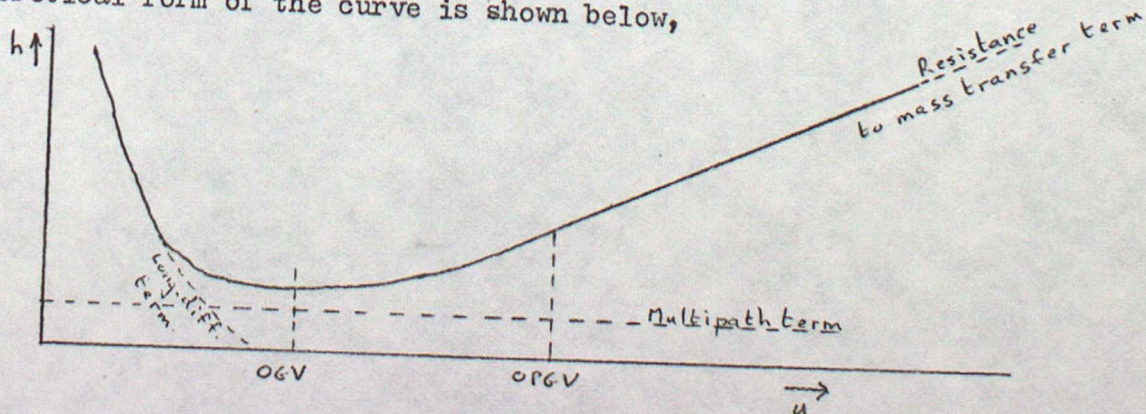
1st term: Multipath term - describes spreading effect due to unequal paths solute has to travel as it winds its way through interstices of support.

2nd term: Longitudinal diffusion term - describes spreading that occurs due to diffusion of solute in gas phase.

3rd, 4th terms: Total resistance to mass transfer term - refers to resistance to mass transfer in gas and liquid phases respectively. They give spreading that results from finite time required for solute to repeatedly transfer between liquid and gas phases.

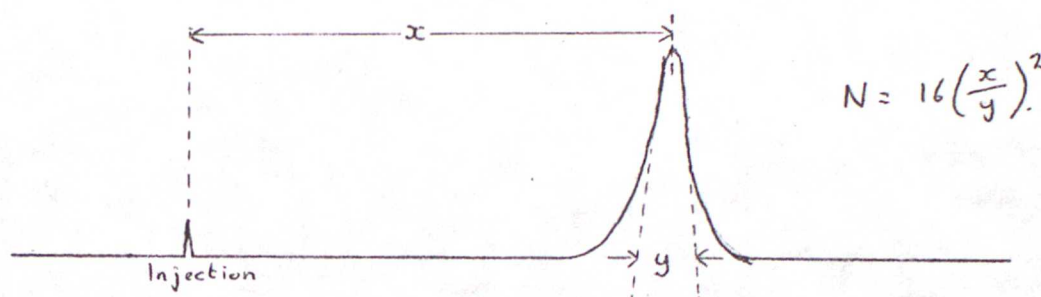
u = linear gas velocity = $\frac{\text{length of column}}{\text{retention time of oxygen}}$

The theoretical form of the curve is shown below,



The minimum of the curve represents the gas velocity at which the column has its maximum efficiency and provides the minimum band width. This is the optimum gas velocity (OGV). By doubling the OGV, one reaches a linear part of the curve with a loss of only 20% of the maximum possible efficiency, but the analysis time is halved. This is the optimum practical gas velocity (OPGV).

Column efficiency is measured by the number of theoretical plates (the discrete plate is however an artificial concept). Theoretical plates can be easily measured from the chromatogram. Tangents are drawn to the peak at the points of inflection (about $\frac{2}{3}$ of the height). The number of theoretical plates, N , is given by $16\left(\frac{x}{y}\right)^2$, where y is the length of the baseline cut by the two tangents, and x is the distance from injection to peak maximum.



N has been measured for the carbon tetrachloride peak for a number of carrier gas flow rates and hence a graph of HETP against linear gas velocity can be produced. The result obtained is shown in figure 8. It can be seen from the graph that the OGV lies around 2 cm/sec which corresponds to a flow rate of about 30 cm³/min. The OPGV is therefore about 60 cm³/min.

Figures

1. Schematic representation of gas chromatograph.
2. Injection port.
3. Electron-capture detector.
4. Typical chromatogram.
5. Exponential dilution flask.
6. Retention time vs boiling point.
7. Peak configuration and area measurement.
8. HETP curve for OV-101 column.

