# Gas Chromatography – an Essay Review 1982

Methods for the Examination of Waters and Associated Materials

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**Methods for the Examination of Waters and Associated Materials**

## Contents

# Warning to users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in properly equipped laboratories. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specification. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before used.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Code of Practice for Chemical Laboratories' and 'Hazards in the Chemical Laboratory' issued by the Royal Society of Chemistry, London; 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No. 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection' Public Health Laboratory Service Monograph 6, HMSO, London.

Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire fighting, and rescue equipment. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

# About this series

This booklet is part of a series intended to provide recommended methods for the determination of water quality. In addition, the series contains short reviews of the more important analytical techniques of interest to the water and sewage industries. This booklet is one such review. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, has issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being issued when necessary. The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users – the senior analytical chemist, biologist, bacteriologist etc, to decide which of the methods to use for the determination in hand. Whilst the attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council. It has nine Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

  1.0  General principles of sampling and accuracy of results
 *2.0  Instrumentation and on line analysis
  3.0  Empirical and physical methods
  4.0  Metals and metalloids
  5.0  General nonmetallic substances
  6.0  Organic impurities
  7.0  Biological methods
 *8.0  Sludge and other solids analysis
  9.0  Radiochemical methods

The actual methods etc are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee. The names of those associated with this method are listed inside the back cover.

Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes for booklets in this series are given in the Reports of the Standing Committee of Analysts, published by the Department of the Environment but sold by the National Water Council, 1 Queen Anne's Gate, London SW1H 9BT. Should and error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in the booklet.

T A DICK
*Chairman*

L R PITTWELL
*Secretary*

*25 September 1981*

*These two Working Groups are in process of being wound up. Their tasks are being redistributed among the other working groups.

# About this booklet

This booklet is one of a series of reviews written for analysts in the water industry and industries discharging effluents which may affect water quality. It is one of three booklets dealing with the major chromatographic techniques.
The other two are:

**Ion Chromatography in the Analysis of Water Samples 1980 and**
**High Performance Liquid Chromatography and other solution Chromatographic Techniques 1982.**

Glossaries of terms relating to Gas Chromatography are given in the IUPAC Compendium of Analytical Nomenclature[1] and in BS 3282: 1969[2]. The definitions listed below are largely derived from these sources.

**Adjusted retention volume ($V'_R$)**
The retention volume less the gas hold-up volume, i.e.
$$V'_R = V_R - V_M$$

**Carrier gas**

The carrier gas (or eluent gas) is the gas used to elute the sample as it passes through the column. The carrier gas together with the portions of the sample present in this phase constitutes the mobile phase.

**Column**

The tube that contains the stationary phase and through which the mobile phase passes.

**Gas chromatography**

Any method of chromatography in which the mobile phase is a gas.

**Gas-liquid chromatography**

Any method of gas chromatography in which the stationary phase is a liquid distributed on a solid support.

**Gas hold-up volume ($V_M$)**

The volume of carrier gas at the column outlet temperature and pressure required to elute an unretarded compound.

**Gas-solid chromatography**

Any method of gas chromatography in which the stationary phase is an active solid.

**Flow rate**

The volumetric flow rate of the carrier gas, measured at the column outlet temperature and pressure.

**Ghosting**

When a chromatogram of a sample or standard is complete and a further injection of pure solvent is made, peaks may appear in this chromatogram derived from the previous injection. This effect is termed 'ghosting' and is most commonly seen when polar compounds dissolved in polar solvents are injected on to polar columns.

**Internal standard**

A compound added to a sample in known concentration for the purpose of eliminating the need to measure the size of sample injected for quantitative analysis.

**Liquid phase**

A substance which is liquid but substantially non-volatile at the column temperature and is sorbed on the solid support.

**Net retention volume ($V_N$)**

The adjusted retention volume multiplied by the pressure gradient correction factor, i.e. $V_N = jV'_R$

## Open tubular column

A column containing stationary phase but having an unobstructed axial channel.

### Partition coefficient (K)

The ratio of the weight of solute in the stationary phase to the weight of solute in the mobile phase at equilibrium i.e.

$$K = \frac{V_S T \rho_L}{273} = \frac{V_N \rho_L}{V_L} = \frac{V_N}{V_L}$$

where
$V_N$ = Net retention volume
$V_L$ = Liquid volume
$\rho_L$ = Density of liquid phase at the column temperature
$V_S$ = Solid volume
$T$ = Absolute temperature

### Peak

The portion of a differential chromatogram showing the response when a component of the sample emerges from the column.

### Peak width

The projection on the horizontal axis of the segment of the peak base intercepted between tangents to the inflection points of the peak.

### Peak width at half height

The horizontal distance between two vertical lines of half peak height joining the peak to the peak base.

### Phase ratio ($\beta$)

The ratio of the gas volume to the liquid volume in a partition column, viz,

$$\beta = \frac{V_G}{V_L}$$

### Pressure gradient correction factor (j)

A factor relating to a column of uniform diameter and composition, which corrects for the elasticity of the mobile phase. If $p_i$ and $p_o$ are the pressures of the carrier gas at the inlet and outlet then

$$j = \frac{3}{2}\left(\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}\right)$$

### Retention time ($t_R$)

The time between injection of the sample and emergence of the peak maximum of a stated component.

### Retention volume ($V_R$)

The volume of carrier gas passing through the column between the injection of the sample and the emergence of the peak maximum of a stated component.

### Resolution

The degree of separation between two peaks.

### Specific retention volume $V_g$

The net retention volume per gram of stationary phase corrected to 0°C

i.e. $\dfrac{273 V_N}{W_L t_c}$ where $t_c$ is the temperature in °K and $W_L$ = weight of liquid phase.

### Stationary phase

The liquid phase, the active solid or the modified sorbent.

### Tailing

Asymmetry of a peak such that, relative to the base line, the front is steeper than the rear.

# 1 Introduction

In gas chromatography (GC), samples to be analysed are normally applied in a stream of carrier gas to a GC column which contains a non-volatile stationary phase, coated on to an inert support. The components of the sample are distributed between the gaseous phase and the stationary phase. As different compounds usually have different distribution coefficients the effect of the column is to separate out the components of the sample into zones. If the stationary phase is chosen carefully and other conditions met, then these zones may be totally separated from one another. The zones move along the column to the end, where a detector is fitted which can produce a response to some or all of the components. After suitable amplification the signal from the detector can be converted to an analogue or digital output and displayed.

Clearly, only compounds with a finite vapour pressure will pass through the column. The compounds may be gases, liquids or solids with a vapour pressure of 0.1 torr or greater at the selected temperature. Such compounds may be described as volatile and it is for the detection and determination of these volatile compounds that GC is used.

Martin and Synge[3] in 1941 first described the model which would define column efficiency and James and Martin[4] in 1952 introduced the first gas-liquid chromatograph. In 1956, Van Deemter et al.,[5] using data from some earlier work, derived equations which gave a theoretical basis for chromatography. Since then GC equipment has deen developed by many manufacturing companies to give increased convenience, accuracy, range of application and selectivity. A range of detectors has been produced for specialised uses and equipment for the automatic display of the results has evolved.

GC techniques are widely used in the water industry for the determination of many organic compounds and for quality control of effluents and waters. Some groups of compounds for which GC analysis is commonly used in the water industry are: carboxylic acids, chlorinated solvents, herbicides, oils, phenols, organo-metallic complexes, pesticides and sterols. Specific compounds, often derived from industrial discharges, have also been extensively investigated using this technique.

There is little doubt that whilst GC above does not allow the primary identification of unknown compounds it can be a most powerful quantitative tool for the determination of a range of specific volatile organic compounds in water.

# 2 Theoretical Aspects of Chromatography

A gas chromatographic column can be represented as a tube containing a dispersed stationary phase, and a mobile phase consisting of a continuous flow of carrier gas. When a mixture of solutes is applied to one end of the tube the components are transported by the carrier gas along the column at rates dependent on the respective partition coefficients (distribution constants). In GC, partition coefficients depend on the vapour pressures of the solutes at the column temperature and their activities in the stationary phase and, provided these are sufficiently different in magnitude, and the column is of sufficient length, the solutes separate into discrete zones. The function of the column in chromatography is to separate compounds of interest from other material as efficiently as possible.

There are certain factors which influence the rate of progression of any compound along the column. These factors (discussed below), which affect the length of time the compound is retained and also affect how much spreading takes place during the passage, must be considered before any analysis is undertaken and modified to optimise the separation of compounds, commensurate with a reasonable analysis time.

## 2.1 Rate of Progression Through the Column

The principal factors influencing the rate of progression of a solute through the column are:
   a. The volatility and polarity of the solute
   b. The temperature of the GC oven
   c. The physical properties of the column
   d. The nature and flow rate of the carrier gas

a. If the solute has a very low vapour pressure at the temperature used it will be retained at the point of addition (commonly referred to as the head of the column) or its rate of progression will be very slow, but volatile compounds of similar polarity

Figure 1  MEASUREMENT OF COLUMN EFFICIENCY

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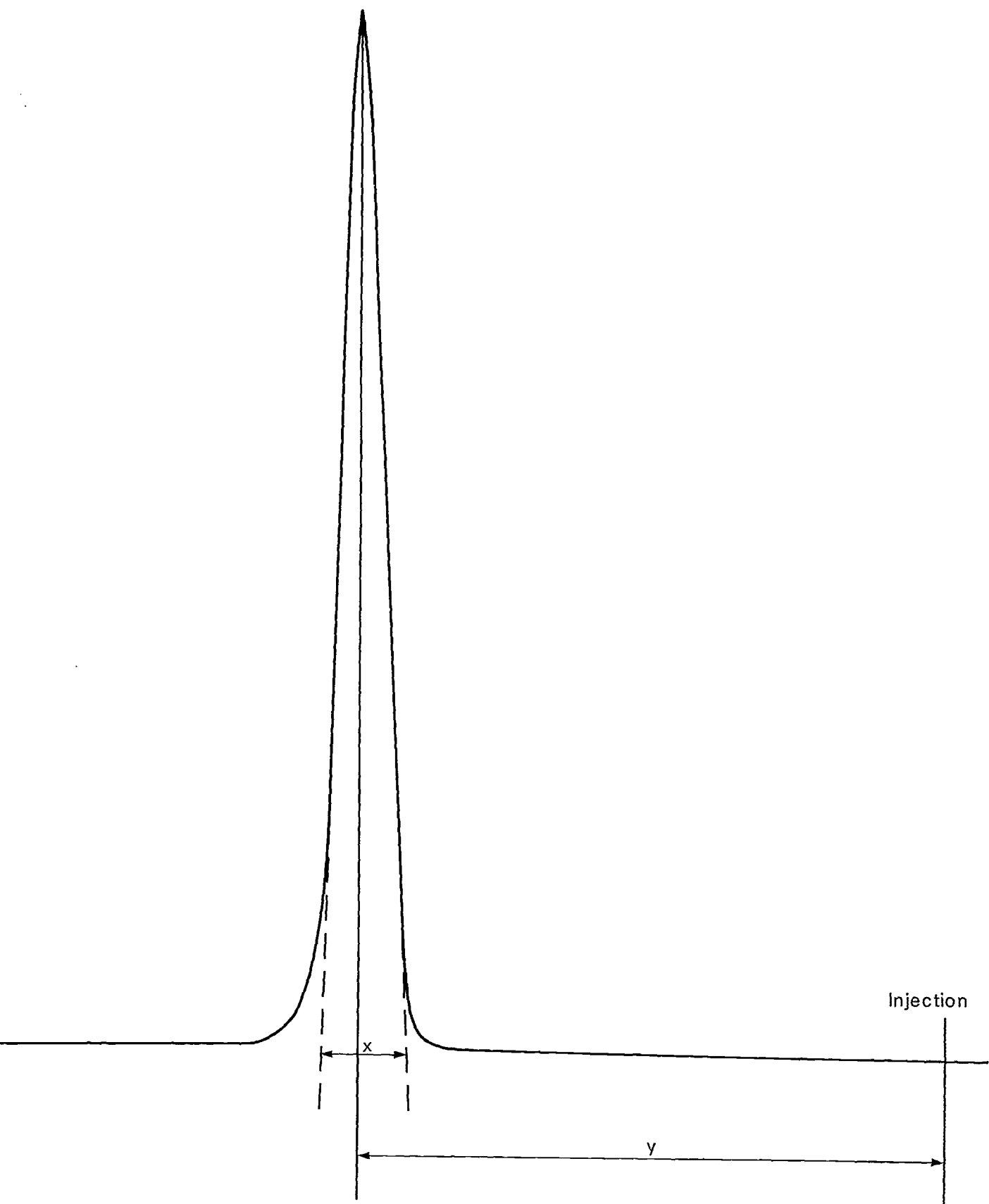
pass more rapidly through the column. The polarity of the solute also affects its partition between stationary and mobile phases of the column and hence the time it is retained. If the stationary phase is non-polar (e.g. silicone or squalene) polar solutes are normally eluted more rapidly than non-polar solutes with the same boiling point.

b. Compounds which at ambient temperature have a very low vapour pressure can be induced to pass along a GC column more rapidly by increasing the temperature. All gas chromatographs are fitted with an oven around the column to achieve this and to extend the range of the compounds which might be analysed. The relationship between the column temperature ($t_c$) and the specific retention volume ($V_g$) is given by the Antoine equation:

$$\log V_g = \frac{B}{(t_c + C)} + A \tag{1}$$

where A, B and C are constants for the particular solute and stationary phase used.