Tables

1. Substances identified using the Met O 15 gas chromatograph.

Figure 1. Schematic representation of gas chromatograph

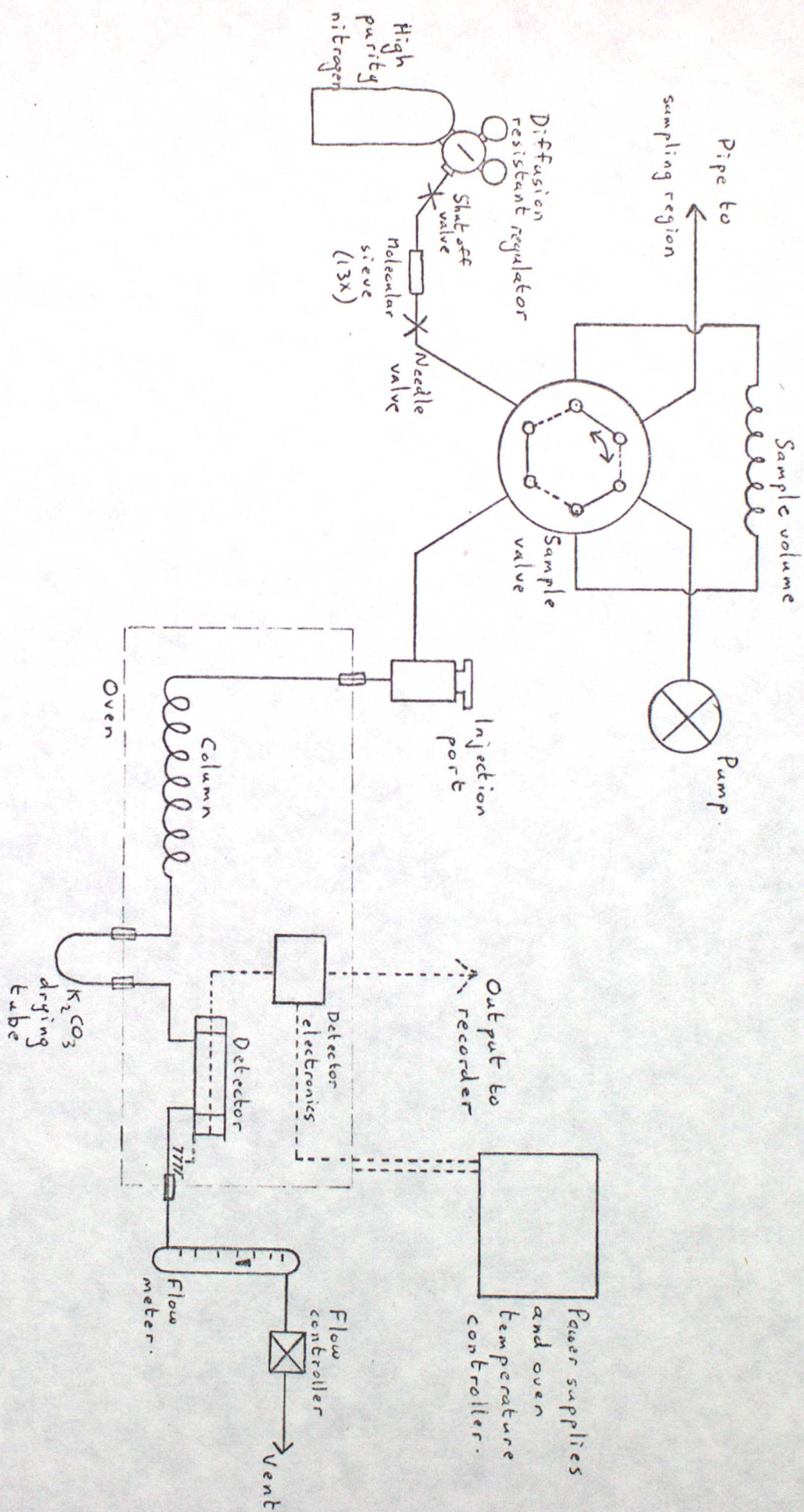


Figure 2. Injection port

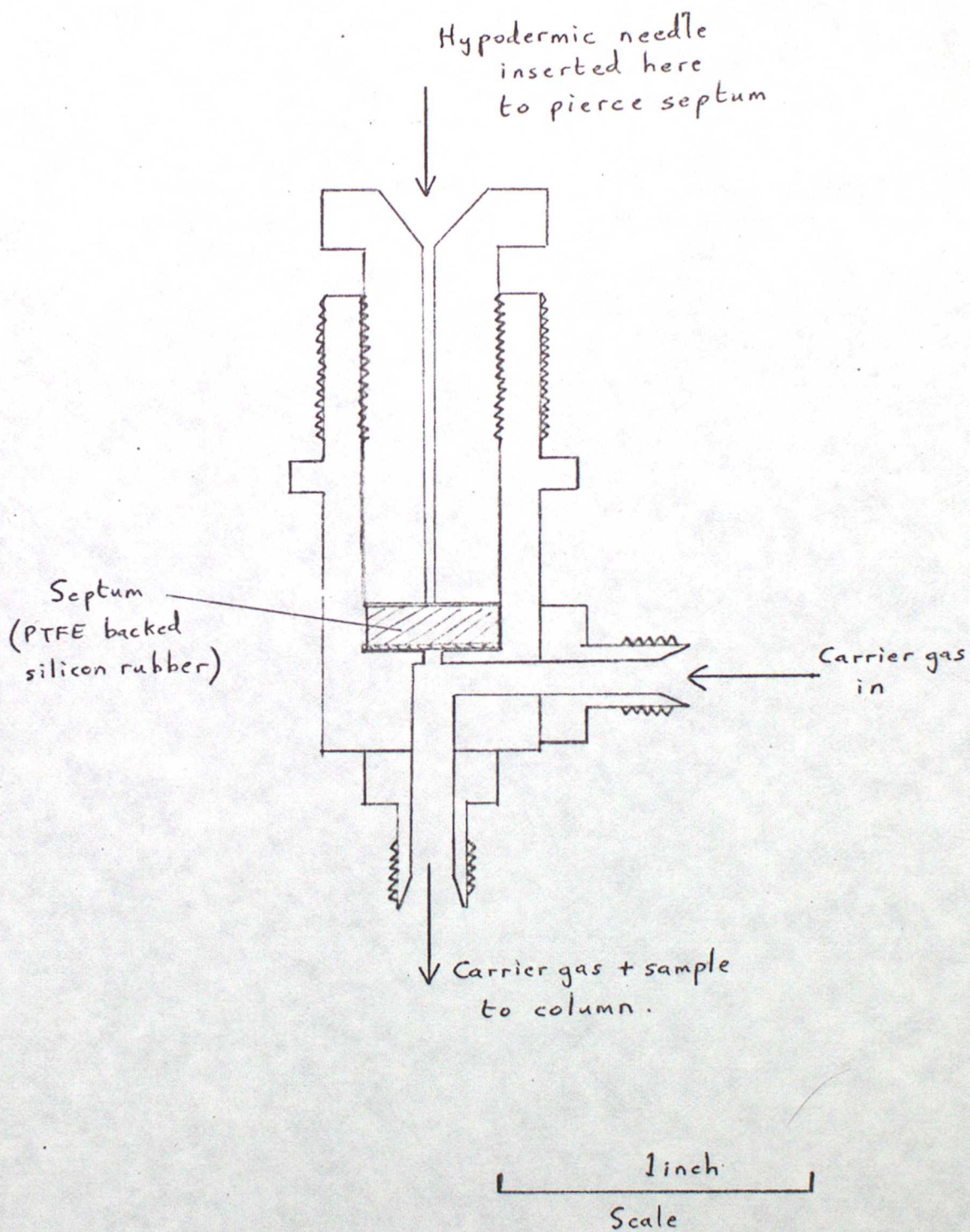


Figure 3. Electron-capture detector

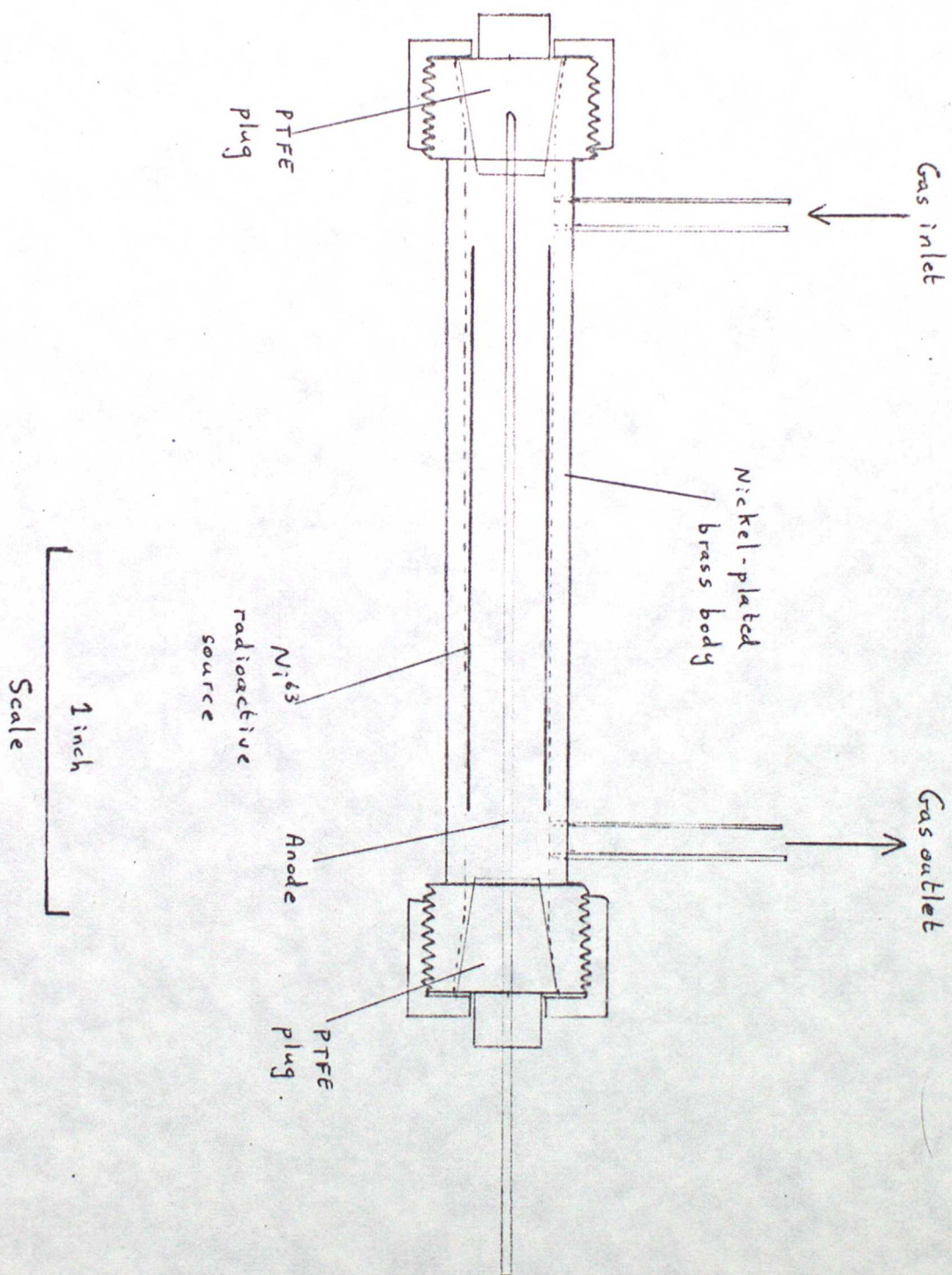
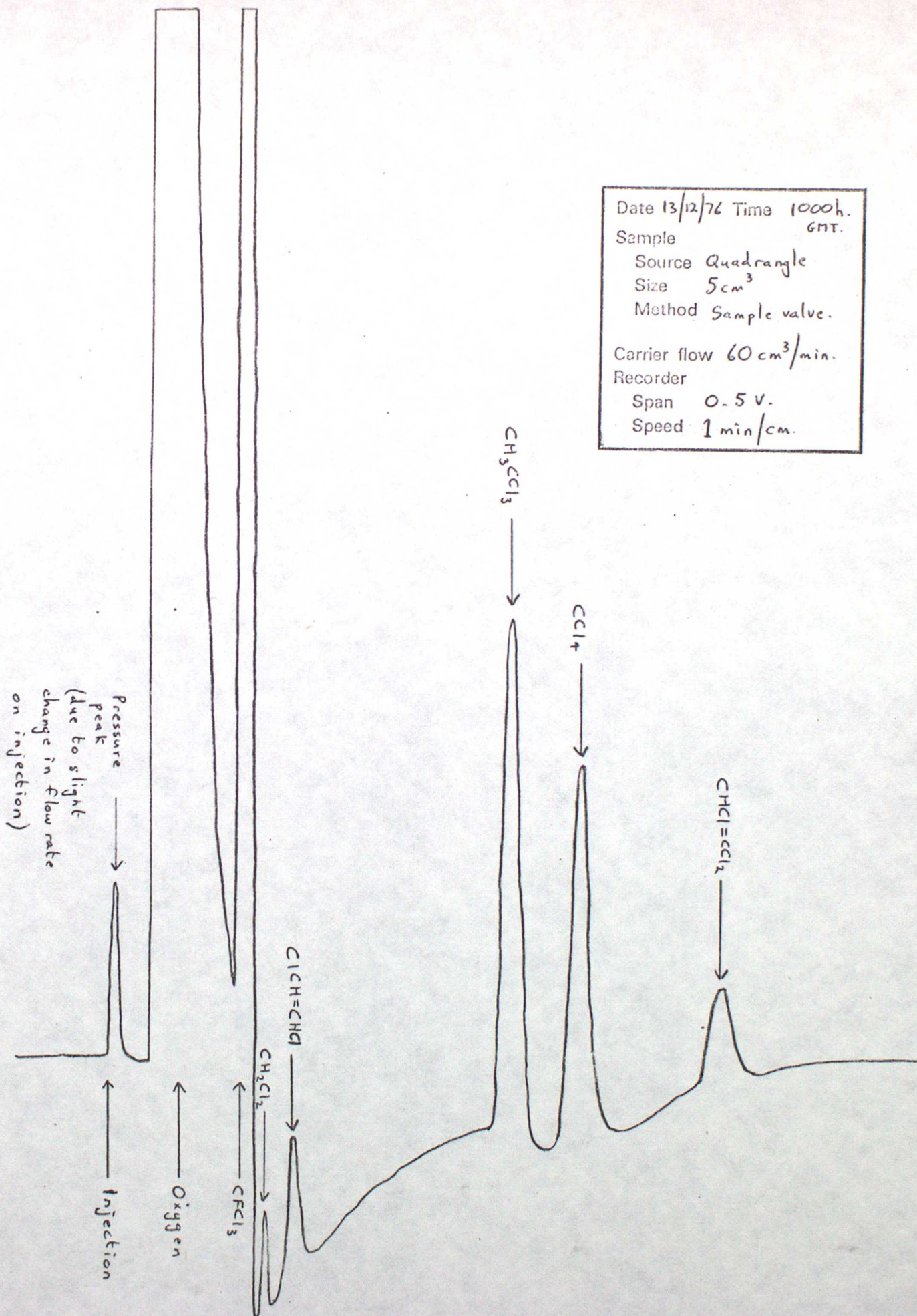