Because the specific retention volume is inversly proportional to the absolute temperature, relatively small variations in the oven temperature will cause considerable changes in retention times and it is important that the oven temperature be precisely controlled.

c. Many stationary phases of varying polarities are commercially available. The effect of the polarity of the stationary phase can be demonstrated by introducing the methyl esters of the $C_{18}$ carboxylic acids into polar and non-polar columns. With a non-polar column the elution order is methyl linoleate, methyl oleate, methyl stearate whilst with the polar column it is reversed, with the saturated methyl stearate eluting first, followed by methyl linoleate.

The rate of progression of a solute through the column under constant conditions depends not only on its polarity but also on the phase ratio (β) which is the ratio of the volume of carrier gas in the column to the volume of liquid phase in the column. If other conditions are equivalent a solute will pass more rapidly through columns of high phase ratio than through heavily loaded columns of low phase ratio. The phase ratio is related to the partition ratio K by:

$$k = \frac{K}{\beta} \tag{2}$$

where K is the partition coefficient.

Columns with a low phase ratio (e.g. most packed columns) give high partition ratios and columns with a high phase ratio (e.g. most open tubular columns) give low partition ratios. For open tubular columns the phase ratio is related to the internal diameter of the column and the thickness of the coating:

$$\beta = \frac{r}{2d_f} \tag{3}$$

where r = radius of the column bore
and $d_f$ = mean liquid film thickness

Another physical property of the column which should be considered, when it is necessary to separate two compounds with very similar retention volumes, is its selectivity. To separate these compounds long or highly efficient columns may be used or, alternatively, columns with a different and more selective stationary phase can be substituted. As the resolution of a column is proportional to only the square root of its length, it is often advantageous to use a different stationary phase rather than to increase the column length.

d. The purpose of the carrier gas or mobile phase is to transport the sample components through the column to the detector. If the flow rate of carrier gas is increased then the solutes will be transported more rapidly, shortening the transport time and hence the time of analysis. Increasing the flow rate of the carrier gas, however, may also adversely affect the separation of the components of the sample and may have an effect on the response of the detector. The nature of the carrier gas also affects the performance of the column and the detector so that selection of an appropriate carrier gas for a particular analysis is often a matter of compromise. In general if the velocity of the carrier gas is low, a gas of high molecular weight gives the best separation, and most chromatographs employing packed columns in the UK use nitrogen as the carrier because of its relatively low diffusion coefficient and low cost. At high velocities of carrier gas, gases with a low molecular weight such as hydrogen

or helium are better, and these gases are normally employed when capillary columns are used[6]. Some detectors work better with one carrier gas than another e.g. the electron-capture detector operating in the pulsed mode gives a better performance with an argon-methane mixture than with the commonly used nitrogen, and with thermal conductivity detectors a carrier gas of high conductivity such as helium often gives the greatest sensitivity. Inevitably therefore, selection of the best carrier gas for a particular analysis depends upon factors which may conflict, as the gas giving the optimal column performance is not always ideal for the detector in use.

### 2.2 The Van Deemter Equation

The mechanism which determines the efficiency of columns is governed by a number of factors expressed in the Van Deemter equation[5]. A shortened form of this equation is

$$H = A + \frac{B}{u} + uC_l \qquad (4)$$

where H = theoretical plate height

- A = a constant dependent on eddy currents in the carrier-gas flow which is affected by the packing geometry, the walls of the column and the turbulence of the gas flow

- B = a constant dependent on diffusion of the sample in the gas and to a small extent in liquid phases; the rate of diffusion is affected by the temperature, by the nature of the carrier gas and the stationary phase, and by the gas velocity

- u = the linear gas velocity

- $C_l$ = the liquid phase non-equilibrium coefficient – a constant dependent on the mass transfer between sample molecules in the stationary phase and the gas phase, which is affected by the effective film thickness of the stationary phase and the diffusion rate of the solute within the stationary phase.

This equation predicts that for maximum column performance the contribution of each term should be minimised whilst a constant linear rate of flow of carrier gas is maintained. It is possible to calculate the values of the constants A, B and C[5] from van Deemter plots of H versus the linear gas velocity u (Fig. 2).

The form of the van Deemter equation is a hyperbola having a minimum at a carrier gas velocity of $(B/C)^{\frac{1}{2}}$ and a minimum value of H at $A + 2(BC)^{\frac{1}{2}}$. If the linear portion of the graph is extrapolated back to the Y-axis the intercept gives the value for A. The constant A is equal to $2\lambda d_p$ where $d_p$ is the particle size and $\lambda$ is a dimensionless constant indicative of how good or bad is the homogeneity of the column packing. Thus if the particle size is known, a measure of the regularity of the packing can be obtained. According to this form of the van Deemter equation, A is the only term which is independent of the linear flow rate.

The B/u term, due to molecular diffusion (longitudinal diffusion in the direction of flow), contributes to zone spreading, as the sample molecules tend to spread in all directions irrespective of whether the carrier gas is flowing or not. It is independent of eddy currents but is dependent on the physical properties of the sample, particularly its volatility. Using the method of least squares, a gradual approximation of B may be calculated from a plot of (H-uC) versus 1/u.

The uC term may be calculated from the slope of the linear part of the van Deemter plot and accounts for non-equilibrium effects. One way of reducing this term and hence increasing efficiency is to make the liquid film thickness as small as possible.

Whilst the validity of the van Deemter equation has been questioned by Giddings[8] and others, who have suggested that the A and uC terms are not strictly additive, the variation of H with the velocity of the carrier gas has the same general form whichever expression is used. Purnell [13] has provided a critical review of the various forms and developments of the van Deemter equation.

As mentioned previously, in order to achieve the best column performance, the three terms in the van Deemter equation should be minimised. Unfortunately, however, the conditions necessary to minimise the effect of one factor are not in accord with those that reduce the effect of another. For example, the B/u term suggests the flow rate of the carrier gas should be high to minimise H, while the uC term suggests that H is

## FIGURE 2 VAN DEEMTER PLOT
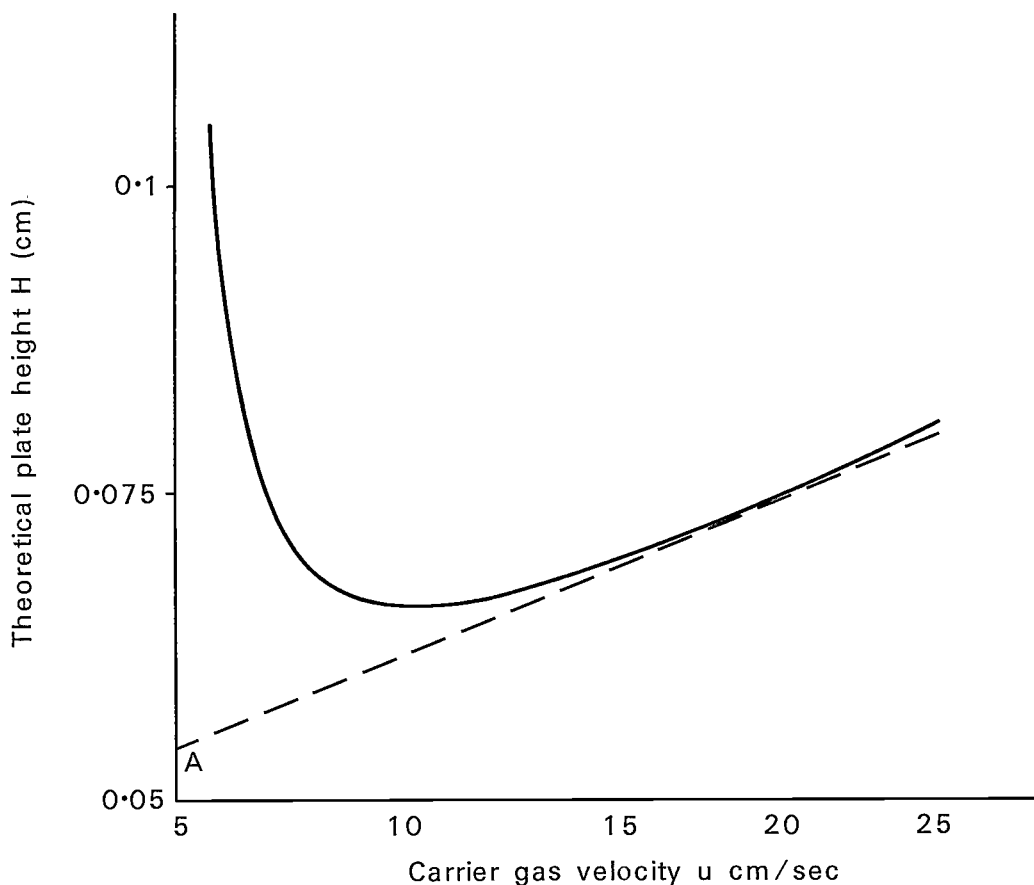


minimised by a low flow rate. Similarly, the diffusion rates in the liquid phase should be high to avoid non-equilibrium effects but equally should be low to prevent longitudinal diffusion. Also, whilst each term suggests that the particle size should be as small as possible, if the particles are too fine the passage of the carrier gas is obstructed.

It is clear, therefore, that H must be minimised by arranging the variables to reach the best compromise. The aim and art of the gas chromatographer is to achieve the ideal compromise for the analysis in question.

The original van Deemter equation has been modified[9-11] to take account of the fact that with lightly loaded and open tubular columns there is always a substantial contribution to the plate height from gas phase non-equilibrium effects ($C_g$).

Golay's[12] modification of the equation takes the form

$$H = A + \frac{B}{u} + (C_l + C_g) u \tag{5}$$

and for open tubular columns where A = O

$$H = \frac{B}{u} + (C_l + C_g) u \tag{6}$$

where the symbols are the same as those used with the van Deemter approach.

Even when a reasonable compromise between the van Deemter variables has been achieved, experience shows that the peak shapes obtained often deviate considerably from the Gaussian ideal. The chromatographic peaks often display asymmetry, often a tailing effect on the trailing edge. It can be demonstrated that, for a compound to give a Gaussian peak, the partition coefficient should be constant during the passage of the peak i.e. Henry's Law is obeyed. This can be shown graphically in terms of distribution isotherms (Fig. 3).

In general, the situation illustrated in Fig. 3(2), where the isotherm shows a positive deviation from the ideal behaviour shown in Fig. 3(1), is caused by physical or

# Figure 3 RELATIONSHIP BETWEEN THE DISTRIBUTION ISOTHERM AND PEAK SHAPE



Concentration of solute in gaseous phase

(1)                    (2)
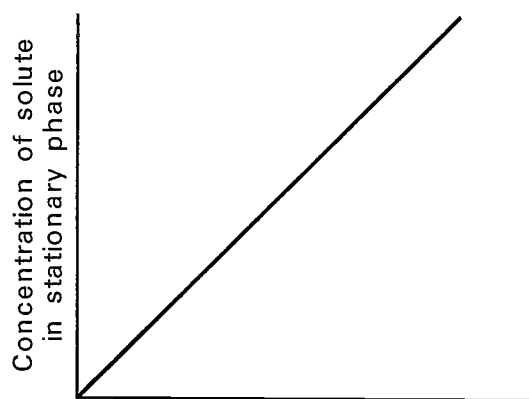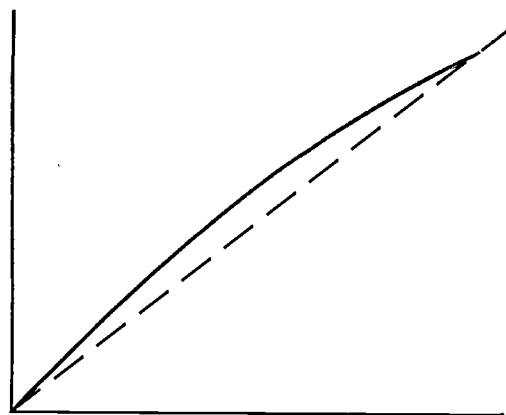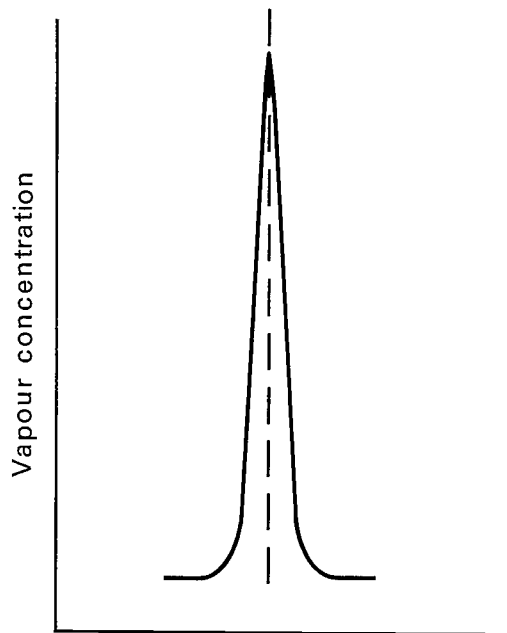
chemical interactions between the solute and the column. For example, the loading of the stationary phase may be too low or the support is unsuitable or the walls of the column may adsorb the solute. Obviously the nature of the column, e.g. its polarity, acidity, basicity and adsorption characteristics, will affect its efficiency, since these properties will all to some extent affect the band widths of the materials being separated and may cause losses of some labile determinands. The columns which are considered suitable for particular analyses will be discussed in Section 3.
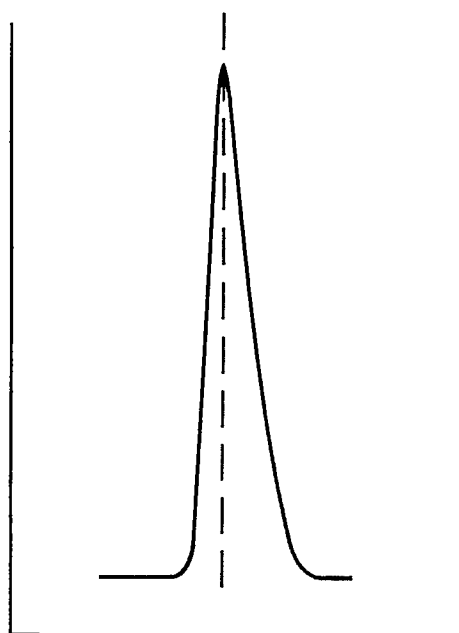
## 2.3 Column Efficiency Measurements

Gas chromatography is normally used to separate components of mixtures from one another and then to detect and tentatively identify these separated components. To achieve good separation it is necessary that the peak associated with a particular compound does not spread out on the column and overlap with any other peak. A column giving peaks which tend to be well separated is described as efficient, and this column efficiency can be measured in a number of ways. Perhaps the most common method is to calculate the total number of theoretical plates the column will yield. This is calculated from any peak in the chromatogram by

$$\text{No. of theoretical plates (n)} = 16 \left( \frac{y}{x} \right)^2 \qquad (7)$$

where $\quad$ x = the projected peak width at the base

$\qquad$ y = distance from the point of injection.

It may prove helpful to increase the speed of the chart recorder to obtain a more accurate estimate of x. The measurements to be made are shown in Fig. 1.

The total number of theoretical plates a column develops is often converted to the height equivalent to a theoretical plate (HETP) or theoretical plate height by

$$H = \frac{\text{total column length}}{\text{number of theoretical plates}} \qquad (8)$$

where H is the height equivalent to a theoretical plate. Alternatively, the measurements of column efficiency can be made using the peak width at 0.6 of the peak height, then the number of theoretical plates is given by:-

$$n = 4 \left( \frac{y}{W_{0.6}} \right)^2 \qquad (9)$$

This method obviates the difficulty of constructing tangents to the inflection points of narrow peaks.

Another method[7] which is often used for measuring the column efficiency, particularly of capillary columns is to measure the separation number, which is a measure of the number of peak widths of a homologous series which will fit between two successive peaks derived from homologues of consecutive carbon number. A series of n-alkanes is normally used for the test. The peak widths are measured at half-height and the separation number ($n_{(sep)}$) is given by:

$$n_{(scp)} = \left[ \frac{d}{Y_1 + Y_2} \right] - 1 \qquad (10)$$

where d is the distance between successive n-alkane peaks
$\qquad$ $Y_1$ is the peak width (half-height) of first selected peak
$\qquad$ $Y_2$ is the peak width (half-height) of selected peak.
Commonly, the two selected n-alkane peaks are between $C_9$ and $C_{20}$. It should be stated which compounds were used for the calculations. In practise the separation number can be related to the number of theoretical plates by

$$n_{(sep)} = K\sqrt{n-1} \qquad (11)$$

where K is a constant which depends on the column properties and varies between 0.1 and 0.2, and n is the total number of theoretical plates.

## 2.4. Tests of Column Performance

To optimise performance, a GC column should give the highest practicable resolution, it should be stable under the temperature and flow conditions used without excessive bleeding of the stationary phase from the column and the results of chromatographic separations should be reproducible over extended periods of time. These properties have been discussed by Grob[14] who describes how they may be measured for capillary columns using a series of tests[15, 16].

The extent of adsorption (caused both by hydrogen bonding and the polar or reactive nature of the column) can be measured by comparing the size and shape of peaks for polar compounds such as 5-nonanone, 1-octanol and naphthalene with those of the n-alkanes. To some extent adsorption may be measured by evaluating the degree of asymmetry of the octanol peak in comparison with the near Gaussian shape of the n-alkanes. This can be calculated from

$$A_s = \frac{a + b}{(a + b) - (a - b)} = \frac{a + b}{2b}$$

where a and b are the two fractions of the peaks as shown in Fig. 4, and $A_s$ is the asymmetry factor.

In addition the asymmetry factor may be used to give an indication of the maximum loading which a column can tolerate. The amounts of alkanes injected are increased and the peak asymmetry factors measured for each injection. The onset of overloading will be indicated by a gradual decrease in the value of $A_s$. Grob states that a column should not be loaded to an extent greater than that which gives a value of 'a' twice that of 'b' (i.e. As < 1.5)[18]. Recently Grob has developed a simple and flexible test which gives a semi-quantitative indication of the separation efficiency, adsorption, acid-base effects and film thickness. The tests can be carried out in a single run under standardised conditions. A test solution which they have evaluated contains twelve compounds in concentrations (shown in Table 1) which are inversely proportional to their sensitivities to flame ionisation detection [17].

Table 1

| Compound | Concentration (mg/l) |
|---|---|
| Methyl decanoate | 42.5 |
| Methyl undecanoate | 41.5 |
| Methyl dodecanoate | 40.0 |
| n-decane | 28.3 |
| n-undecane | 28.7 |
| 1-octanol | 35.5 |
| Nonanal | 40.0 |
| 2, 3-butanediol | 62.0 |
| 2, 6-dimethylaniline | 32.0 |
| 2, 6-dimethylphenol | 32.0 |
| Dicyclohexylamine | 31.3 |
| 2-ethylhexanoic acid | 38.0 |

The hydrocarbons are used as a check that the attenuation is correct for precise measurement of the other peaks. The nonanal, 2, 3-butanediol and 1-octanol standards are all used to give a measure of the different types of adsorption that may occur on the column. The alcohols and amine are more likely than the aldehyde to be adsorbed, by hydrogen bonding, to Si-OH groups in the glass.

The methyl esters (which were chosen because of their similar retention times on the different stationary phases and because they are less likely than alkanes to cause column overloading) are used for the measurement of separation numbers (Equation 10). (Grob et al.[17] have found that the average of the two separation number values calculated from the three ester peaks is similar to the value calculated from the alkane peaks.)

Finally the DMA, DMP, dicyclohexylamine and 2-ethylhexanoic acid are used for acid-base tests. These and other tests have been discussed by Jennings[19] particularly for use with fused silica columns.

# 3 Uses of Gas Chromatography in the Water Industry

The Handbook of Chromatography[20] lists many thousands of separations which have been performed by gas chromatography. In the water industry a number of groups of compounds are analysed routinely using this technique and many others on an occasional or ad-hoc basis. The most commonly used analyses are for oils, phenols, organo-chlorine pesticides, polychlorinated biphenols organophosphorus pesticides, herbicides, haloforms, organo-metallic compounds, the lower carboxylic acids in sludges, chlorinated solvents, and digester gases. Other analyses for specific compounds such as acrylamide, methanol and pyrethrins, are also performed occasionally together with those designed to provide information about specific

## Figure 4 MEASUREMENT OF ADSORPTION

n-alkane

l-octanol
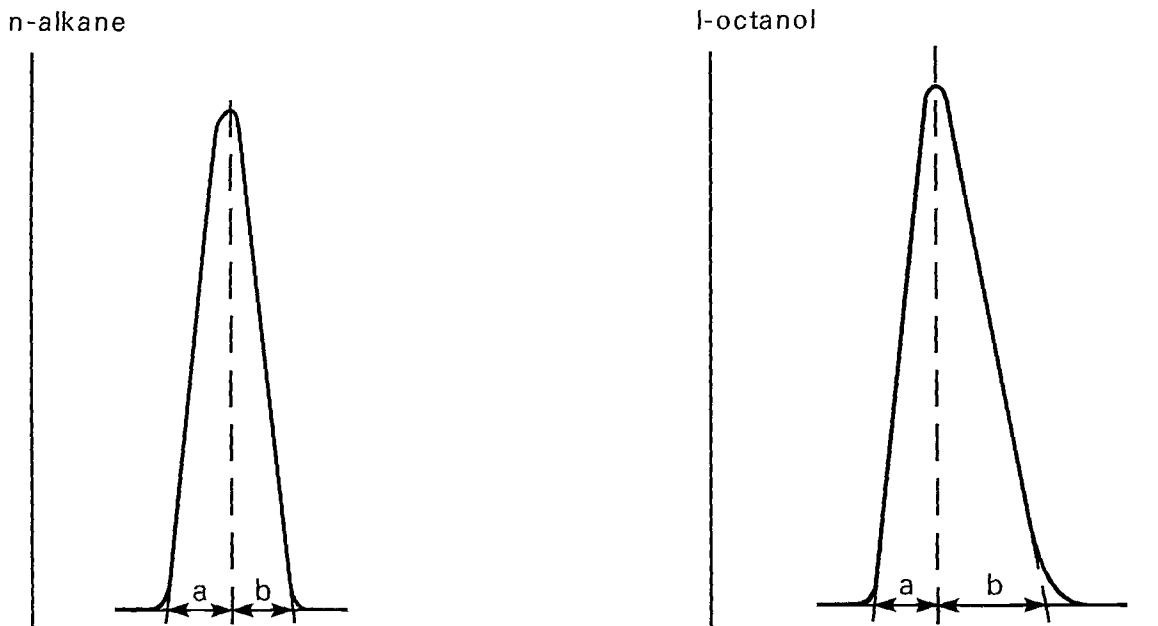


effluent problems. In combination with other techniques, GC may also give background information about the types of compound present in the aqueous environment, particularly those which are considered toxic in some way. GC is also sometimes used as a device to separate pure compounds from mixtures when simple methods of accomplishing this are unsuitable.

The types of sample which might be analysed include drinking water, river water, sewage, sewage effluent, sewage sludges, industrial effluents, waste tip leachates, fish and aquatic organisms, mud and occasionally air samples when an odour problem is apparent.

Most of the common analyses are described in other SCA publications in this series, but an outline of some of these methods may be useful here.

### 3.1 Oils

Oils are normally quantified by an infra-red technique but characterisation of oil pollutants is often carried out by GC. The sample is injected on to the column with a syringe or alternatively a probe or tube injector may be used. A non polar column e.g. OV1 is used with a flame ionisation detector and oven temperature programming employed. A characterisation of the oil is obtained by comparison of the disinctive features in the chromatogram with reference samples of oils. This process is somewhat dubious, owing to the variability of the samples but is in common use. Mineral oils, tars and some vegetable oils may be characterised in this way.

Sometimes it is necessary to compare an oil pollutant with a suspected source, in which case high resolution capillary column chromatography is used to enable detailed comparison of the fine structure of the chromatograms to be made. Natural oils and fats are characterised by saponification of the fatty material and conversion of the fatty acids formed to their methyl esters before the GC analysis.

### 3.2 Phenols

Colorimetric analysis for phenols provides a phenolic index which varies with the method used and gives a varying response depending upon which individual phenols are present in the sample. GC offers a better approach when phenols other than phenol itself are present. The sample is extracted and silylated with bis (trimethylsilyl) acetamide to produce derivatives which give well shaped peaks in the chromatograms. Internal standards may be used and a measure of total phenols obtained by summing the concentrations of the individual phenols determined.