Figure 4. Typical chromatogram



Date 13/12/76 Time 1000h. GMT.

Sample

Source Quadrange

Size 5 cm³

Method Sample valve.

Carrier flow 60 cm³/min.

Recorder

Span 0.5 v.

Speed 1 min/cm.

Figure 5. Exponential dilution flask

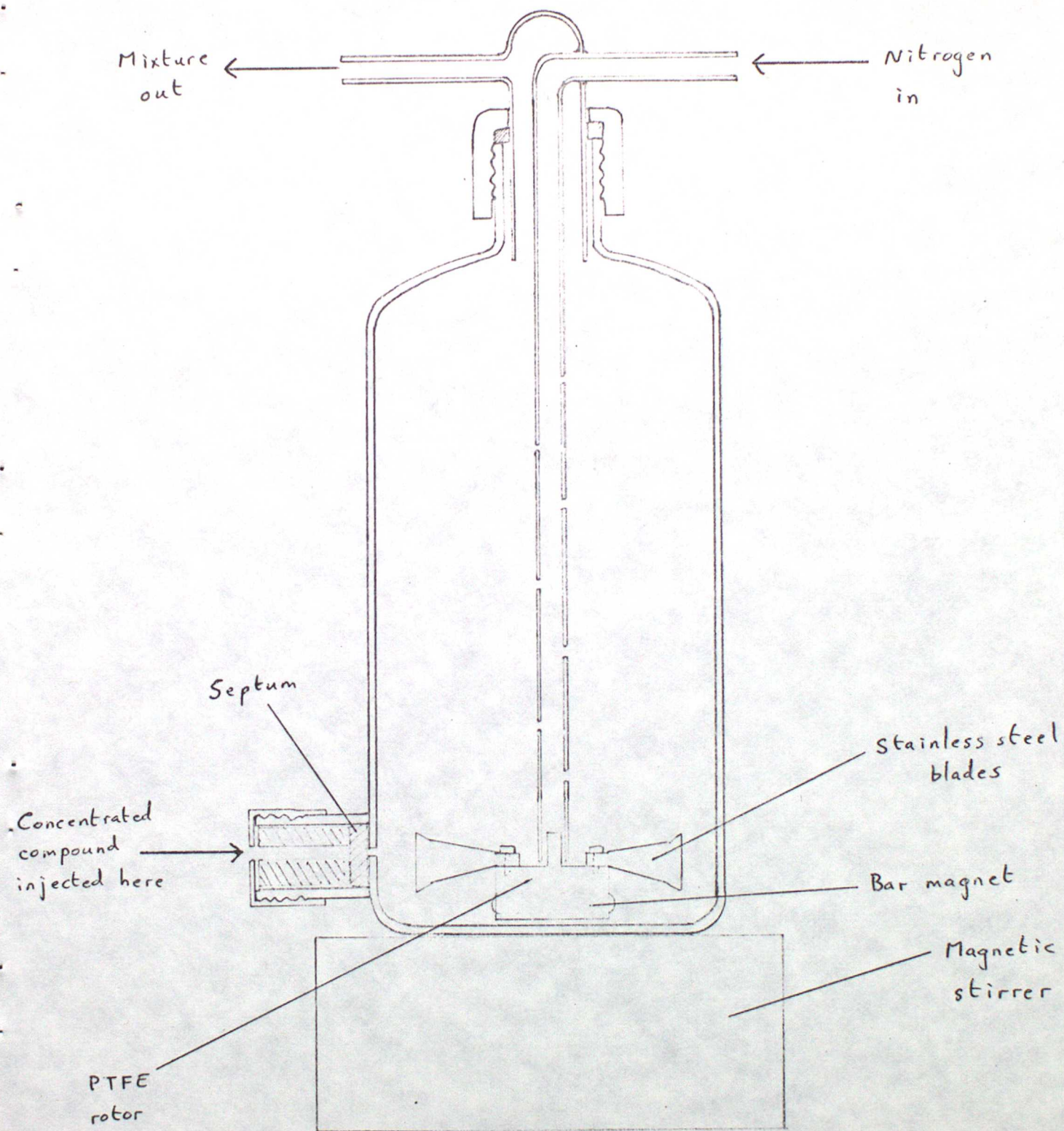