## 3.3  Organochlorine Pesticides and PCB

This analysis is normally carried out on samples containing only residue levels of the determinands. The extraction, clean up, and separation techniques tend to be elaborate and are normally carried out by experienced analysts. The columns used vary widely and it is appropriate to use more than one column to increase the chance of successful identifications. DEGS, OV1, Apiezon L and mixed OV1/QF1 columns are often used. The column oven is run under isothermal conditions and the eluted compounds detected by an electron-capture detector which is particularly sensitive to halogenated compounds.

## 3.4  Organophosphorus Pesticides

These compounds are extracted with hexane and/or dichloromethane, concentrated, and injected on to the chromatographic column. Commonly, a non-polar column is used with an initial run using temperature programmed operation followed by an isothermal run at an appropriate temperature if the retention time of any peak present in the initial chromatogram corresponds to that of any known organophosphorus pesticide. A flame thermionic or preferably flame-photometric detector is used. These are very selective detectors and normally no prior clean-up of the sample is necessary.

## 3.5  Herbicides

Phenoxyalkanoic acid herbicides are determined by extraction with ether followed by conversion to the butyl ester. Methyl esters are sometimes prepared but there tends to be more interference, derived from co-extracted material, in the chromatograms at the retention times associated with the methyl esters compared to those present at the longer retention times when the butyl esters emerge. A non-polar column is used under isothermal conditions with an electron-capture detector. MCPA (2-methyl, 4-chlorophenoxyacetic acid) which is a commonly used herbicide, gives only a poor response when an electron capture is used and a mass spectrometer in the single or multiple ion mode is a more satisfactory detector for this substance.

## 3.6  Haloforms

These are extracted from water samples with 30–40°C petroleum ether or pentane and are examined without concentration by electron-capture gas chromatography using a polar column run under isothermal conditions (100°C for FFAP). The absence of a concentration step ensures that losses of haloforms by evaporation are minimised.

## 3.7  Fatty Acids

The presence of high concentrations of the lower ($C_2C_5$) carboxylic acids in digesting sewage sludge is indicative of digester malfunction and it is quite common to analyse for these acids in such material. The sample is acidified with formic acid and the supernatant aqueous solution containing the acids is injected directly on to a polar column (Carbowax 20 M or FFAP) under isothermal conditions at 135°C using a flame ionisation detector. This analysis is normally free from interference but ghosting effects (qv) always occur.

## 3.8  Chlorinated Solvents

The presence of chlorinated solvents even at low levels impedes or stops the satisfactory digestion of sewage sludge. It is common therefore to examine sludge from digesters which are not functioning properly for these volatile chlorinated hydrocarbons. The sludge sample is steam distilled into pentane or ether cooled in a freezing mixture and the solution so formed injected directly into a chromatograph fitted with an efficient non-polar column and an electron-capture detector. The column oven is maintained isothermally at low temperature, normally 30°C.

## 3.9  Digester Gases

Anaerobic digestion is frequently used to digest sewage sludge and it is common to monitor the performance of the digesters by analysing the gases produced using a gas chromatograph fitter with a kathorometer or thermal conductivity detector. The carrier gas used is often helium although argon, nitrogen and hydrogen are sometimes

preferred. The stationary phase used often consists of cross-linked polystyrene beads, termed Porapak R, S or T or molecular sieve 5A or 13X. The GC oven is programmed from ambient or subambient to 100°C, when water vapour, hydrogen sulphide, methane, carbon dioxide, oxygen and nitrogen can be separated and detected.

## 4 Instrumentation

A gas chromatograph consists essentially of a column whose temperature can be varied, an injection assembly, a detector to detect the presence of material eluting from the column, and an amplifier to increase the detector signal strength so that its response can be displayed on a recording device such as a chart recorder. McNail [21] has reviewed the main features of chromatographs available from fourteen manufacturers to provide information to potential customers.

Columns are of two main types, packed and capillary. Packed columns are the most commonly used, and have some advantages over capillary columns. They are much easily prepared in the laboratory, they are less fragile and they will often withstand higher temperatures than capillaries. Packed columns contain an inert granular material (support) coated with the chosen stationary phase. Capillary columns are, however, being increasingly used because of the very much higher efficiencies of separation which can be achieved with them. These columns are normally long coiled tubes whose inner surface is coated with the stationary phase.

### 4.1 Packed Columns

These are normally constructed of glass or stainless steel and range in length from 0.5 to 6.0 metres. Analytical columns are usually sold with nominal outside diameter (OD) of ⅛″ or ¼″ although preparative columns may be purchased with diameters of ⅜″ or ½″. The internal diameter of the column determines the optimum flow rate of carrier gas which can be used. Columns of narrow bore tend to give better separations than columns of wide bore but can be more easily overloaded if the amount of material present in the sample is large. In general, if the internal diameter of the column is large, a longer column will be necessary to achieve the same efficiency but will have a higher working capacity than that of a narrow-bore column. Columns of ⅛″ OD, which normally have an internal diameter of about 2 mm, are more difficult to pack than ¼″ OD colums but are preferred in temperature-programmed work as they come to the equilibrium temperature more rapidly. The OD of the column used is determined by the make of instrument in use and it is worthwhile to consider the type of analysis envisaged before a new instrument is purchased which may restrict the user to a particular column diameter. The column length is determined by the user and suitable columns can be purchased of any length to suit the analytical requirements. When the peaks tend to overlap a long column is required, but little increase in the resolution of packed columns is obtained beyond 6 m. Long columns increase the analysis time, so that for efficient working the length of the column should be sufficient to achieve the required separations but not so long that analysis time is excessive. For most analyses commonly carried out within the water industry packed columns of lengths from one to three metres are employed

### 4.1.1. Support materials

To produce an effective column it is necessary initially to choose a suitable support material. The ideal support would be chemically and physically inert with no properties which could produce catalytic decomposition of the samples. It would have a high resistance to mechanical fracture, a high porosity to minimise pressure drop, and would not tend to adsorb solutes. The specific area would be large and the granules of uniform size. The most commonly used supports in practice are Chromosorb W and Chromosorb G. These are prepared by the manufacturers from diatomaceous earth (keiselguhr) by heating at 900°C with sodium carbonate; the calcined product contains about 3.6% of $Na_2O$ [22] and the remainder is siliceous material. Chromosorb G has a small specific area in comparison with Chromosorb W giving columns of high permeability with good mechanical strength, making the column easy to pack without the production of 'fines'. The softer Chromosorb W is, however, more inert and is preferred for use when compounds which may break down on the column are being determined. Grob[23] suggests, as a rule of thumb, that Chromosorb G can normally be used rather than Chromosorb W if stainless-steel columns are satisfactory for the analysis, the implication being that if the determinands are insufficiently labile to break down on stainless steel they will not break down on Chromosorb G either. Otterstein[24, 25] has published reviews on solid supports, in which he discusses the properties of these and other support materials.

Before the support is used it is normally washed in acid to remove the mineral impurities present which may cause decomposition of the samples. Some of the fines present are removed by flotation at the same time. The material is washed with hydrochloric acid followed by water until the washings are neutral. Acid-washed (AW) supports are available commercially and it is not usual to carry out this procedure in the laboratory.

Most columns, however, require the application of a stationary phase to the support and the choice of a suitable phase can often be the most important variable in the success of the analysis. GC suppliers often publish lists and tables of phases suitable for various applications but perhaps the most reliable and convenient source of information is found in the abstracts published by the Chromatography Discussion Group[26] which include useful cumulative indices of phases used for all types of GC analysis.

### 4.1.2. Loading of columns

The speed of analysis and the efficiency of separation can be improved by using columns lightly (<5%) loaded with the stationary phase. With these columns, the effect of the support on adsorption is greater than with heavily loaded columns. It is possible to reduce adsorption, particularly noticeable with polar compounds, by a number of treatments, the most common of these being deactivation with dimethyl-dichlorosilane (DMCS). This operation is carried out in *the vapour phase by passing a* stream of nitrogen saturated with DMCS through a U-tube containing the support. After treatment the support is washed with methanol and dried at 100°C in an oven. Silanised supports are also available from GC suppliers and it is usual to buy these rather than to prepare them in the laboratory.

An alternative procedure stems from the discovery by Aue *et al.*[28] that when the polyglycol Carbowax 20M was coated on to Chromosorb W and this was heat-treated under nitrogen at 280°C and exhaustively extracted with methanol, a highly efficient deactivated packing with very low bleed characteristics was produced. This material was considered to have a non-extractable permanently bonded layer (nominally nonomolecular) of Carbowax in contact with the support surface. Whilst the technique is more established for use with capillary columns[29] its use makes an interesting alternative to silanisation with DMCS or hexamethyldisilazane (HMDS).

Another factor to be considered in the choice of support is the mesh size. The van Deemter equation (Equation 5) suggests that the column efficiency increases with decreasing particle size. Dal Nogare and Chin[27] found that use of a support with 80–100 mesh gave a column three times more efficient than one packed with the larger diameter 30–35 mesh material. However, as the particle size decreases so also does the pressure drop along the column, and furthermore the fine particles are more difficult to pack uniformly. In practice the compromise particle sizes used are normally 60–80 mesh or 100–120 mesh. The larger diameter particles are used to reduce pressure-drop in very long columns. The particle diameter of 60–80 mesh supports is between 0.20 and 0.25 mm, while 100–120 mesh supports vary in diameter between 0.125 and 0.15 mm.

### 4.1.3. Gas-solid chromatography

Columns are sometimes packed with an active granular solid, the technique being described as gas-solid chromatography. This technique, which apparently depends upon the adsorption of the solutes directly on to the packing material is used mostly for the determination of gases, low-boiling compounds and short-chain polar compounds. The types of adsorbents used are usually porous polymers such as Porapak, Tenax GC and Chromosorb Century 101–108. Carboranes such as Dexsil are also used in gas-solid chromatography where great stability is required at high temperatures, the maximum temperature limit for these materials being 450°–500°C. Kieselev and Yashin[30] have published a review of adsorption chromatography, stressing the theoretical aspects, while Jeffery and Kipping [31] have reviewed practical applications of the technique.

### 4.1.4. Preparation of packed columns

For a column to give maximum efficiency it is essential that the stationary phase should be coated evenly on the support and that the column be efficiently packed.

Columns can be purchased, ready-made, from all chromatography suppliers but these tend to be expensive and many analysts prefer to prepare their own.

The first step in preparing a column is to dissolve the liquid or stationary phase in a suitable solvent. Solvents suitable for individual phases are listed in manufacturers' catalogues, and a representative selection is given below:

| Stationary phase | Solvent |
| --- | --- |
| Apiezon L | Toluene |
| Carbowax 20M | Chloroform |
| FFAP | Chloroform |
| OV1 | Toluene |
| OV17 | Acetone |
| OV210 (QFI) | Acetone |
| SE30 | Toluene |

The amount of stationary phase to be dissolved in the solvent depends upon the weight of support being coated and the column loading. Some liquid phases, e.g. OV1, take a considerable time to dissolve and are best left in contact with the solvent overnight. The amount of solvent used should be sufficient to enable a slurry to be made with the support phase, but is typically about 3 ml of solvent per gram of support material to be coated.

The prepared solution is slurried with the support, usually by stirring in a beaker with a glass rod, and the solvent is then evaporated. This may be accomplished in a rotary evaporator, possibly using a filter pump to speed up evaporation. Another technique which has been used is to spread out the slurry on a large (9″ diameter) watch glass and to stir gently with a glass rod every few minutes, exposing fresh surfaces for evaporation, until the material flows freely. Essentially, whichever technique is used the stationary phase should be coated as evenly as possible on the surface of the support and the necessary agitation kept to a minimum to prevent disintegration of the support material.

When the column packing has dried, it must be packed into the column. This is accomplished by attaching a filter pump and water trap to the end of the column which will eventually fit into the detector. A small funnel is joined to the front end of the column with flexible tubing and the coated packing added to the funnel. The packing should then be sucked to the far end of the column where it is retained by a frit or plug of silanised glass wool. Repeated additions of packing to the funnel may enable the column to be filled, but sometimes it is necessary to augment the filter pump by removing the funnel and blowing the packing to the far end of the column with an air-line before proceeding as before until the column is packed. The use of a vibrator to pack columns often cracks the support, leading to fines and active sites in the packing. However, gentle manual tapping can be used to assist in column packing without damage to the support. When the column has been packed to an appropriate level the packing may be held in place with a plug of silanised or deactivated glass wool. This prevents blow-back of packing material if the column-head carrier-gas pressure is inadvertently released, although adsorption can take place on the glass wool and some analysts prefer to use the pressure of the carrier gas to hold the packing material in the column.

After packing, the column is inserted into the chromatograph oven with a low flow rate of carrier gas (5–10 ml/min) and with no connection to the detector. The column is then conditioned at its maximum working temperature for at least 48 hours. This process removes contaminants, residual solvent, and excess stationary phase. After conditioning, the column is ready for use, although it is quite common for its performance to improve dramatically after a few injections of standards and/or samples have been made. Adsorption sites on the column are deactivated and the resolution improves after the "running-in" injections.

## 4.2. Capillary Columns

The use of capillary columns is increasing because of the greater efficiency of this type of column and the more efficient separations which can be achieved. An example of

this from the water industry might be the separation of the chlorinated solvents Arklone (1, 1, 2-trichloro-1, 2, 2-trifluoroethane) and dichloromethane which can occur in steam distillates from sewage sludges. This separation is difficult to perform using packed columns, but complete separation of the two peaks is easily achieved when a 50-m capillary column coated with an SP1000 stationary phase is used.

Open tubular capillary columns consist of narrow bore tubes coated on the inner wall with a layer of stationary phase giving an unrestricted carrier gas path down the centre. This gives this type of column very high permeability so that very long columns can be used without substantially increasing the head pressure of the carrier gas. In this way greater total column efficiencies are achieved.

The use of open tubular capillary columns was first suggested by Martin in 1956, and in 1958 Golay[32] published the theoretical and practical considerations necessary for their use.

The use of capillary columns is not without its difficulties, but should be considered when well-separated peaks are required for quantitative work. Interferences in a method can often be elminated by the use of these columns as the peaks associated with interfering compounds, apparently having the same retention time as the determinand when packed columns are used, may be completely separated leaving no difficulties in quantitative interpretation of the chromatograms.

The capillary columns are usually made from glass, fused silica or stainless steel, although nylon and PTFE tubes have also been used. Stainless-steel tubing is much less fragile than glass and is suitable for the separation of stable non-polar compounds such as mineral-oil components, but for labile compounds, where decomposition might occur, glass or fused silica capillary columns should be used. Capillary columns are normally described as WCOT, PLOT or SCOT columns, although there is some ambiguity about these terms. WCOT columns are wall-coated open tubular columns where the internal surface of the tube is coated with a thin layer of the stationary phase. PLOT columns are porous-layer open tubular columns where the internal surface is coated with a layer of adsorbent support. SCOT columns are support-coated open tubular columns where the internal surface is coated with a support which in turn is coated with the stationary phase. Wall-coated columns give the most efficient separations although SCOT and PLOT columns have a longer life with a higher sample capacity and are less easily overloaded. WCOT columns are the most commonly used, however, because they give the highest efficiencies of separation.

It is unusual to prepare these columns in the laboratory. They are expensive to purchase but the effort involved in their preparation is considerable. Tranchant[33] includes a procedure for the preparation of capillary columns and Grob [34, 35] has given practical details of his own preparation procedures.

Because of the increased efficiencies of capillary columns (separation numbers are commonly 30-40, equivalent to about 100,000 theoretical plates in contrast to the 5000 theoretical plates typical of a packed column) it is unnecessary to use such a wide variety of stationary phases, and most analyses can be accomplished using a non-polar (e.g. OV1) and mid-polar (e.g. OV17) or a polar (e.g. Carbowax 20M) column. In order to achieve maximum performance, however, other factors must be considered, in particular the injection device, the carrier gas and its flow rate, and the technique of connecting the columns so that 'dead spaces' are eliminated. These factors will be discussed later.

### 4.3. Manual Injection

Samples are usually injected into a chromatograph with a calibrated microlitre syringe through a flexible septum. The syringe commonly used has a capacity of 10 $\mu$, with a sharply tapered point for septum penetration and a plunger guide to minimise the risk of accidental damage. The volume of sample injected on to packed columns is usually 1 to 5 $\mu$ and common practice is to make the volume injected constant, varying the concentration of standards and the dilution of samples rather than altering the volume of sample. This is because the syringe has a needle volume of at least 1 $\mu$ and if an injection block heater is used all of this will pass on to the column. Thus an injection of nominally 1 $\mu$ will in fact be 2 $\mu$ and a nominally 2 $\mu$ injection will be 3 $\mu$ and so on, so that when the responses from different volumes of sample and standard injections are made the comparisons may be grossly erroneous. Other syringe techniques are, however, possible (e.g. "sandwich" injections) and are in fairly common use, but

compensation is always made in some way for the needle volume. The precision of some of these alternative techniques is poor and should be checked against the standard procedure before use. Normally, the sample is sucked into the syringe and emptied several times before filling to slightly over the required volume, bubbles of air or vapour being eliminated if any are present. When very volatile solvents are being used in warm conditions, storing the syringe in a refrigerator between injections eliminates the problem of bubbles. The volume of sample in the syringe is then adjusted and the plunger withdrawn so that all the sample is contained within the barrel. The needle is wiped with a tissue, and inserted through the septum, and the plunger is rapidly depressed. Usually the syringe is then immediately withdrawn. Alternative injection techniques can be used, as it is possible to generate errors using the above procedure. Syringes in which the plunger passes down the needle are sometimes used when all the sample is contained within the needle. In recent years the design of these syringes has been improved so that they are now leak-free, but they still have the disadvantage that bubbles inside the barrel cannot be seen and eliminated.

One aspect of injection technique which can generate errors is the time the needle spends in the injector. When the syringe is withdrawn immediately after injection there is discrimination against the high-boiling components of the sample. These may recondense on the outside of the needle which has not yet reached the injection temperature. The precision achieved for these compounds may thus be poor. If the needle is left in the injector for about three seconds before the plunger is depressed, and about 5 seconds after injection, this problem is overcome, but degradation of labile compounds may occur on the hot metal surface and the peaks will broaden. Whichever technique is selected it is important that it is consistent and appropriate for the analysis being performed.

## 4.4. Automatic Injection

It may be considered that the number of samples requiring a particular analysis is so large that automatic injection into the chromatograph is desirable. Automatic injectors are normally operated pneumatically and are controlled by programmable electronic devices. The samples are contained in cups mounted in a rotating tray which advances one step after each injection has been made. The syringe is automatically flushed several times in the sample. It is then filled and the needle forced through the septum. The plunger is pushed down, injecting the sample, and the syringe is withdrawn. The cycle is repeated on the next sample or standard after a pre-set time has elapsed. These automatic injection devices are often more precise than manual injections and their use prolongs the life of the septum. Care must be taken, however, to minimise evaporation of solvent in the sample tray if quantitative results are required. Metal foil, polyethylene, or septum vial caps are normally used for this purpose.

After injection into the chromatograph, the sample passes directly or indirectly on to the column. When the injection is made directly into the column packing the process is described as 'on-column' injection. On-column injection without the use of an injector heating block has the advantage that decomposition of thermally labile compounds is minimised, but if the temperature of the chromatograph oven is low at the start of a run, e.g. in temperature-programmed work, the peaks tend to spread. If however, isothermal high-temperature operation is being used, on-column injection gives good reproducibility with minimal degradation. More commonly the sample is instantaneously vaporised at the head of the column by means of a heated metal block, and the carrier gas carries the vaporised sample in a narrow band on to the column. Grant and Clarke[36] have studied the effects of injection variables on the precision and accuracy of the peak heights and areas using a syringe in which the plunger passes into the needle. On-column injection gave significantly better precision for narrow boiling-range mixtures but injection by flash vaporisation gave better results when wide boiling-range mixtures were used. They concluded that the best compromise would be to use on-column injection with additional heat supplied by a vaporiser.

It is sometimes advisable to use a column liner, which normally consists of a short glass tube fitting inside the column. It may be packed with the support, with the support coated with the stationary phase, with silanised glass wool, or may be unpacked. The function of the column liner is to prevent non-volatile material which might be present in the sample from passing on to the column itself. After several

samples containing non-volatiles have been injected, the liner may be removed for cleaning or replacement. This process prevents the accumulation of non-volatile materials on the column packing which could eventually lead to loss of efficiency of the column. Column liners should be cleaned and deactivated before use in the same manner as that described for the column itself.

### 4.5. Capillary Column Injection

When capillary columns are used, injection systems are often complex. Grob[37] has described an on-column injection system for capillary columns which offers the advantages of minimum thermal degradation of the sample but it is currently more usual to use a heating block to effect flash-vaporisation of the sample. Capillary-column injectors can be operated in 'splitless' or 'split' modes. When a splitless injection system is used all the sample (normally 1 μ) is swept on to the column by the carrier gas. Some residual material, however, particulary the solvent, remains in the injection port and as it is slowly passed on to the column it causes the solvent peak to tail badly and may cause broadening of some or all of the other peaks. To prevent this the injection port is backflushed with carrier gas after most of the sample has been swept on to the column. The flow rate of the backflushing gas is normally about 30 ml per minute and the process is carried out between 10 and 15 seconds after injection. A similar process is used to purge the septum by sweeping it with the carrier gas to remove volatile silicones and plasticisers, which would otherwise pass on to the column and cause spurious peaks in the chromatograms. This effect is commonly encountered when the septum has recently been changed, although it can be minimised by preconditioning the septa in an oven in vacuo.

When a sample or standard is injected on to a capillary column at low temperatures the solvent forms a new temporary liquid phase on the first part of the column and this impedes the progress of the sample components. This causes the components eluting close to the solvent to narrow their band widths from the original spreading on injection, resulting in narrower peaks and better column efficiency. This process is sometimes called the 'solvent effect'.

Commercial capillary-column injectors normally also have provision for split injections. This type of injection is often used for high-temperature isothermal operation. Here only part of the sample passes on to the column, the proportions being pre-set by arranging that the carrier gas passed onto the column and out through a vent in a fixed ratio. The split ratio is defined by:

$$\text{Split ratio} = \frac{\text{flow (vent}}{\text{flow (column)}}$$

It is possible that the compostion of the mixture of compounds passing on to the column is not the same as that in the sample i.e. the splitter discriminates against certain components. This effect is usually seen when mixtures of compounds with widely differing molecular weights are injected. The effect has been minimised in modern commercial capillary-column injectors and these also have the advantage of being automatic and being constructed with all the internal surfaces made entirely of glass.

### 4.6. GC Ovens and Temperature Programming

In all gas chromatographs, the column, whether packed or capillary, is mounted in an oven. Increasing the temperature of the oven shortens the retention times of eluting components and the temperature or temperature range of the column oven is set such that adequate peak separation is obtained in the shortest possible time. It is important that the temperature control of the oven is accurate and consistent, as otherwise the retention times of the samples and standards will vary and identification and quantification of the peaks rendered much more difficult. In all modern instruments a forced-air circulation is used in conjunction with various types of control unit. Most of these units use a platinum resistance thermometer to control the temperature of the oven, although microprocessor-controlled feedback units are now fitted on some commercial equipment. For most quantitative applications the instrument is operated in the isothermal mode at an appropriate temperature. This has the advantage that the retention times are accurate but the disadvantage that the early peaks will be sharp and close together but late peaks will be low and broad. Also high-boiling components may not be detected or may elute during the course of a later run.

These problems can be avoided by changing the oven temperature in a controlled manner during the course of the run (temperature programming). This technique is often used for the analysis of complex mixtures in environmental samples. The most useful type of temperature programmer is one which allows the initial temperature to be set and maintained for a pre-set time followed by a linear increase in temperature at a pre-set rate directly proportional to the elapsed time. The upper temperature is also pre-set and the oven is maintained at this temperature for any desired period. On many instruments the oven door can be made to open automatically and the oven heaters turned off while the oven cools, enabling more efficient operation and the possibility of performing temperature-programmed chromatography with automatic sample injection. Low thermal mass ovens, usually constructed of stainless steel, have the advantage that the cooling rate is more rapid, allowing more temperature-programmed analyses to be performed during the working day.

## 4.7. Detectors

Components of a mixture which have been separated by the column are eluted from the end of the column and pass into a detector. The function of the detector is to react to changes in the chemical composition of the gases passing through it and to produce an electrical response proportional to the amount of the component emerging from the end of the column. Some detectors give a much enhanced response to certain groups of compounds and are described as selective, but the most commonly used detector, the flame ionisation detector (FID) (Fig. 5) responds to most organic compounds present in the vapour phase.

### 4.7.1. *Flame ionization detector*

The stream of carrier gas containing the compounds eluted from the column is mixed with hydrogen and passed through a jet where it is mixed with air and ignited in the body of the detector. A collector electrode is mounted over or around the flame maintained at a potential of 100–300 V with respect to the earthed detector body. Thermal ionisation of the eluted components allows a current to pass between the collector and the body which is proportional to the number of ions being formed in the flame at that moment[38]. For any one compound, therefore, the current produced is proportional to its concentration in the detector. The current flowing is amplified and the amplified signal normally displayed on a chart recorder.