Figure 6. Retention time vs. boiling point

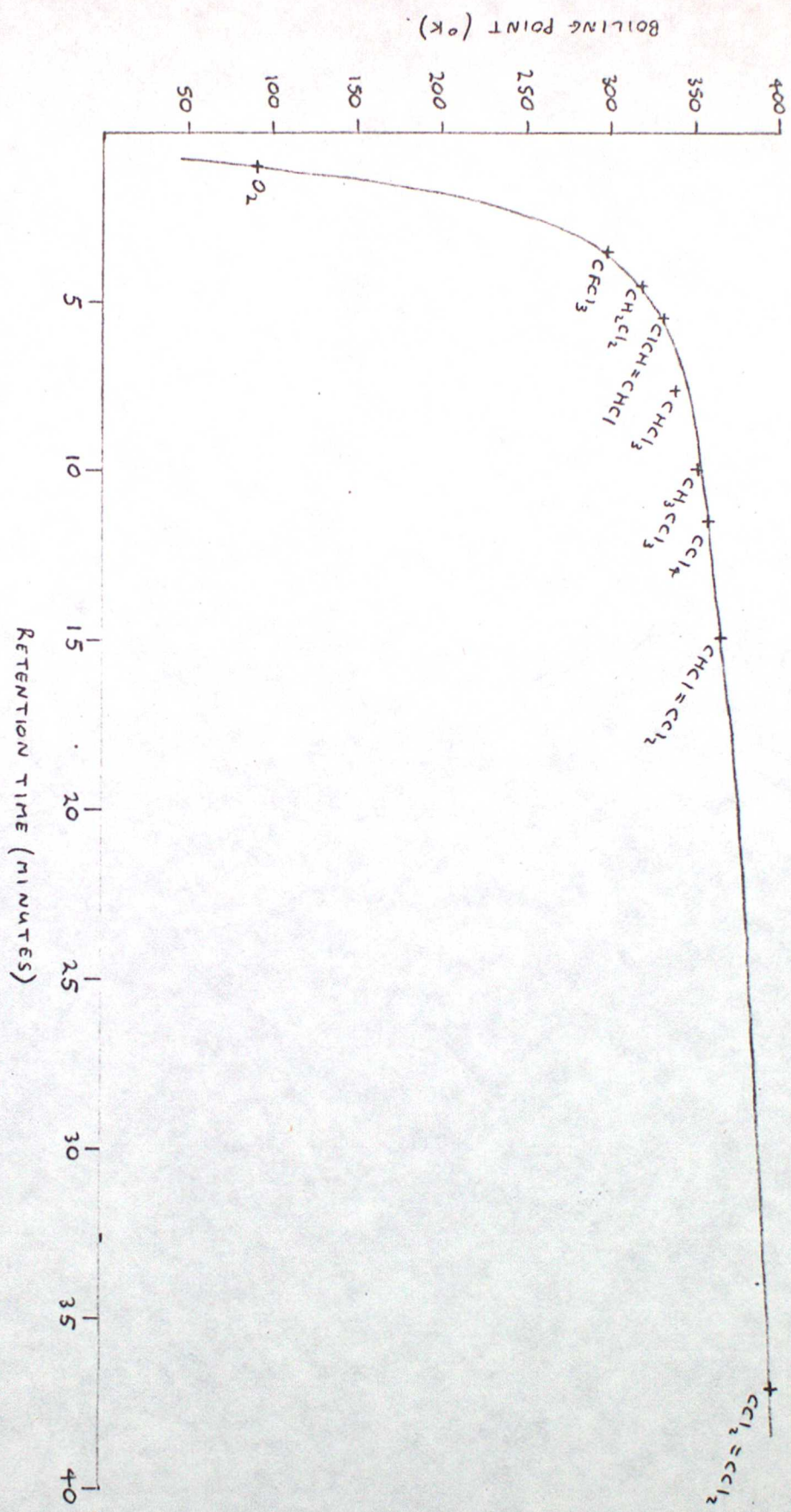


Figure 7. Peak configuration and area measurement

The purpose of these diagrams is to show a few typical peak configurations and the areas that are measured. The dashed lines mark the area boundaries.