Flame ionization detectors are sensitive and have a wide linear range. The flow rates of the carrier gas, hydrogen, and air supplied to the detector are normally stated in manufacturers' recommendations, but as a general guide the flow rate of hydrogen should be 10% higher than the flow rate of carrier gas and the flow rate of air should be ten times that of the hydrogen. For a ¼″ column with a carrier-gas flow rate of typically 30 ml per minute, the hydrogen would be set at 33 ml per minute and the air at 330 ml per minute. These flow rates can be checked with a soap-bubble flow meter.

### 4.7.2. *Electron capture detector*

The electron capture detector (ECD) (Fig. 6) is used to detect compounds which have an affinity for electrons and one of its forms was first described by Lovelock and Lipsky in 1960[39]. Its principal use is to detect halogenated compounds, e.g. herbicides, pesticides, PCB and haloforms. The detector normally consists of a cylindrical body housing a radioactive source and a concentric probe acting as the cathode. The detector body is earthed whilst the central probe is maintained at a potential which depends upon the type of detector employed. The radioactive source is normally $^{63}$Ni which has largely replaced the tritium sources used in former years because of its greater thermal stability. The mechanism of the electron-capturing process has been described by Wentworth et al.[40–42] and has been reviewed by Pellizzari[43].

There are three common ways in which a potential is supplied to the ECD. The simplest of these is a constant dc voltage, often of about 30 V, although this is normally optimised for the determinand and the instrument in use. In the second type the voltage supplied is pulsed, typically with a pulse space of 15 μs, and in the third type the interval between the pulses supplied is varied to maintain a constant detector current. Since the detector response is proportional to the available standing current in the detector, maintaining this current at a constant value results in a response which

# Figure 5 SECTION THROUGH
# LENGTH OF FLAME IONISATION DETECTOR

Ignitor

Gas outlet

Collector lead

Collector electrode

Frit

Jet

Air inlet

Hydrogen inlet

from column

# Figure 6 ELECTRON CAPTURE DETECTOR



Figure 6 ELECTRON CAPTURE DETECTOR

- Probe connection
- Insulator
- Central anode
- Gas outlet
- Detector body
- Ni$^{63}$ source
- Purge or make-up gas
- Column coupling
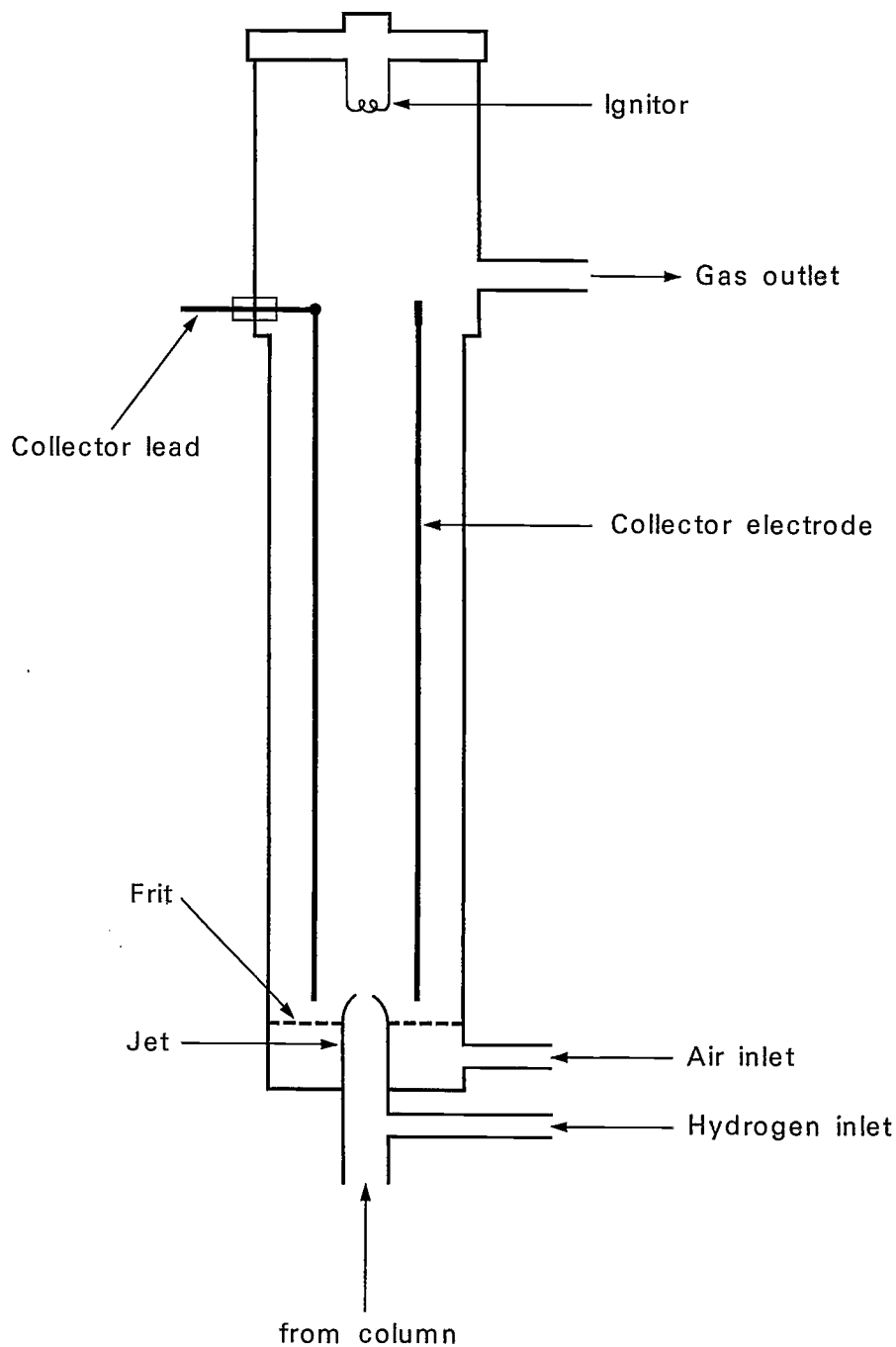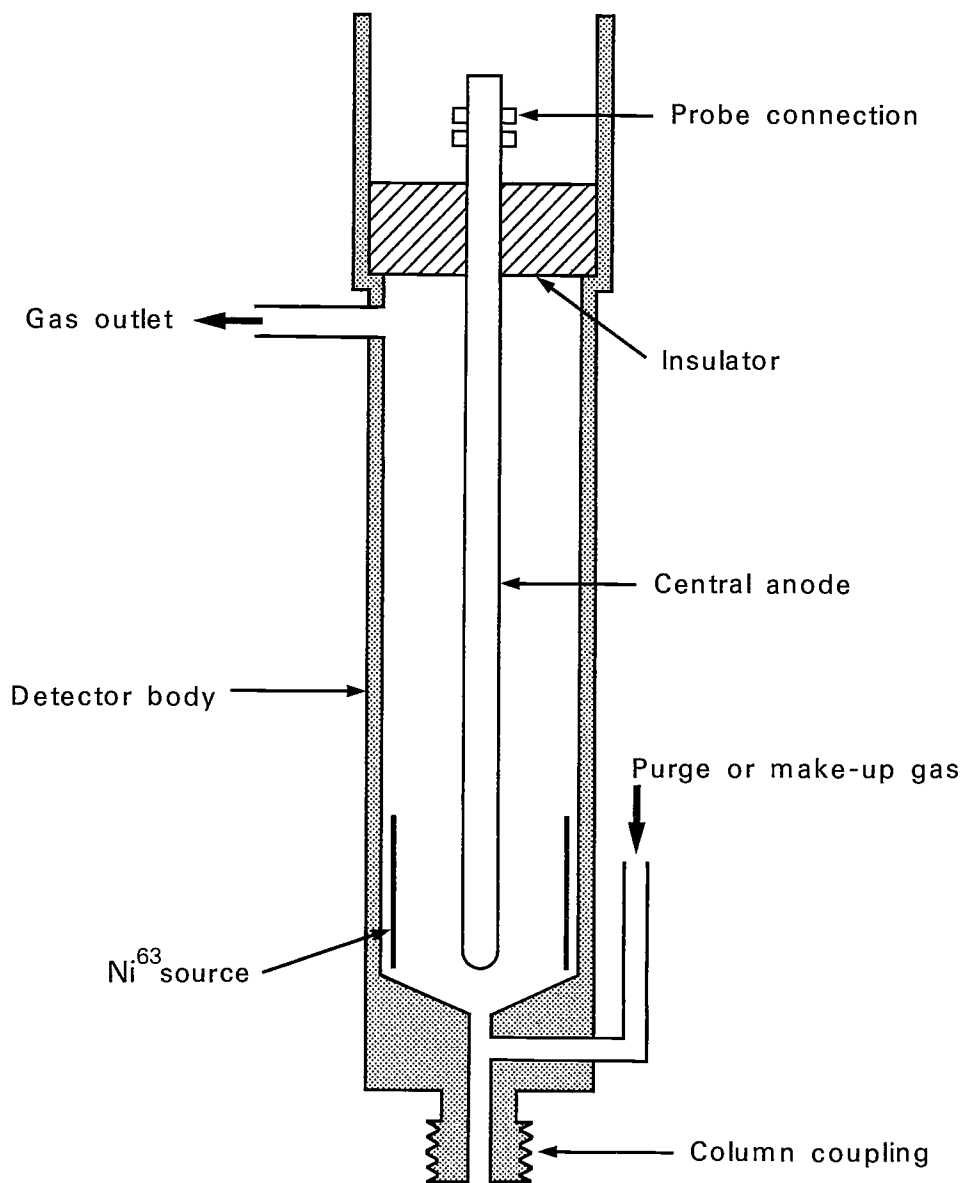
is linear over a wide range and produces increased detector sensitivity. There is little doubt that the third type is the most satisfactory, especially as the effects of contamination on the detector are minimised and as limited temperature programming may also be possible.

For certain compounds the ECD is extremely sensitive e.g. it is possible to detect 0.1 pg of γ-hexachlorocyclohexane, and this detector is much used in pesticide residue analysis. A problem in its use, however, is contamination and consequent loss of performance. Problems may arise from impure supplies of carrier gas, from the septa, from column bleed, and from the samples themselves. When detector contamination has occurred the standing currents are lowered and the trailing edges of the peaks tend to dip below the baseline. In these circumstances the detector should be returned to the manufacturer for cleaning. Although cleaning is a simple operation, only trained personnel in laboratories properly equipped to deal with radioactive substances should attempt to clean these contaminated detectors.

### 4.7.3. *Thermal conductivity detector*

The katharometer or thermal conductivity detector is a simple device which is often used in the analysis of gases produced by anaerobic sludge digestion. In this detector a constant electric current is passed through a temperature-sensitive element, often of platinum wire. After initial equilibration, the temperature of the wire is a function of the current, the thermal conductivity of the carrier gas surrounding the wire, and other constant energy losses. If material is eluted from the column the thermal conductivity of the gas surrounding the wire is altered and the thermal equilibrium is modified; the temperature of the wire changes and consequently also its electrical resistance. In practice the katharometer is inserted into a Wheatstone bridge circuit together with a reference cell, the two cells being housed in an insulated metal block. The changes in resistance and hence the change in current flowing across the bridge are conveyed to a chart recorder. The main disadvantages of this detector are its lack of sensitivity, and that quantitative analysis requires a calibration for each eluted component in relation to any carrier gas used although some detectors now employ constant filament current operation when both sensitivity and linearity are greatly improved.

### 4.7.4. *Flame photometric and flame thermionic detectors.*

The flame photometric detector[44] (Fig. 7) is a sensitive and specific detector for the determination of compounds containing sulphur and phosphorus, which is frequently used for the determination of organo-phosphorus pesticide residues. In this detector the column eluate is passed into a hydrogen-rich flame, when compounds containing sulphur or phosphorus, undergoing combustion, emit characteristic radiation at 394 nm and 526 nm respectively. This radiation passes through a glass heat-shield and a selective filter on to a photomultiplier, and the amplified signal from the photomultiplier can then be recorded. The use of two detectors arranged on either side of the flame allows the simultaneous determination of both sulphur and phosphorus compounds. The response of the detector to phosphorus compounds is linear, but with sulphur compounds the square root of the response is proportional to the concentration. This effect, and the mechanism by which the chemiluminescent species are formed, have been discussed by Adlard[45].

The flame thermionic detector (Fig. 8) is also used to determine phosphorus-containing compounds, although it also responds to halogenated and nitrogen-containing compounds. It is still in common use for the determination of organo-phosphorus pesticides although most workers now prefer the flame-photometric detector which is simpler to operate. The detector is similar in construction to the FID except that a collar of an alkali metal salt is mounted in or around the flame. The effect of this collar, normally constructed of caesium bromide or rubidium chloride, is to enhance the phosphorus signal relative to, say, hydrocarbons. The mechanism of this process is not entirely clear but has been discussed by Sevcik[46] and is temperature-dependent. Hence it is dependent upon the hydrogen flow rate, which must be optimised in any analysis carried out with this detector.