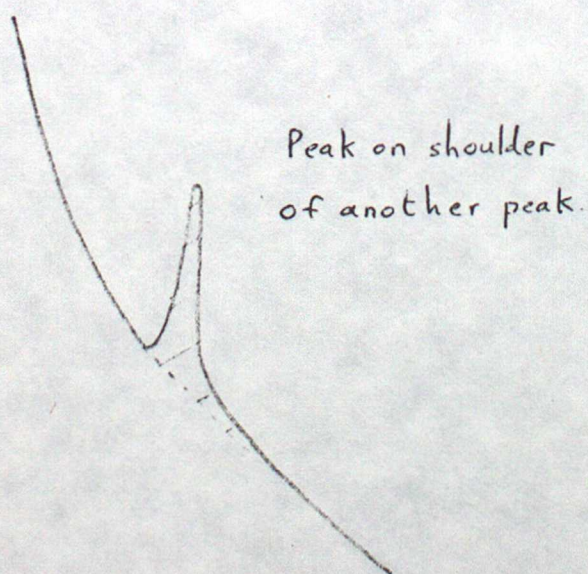
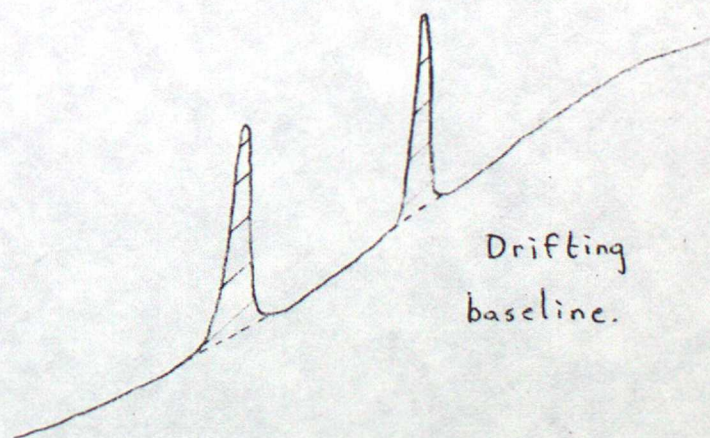
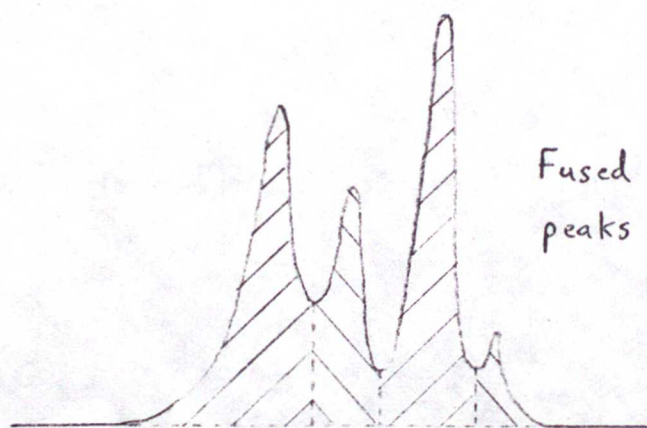
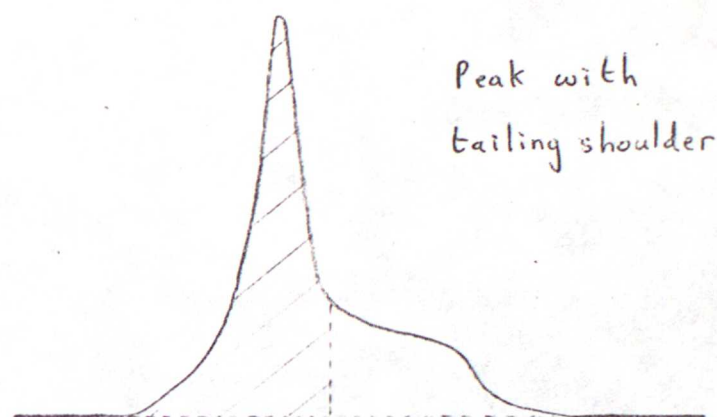
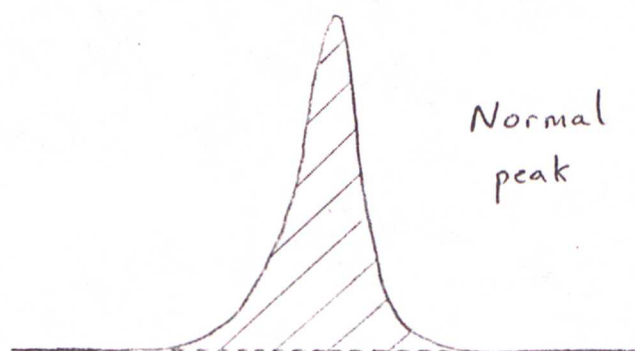


Figure 8. HETP vs. linear gas velocity

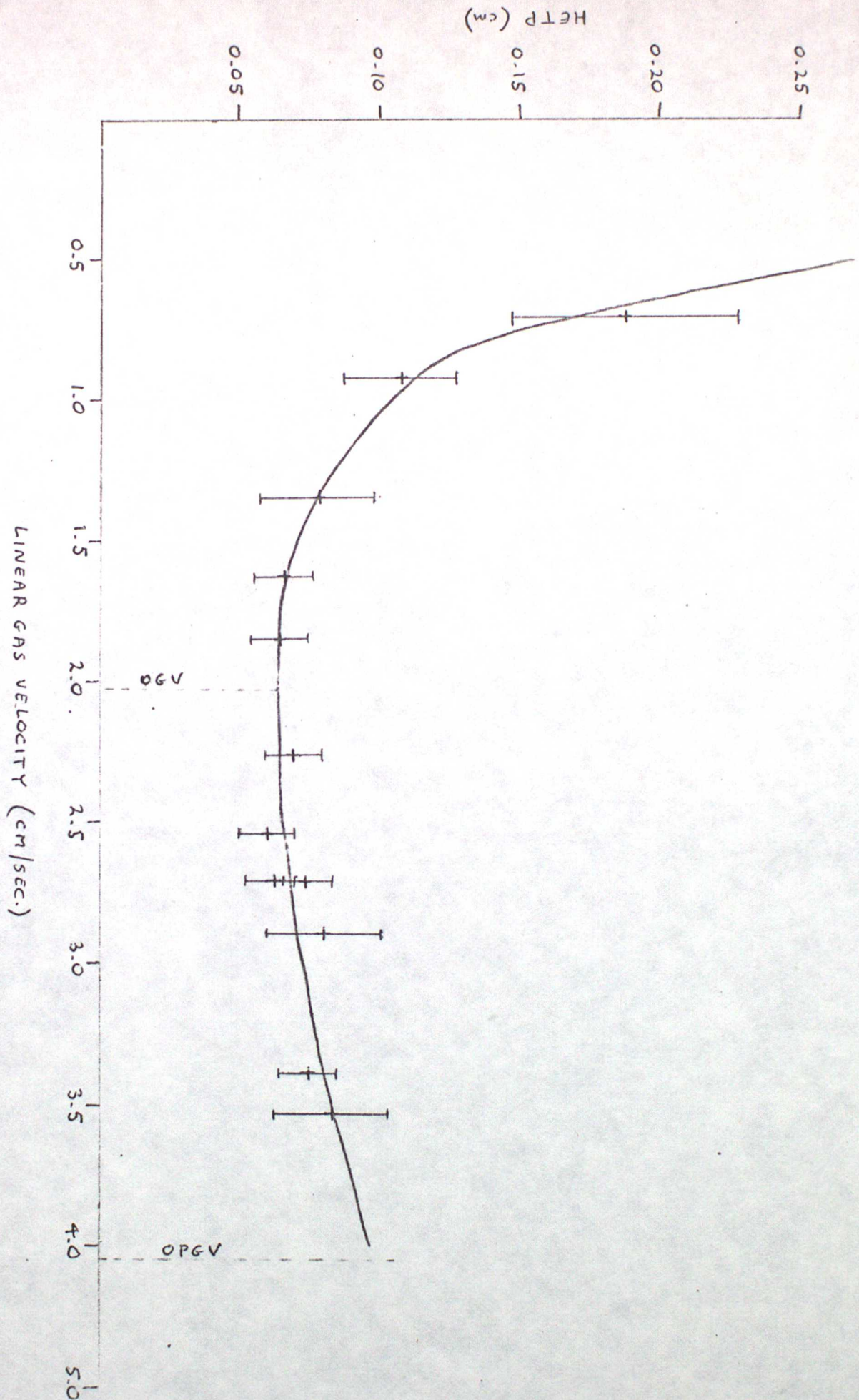


Table 1. Substances identified using Met O 15 G.C.

Compound	Formula	Boiling point ($^{\circ}$ K)	Retention time (mins)
Oxygen	O_2	90	1.2
Trichlorofluoromethane (Freon-11*)	CCl_3F	297	2.6
Methylene chloride	CH_2Cl_2	314	2.9
1,2-Dichloroethylene	$ClCH=CHCl$	321	3.6
Chloroform	$CHCl_3$	334	5.2
1,1,1-Trichloroethane	CH_3CCl_3	347	7.6
Carbon tetrachloride	CCl_4	350	8.8
Trichloroethylene	$CHCl=CCl_2$	360	11.5
Tetrachloroethylene	$CCl_2=CCl_2$	394	28.5

* Du Pont Trade name.

(Retention times for carrier gas flow rates $60\text{ cm}^3/\text{min}$).