### 4.7.5. *Mass spectrometry*

The mass spectrometer used as a GC detector can be made very specific for individual compounds or can be used as a qualitative tool to identify the components eluted from

the GC column. It is highly sensitive and specific for thermally stable volatile compounds, but the equipment is very expensive and considerable expertise is needed in its operation. When the mass spectrometer is tuned to a particular mass, which may be the molecular ion or a prominent fragment ion of the compound of interest, interferences in the analysis can be virtually eliminated except for similar isomers eluting at the same time.

In the mode where identification of all the peaks in the chromatogram is required, the mass spectrometer is set to scan all the mass/charge ratios in a pre-set range (m/e = 40 to m/e = 440 is a commonly used range) and a chromatogram of the total ion current produced is recorded. The masses and intensities of the molecular and fragment ions derived from each peak can be interpreted to give an identification of the eluting peak. The use of a coupled data-system considerably aids interpretation of the spectra produced and increases the chance of successful identifications. A good introduction is given by Hill[47] who provides a large section devoted to the interpretation of the spectra produced from many commonly occurring compounds.

### 4.7.6.  *Other detectors*

There are a number of other GC detectors which have been developed but these are less commonly used. Grob[48] lists the salient features of most of these and provides references for further information.

### 4.8  **Amplification of the Detector Signal**

The current generated by the detector is very small ($10^{-10}$ amp for the FID) and it is therefore necessary to convert the detector signal electronically to a voltage sufficient to drive a chart recorder or other output device. Most of the amplifiers available utilise high-impedence, low-noise circuits in conjunction with several feedback resistors to produce a linear current-voltage converter. Part of the output is fed back to the input through the feedback resistors to stabilise the output. The amplifier is fitted with several controls, the range or attenuator control, the backing-off control and zero adjustment. The attenuator allows the total amplification required to be selected, the scale being graduated in linear or geometrically progressive steps, the lowest value of which gives the highest amplifier gain. As there is a background signal generated by the detector when no sample is present, it is necessary to offset this electrically prior to amplification. This is accomplished by adjusting the backing-off control which subtracts this offset current using a variable voltage and resistor circuit. The zero control offsets any voltage imbalance in the amplifier so that there is no output when the input signal is absent.
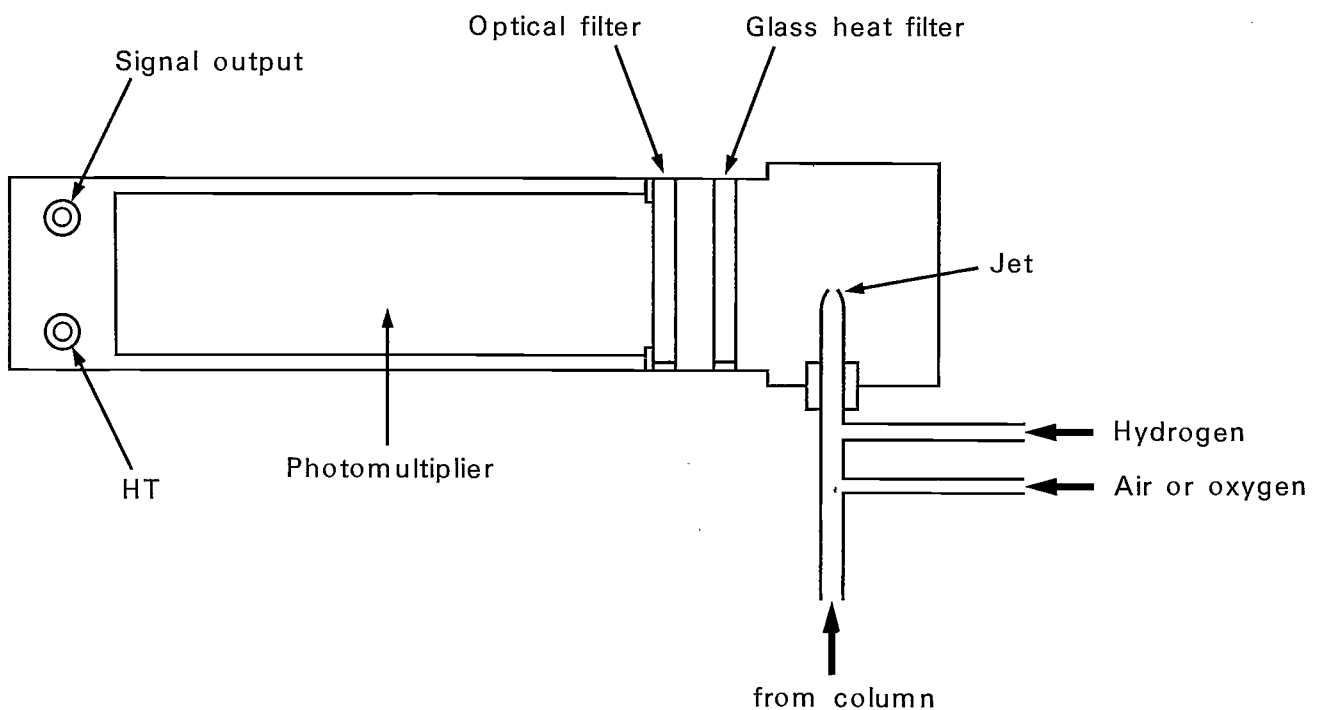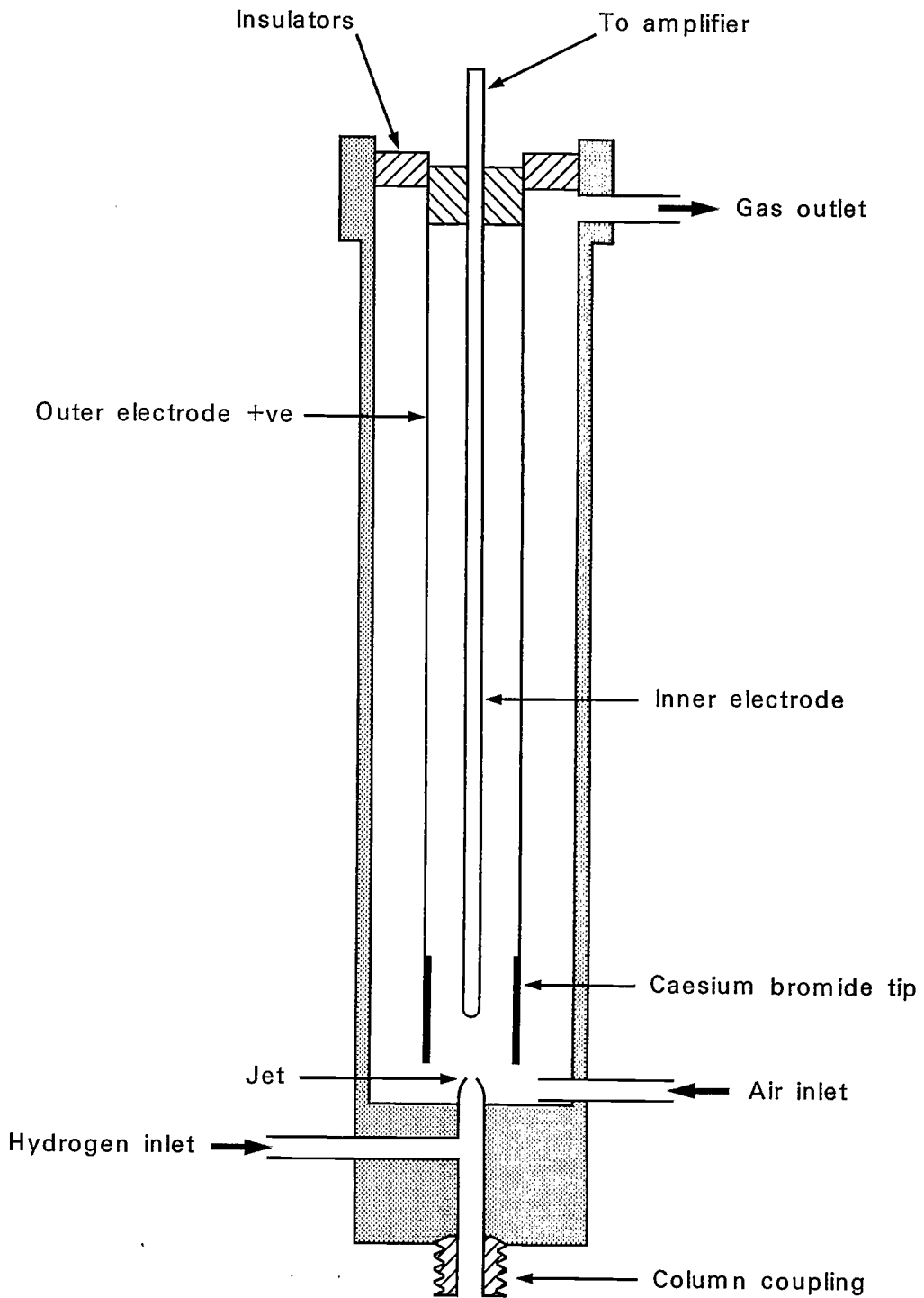
## Figure 7 FLAME PHOTOMETRIC DETECTOR

# Figure 8 SECTION THROUGH THERMIONIC DETECTOR

Insulators

To amplifier

Gas outlet

Outer electrode +ve

Inner electrode

Caesium bromide tip

Jet

Air inlet

Hydrogen inlet

Column coupling

Many modern chromatographs utilise a different type of amplifier employing transistor feedback[49]. It consists of two amplifiers in series, the first of which has a logarithmic output to cope with the wide dynamic range of the input from the detector, and the second is an exponential converter to restore overall linearity to the amplifier. These amplifiers do not cause a shift in baseline when the attenuator ranges are changed and, when used in conjunction with an integrator, enable samples with widely differing concentration ranges to be determined without repeat injection. This is very useful if an automatic injection system is employed and the chromatograph is left unattended overnight. The system can be made fully automatic and on some instruments the need for amplifier adjustments has been eliminated.

## 4.9. Recorders

A recorder chart is an analogue device used to record graphically, the output of the GC amplifier. Normally a paper-strip chart is used, recording variation of the detector response (and hence concentration of the determinand) with time. A number of factors are important in the choice of a recorder. The pen response time (which is the time taken of the pen to restabilise after an abrupt change in the input) should be short enough to record any rapid changes in the input signal, and should be as short as possible if high resolution capillary columns are used although with packed columns where the peaks are much broader this factor is insignificant. The linearity and resolution of the recorder is dependent upon its slidewire construction and resistance, but when modern recorders are used errors from these sources are negligible.

It is useful if the recorder is versatile, i.e. there is facility for altering the range, e.g. from 0.1 mV to 1 V, and that a wide range of chart speeds is possible. Experience has indicated that flat bed recorders are generally the most convenient and pens which write consistently are desirable. Some recorders use heat-sensitive paper which eliminates problems with pens, but some do not allow inspection of the trace until it has emerged from the enclosed writing head, two or three minutes after it has been drawn. If it is necessary to change the attenuation during the course of the run this delay might be too long for convenient operation, especially if capillary columns are being used. The use of two-pen or multi-pen recorders may be advantageous for some applications. It is possible to obtain a chromatogram using two pens, one giving 10 times magnification of the other. Alternatively more than one chromatograph or detector output can be fed to the same chart recorder.

## 4.10 Integrators

The most common method of quantifying a chromatographic peak is by measuring its height and comparing this with the height of a peak derived from a known standard run under the same conditions. Sometimes, however, a measurement of the peak area is more appropriate or convenient. In these circumstances estimates of the area can be made manually by triangulation, by cutting out and weighing, or by the use of planimeter. None of these methods, however, is entirely satisfactory as they are time-consuming and inaccurate, and the use of an integrator is much more successful. Mechanical or disc integrators which follow the track of the recorder pen have been widely used but have now been superseded by electronic integrators.

These normally use a microprocessor to control the way in which the chromatographic peaks are integrated and the same instrument sometimes can also control the function of the GC from the input keyboard as well as performing a range of calculations on the stored data from a GC run. Most instruments allow a wide variety of parameters to be preset to compensate for imperfectly separated peaks and elevated baselines; small peaks can be rejected and tangential skimming algorithms used to differentiate small peaks from a large underlying peak. Some types of integrators embody a printer-plotter which draws the chromatogram and then prints out the retention times and peak heights, peak areas or concentrations of all the peaks in the chromatogram relative to an internal or external standard. The more expensive systems use some method of data storage such as floppy discs or tapes so that the data from any run is not lost when the succeeding run starts and a visual display unit is often provided for the inspection and manipulation of stored and current data. Many systems will record monitor functions such as the carrier gas flow rate and will also store records of the sample code, the date and the analysis parameters used. In general, integrators are useful when many routine analyses are performed. The algorithms used for peak sensing and correction approach the reliability of a trained chromatographer. The

provision of data storage facilities with a screen for visual inspection and manipulation of data using appropriate software considerably eases the burden of the analyst.

The use of one of these integrators coupled to a chromatograph fitted with a wide-range amplifier and automatic injection equipment can allow suitable samples to be run unattended for long periods with only minimal effort from the operator. Such a system has been in use at the Water Research Centre for five years, determining concentrationss of volatile fatty acids[50].

## 5 Sample Preparation

It is most unusual for any sample to be run directly on the chromatograph with no preliminary preparation. It is much more usual to extract the compounds of interest into an organic phase and to inject an aliquot portion of this organic extract into the chromatograph after the completion of any separation, concentration, derivatisation, or clean-up procedure which is necessary for the particular analysis. Waggott[51] has outlined a number of procedures which have been used to extract a wide range of organic compounds from aqueous samples. Recovery of the organic constituents of the sample is always imperfect and preliminary experiments are necessary to ensure that the recovery is adequate.

### 5.1. Solvent Extraction

Solvent extraction may be carried out manually in the bottle in which the sample was taken or in a separating funnel. Alternatively a continuous separation may be performed in a liquid-liquid extractor of a type depending upon whether the extracting solvent has a higher or lower density than the sample

### 5.2. Steam Distillation and Headspace Analysis

Steam distillation is used to separate more-volatile components e.g. chlorinated solvents, especially when the test material is sewage sludge[52]. The volatile compounds may be distilled into a solvent such as ether or pentane, thus acccomplishing a concentration step as well as separation.

Another technique, whereby volatile organic compounds are stripped from aqueous samples by bubbling air or nitrogen through the sample and are collected on a carbon filter, has been described by Grob[53]. The purging gas is recycled by a pump through the sample and the filter for a specified time, the temperature of the sample being maintained (usually at 30°C) by means of a water bath. After the sample has been purged the carbon filter is washed with 5–15 μl of pentane, dichloromethane or carbon disulphide to yield the extract for injection into the chromatograph. This technique gives good recoveries of volatile compounds up to n-$C_{18}$ alkane and the filter extract is free from the less-volatile components. A related technique has been described by Bellar and Lichtenburg[54] which employs gas stripping with a relatively small sample volume, followed by trapping. It is used by the US Environmental Protection Agency and others, and is normally termed the VOA (volatile organic analysis) technique.

A simple static headspace technique, described by McAuliffe[55], involves equilibration of a portion of the aqueous sample with an equal volume of an inert gas. Components with a significant vapour pressure and limited water solubility are transferred to the gas phase in a reproducible manner giving a headspace concentration proportional to the concentration in the aqueous sample. An aliquot portion of the equilibrated gas is injected directly into the chromatograph with the advantage that no solvent is introduced. It is common to use a septum-capped vial or a standard glass hypodermic syringe for the equilbration, although many variations of the basic technique are in common use[56].

### 5.3. Resin Adsorption

Another technique for the concentration and extraction of organic residues from waters and effluents[57–59] involves adsorption of these compounds on non-ionic macroreticular resins such as Amberlite XAD2. It is not a simple technique, since thorough purification of the resin is necessary, and pH value and flow rate have significant effects on the recoveries. The resin is freed from organic impurities by successive Soxhlet extractions for 6 h with hexane, ether and methanol and the

purified material is stored under methanol until required. The prepared column of resin is washed with distilled ether, the sample is passed through at a low flow rate; and the organic compounds retained by the column are subsequently eluted with methanol or diethyl ether. This methanol or ether extract may be injected directly or may be dried and concentrated by evaporation or freeze-drying before injection into the chromatograph.

### 5.4. Extraction of Solid Samples

Solid samples such as muds and sludges are often extracted with solvents in a Soxhlet apparatus. When the samples are wet, extraction may be incomplete and it may be necessary before they are extracted to mix the sample with roasted sodium sulphate until a free running powder is obtained.

### 5.5. 'Clean-Up' and Derivatisation Techniques

With some samples, whichever method of extraction is used, co-extracted compounds will interfere in the GC analysis, i.e. the peaks associated with the compounds sought will be obscured by those derived from co-extracted compounds having a similar GC retention time. One solution to this problem is to separate the interfering compounds from the determinands before the sample is injected into the chromatograph. Often, column chromatography using alumina, Florisil or silica-gel columns is used for this purpose and the process is termed 'clean-up' of the samples. The process may involve adsorption chromatography, such as that used to separate polar constituents in mineral oil determinations, or partition chromatography such as that often used to remove interfering compounds in determination of residues of organo-chlorine pesticides.

Another approach may be to use a specific detector, e.g. electron-capture or flame-photometric detectors, which enhance the response of particular types of compound relative to others. This approach is not possible unless a suitable specific detector is available, but it may be possible to convert the compound sought to a derivative which gives a good response with a specific detector, with the advantage of the increased sensitivity obtained by the use of a detector such as the ECD. Derivatives such as pentafluoro-benzyl ethers or esters may be prepared from phenolic or acidic compounds to produce chromatograms showing an enhanced response for low levels of determinand. Derivatisation is also used to produce chromatographic peaks which are better shaped and hence better resolved from each other. The derivatised compounds may be more volatile than the original compounds or the polarity may be altered. Careful choice of derivative and column may result in more efficient separations and lower detection limits. The use of a silylating reagent in the GC/FID analysis to phenols, where the phenols are converted into the more-volatile and less-polar silyl ethers, is an example of the use of derivatisation.

A wide variety of sample preparation procedures have been described for various analyses. Some of the more useful techniques for water industry analysts are described in the AOAC Methods Book[60] which also includes a considerable bibliography.

## 6 Interpretation of Results

In GC, a compound which elutes with an identical retention time to that of a standard compound run under the same conditions can be tentatively identified as that compound. Confirmation of the identity of the unknown peak can be obtained by the use of two or three columns of different polarities, by chemical tests, or by using a primary identification technique e.g. mass spectrometry. If it is presumed that the eluted peak is associated with the compound sought, it is usual then to quantify the amount present by comparison of the instrument response given by the sample and by

known compounds is being performed. At the outset a full set of calibration standards is injected and the linear range of the GC system established. It may be assumed that if the systems is properly maintained this linear range will not alter appreciably over an extended period, so that it is unnecessary to run a complete calibration for each set of samples, so long as the amount of the determinand injected falls within the pre-determined linear range. This should be checked at intervals. Duplicate injections of a mid-range standard should be made and, if these agree closely, a line from this point through the origin gives the calibration graph for the analysis on that occasion.

Difficulties in interpretation sometimes occur when peaks of interest overlap, or when an interfering peak is present overlapping that of the determinand in the chromatogram. The best solution is normally to change the analytical method or the chromatographic conditions such that this does not occur. Sometimes decreasing the oven temperature will achieve the desired effect and sometimes it is necessary to change to a different type of column, e.g. a packed column supporting a different stationary phase or a more efficient capillary column. If, however, there is a distinct valley between peaks which are partially overlapping it is possible to obtain consistent results by measuring peak heights or by allowing an integrator to measure the peak areas, effectively by dropping a perpendicular from the nadir to the baseline.

On occasion peaks of interest appear on sloping baselines derived from another major peak or from bleeding of the stationary phase from the column. In these circumstances, if the analytical conditions cannot be altered to avoid the problem, it is necessary to draw a tangential baseline following the line of the slope either manually or electronically if an integrator is used. Inevitably, however, there is some loss of accuracy when this procedure is followed.

In the interpretation of the results it is also important to pay regard to experimental variation before conlusions are drawn. Factors such as baseline noise or signal to noise ratio must be considered and a limit of detection calculated by analysing replicate blanks or very low level samples to give an estimate of the standard deviation and hence the detection limit under the conditions used. Methods for testing the precision and performance af analytical methods are often given in the texts of the SCA methods and in other publications[61].

A chapter in the book edited by R L Grob[23] gives more detailed consideration to the quantitative aspects of GC analysis.

### 6.1. Kovats Indices

Many aqueous samples contain large numbers of components which can be separated by the GC column, and it may be desirable to name these compounds tentatively, or to compare them with published data, without using any form of primary identification of the eluted components. The use of retention times for this purpose is unsatisfactory since these depend on the conditions of the analysis, but when retention indices[62] are used comparability between chromatograms is much improved as this parameter depends only on the stationary phase employed, the temperature and the compound being analysed. The retention index is a number which relates the retention volume of an eluted component with that of two bracketting normal paraffins. Each n-alkane is arbitrarily allotted an index of 100 times its carbon number and the retention index number (Kováts index) of any component obtained by logarithmic interpolation.

These relationships can be expressed by:

$$L_A = 100\,N + 100\,n\,\frac{\log V'_R(A) - \log V'_R(N)}{\log V'_R(N+n) - \log V'_R(N)} \quad,$$

where $L_A$ = retention index of a substance A,

  $n$ = carbon number of the n-paraffin smaller than $V'_R(A)$,

  $N$ = carbon number of the n-paraffin larger than $V'_R(A)$,

  $V'_R(N)$ and $V'_R(N+n)$ = adjusted retention volumes of the n-paraffins bracketting A,

  $V'_R(A)$ = adjusted retention volume of A.

In practice the retention index is simply derived from a semi-logarithmic graphical plot of the adjusted retention time (i.e. the retention time of a component minus the retention time of an unretained peak) versus 100 times the carbon number of a series

of n-alkanes which bracket the GC peak of interest. The logarithm of the adjusted retention time of the unknown is calculated and the Kováts index determined from the graph.

When the Kováts index for an unknown peak had been calculated it is possible to compare this with published or previously obtained data and thus tentatively to identify the peak. Ramsey, et al.[63] have listed indices for 296 compounds and have discussed the value and accuracy of such comparisons. Retention data of this type have been stored in a retrieval system (e.g. by ASTM) and if the initial information used is sufficiently accurate, comparisons made between unknown chromatographic peaks and stored data could assist in the interpretation of complex chromatograms. Problems in the use of Kováts indices can arise in capillary-column work when a non-polar WCOT column is used which has been pre-coated with Carbowax 20 M to fill up active sites. It is possible for such a column to behave as though it contained a mixture of phases, producing considerable distortion of the Kováts retention indices.

The use of retention index measurements on temperature programmed GC runs would enable a wider range of compounds to be tentatively identified by comparison with stored or published data. It is, however, important to measure these indices accurately using well-defined chromatographic conditions. Linear interpolation is not sufficiently accurate but the use of cubic spline or polynomial interpolation[69] may give useable results.

# 7 Comparison of GC With other Techniques

Gas chromatography is essentially a technique for separating mixtures of volatile organic compounds, usually followed by quantification of the separated peaks. The other forms of chromatography which separate components in a similar manner are thin-layer chromatography (TLC), high-performance liquid chromatography (HPLC), column chromatography, and paper chromatography. Column chromatography is often used for the 'clean-up' of samples and in preparative work but neither this technique nor paper chromatography is nowadays commonly used for analysis. TLC has the advantages that the equipment necessary is inexpensive unless a plate scanner is used and that it will deal with some non-volatile compounds, but the accuracy of the results obtained is ofter rather poor. HPLC can also be used for non-volatile compounds and with modern instruments the resolution between the peaks is frequently good. The cost of the equipment necessary and the expertise needed to use it, however, are comparable to that for GC.The detectors normally used for HPLC work are ultra-violet or fluorescence detectors which, whilst providing an advantage of some selectivity with certain determinations, do not respond to almost all organic compounds in the same way as does a flame-ionisation detector.

In general, the advantages of GC compared with other chromatographic techniques are that it gives the most efficient separation of complex mixtures especially when capillary columns are used, that it offers a method of quantifying nearly all volatile organic compounds, and that the detectors available are sensitive and may also be selective. The disadvantages are that only compounds with sufficient vapour pressure to pass through the column at its maximum operating temperature can be analysed, that it is fairly expensive, that sample pretreatment is almost invariably necessary, and that it is not a primary identification technique unless coupled to a mass spectrometer or suitable infra-red spectrophotometer. Like all other chromatographic techniques it may not be entirely free from interference from co-extracted compounds which elute at or about the same point as that of the determinand.

Gas chromatography, whilst it compares favourably with other forms of chromatography for volatile organic compounds, is frequently not the only method which can be used for any particular analysis and may not be the most satisfactory. Colorimetric techniques, both manual and automatic, infra-red, gravimetric and polargraphic techniques are frequently used instead. In general, however, GC achieves greater specificity than other methods. In the colorimetric determination of phenols using 4-amino antipyrine, for example, a 'phenolic index' result is produced which depends upon which phenols are present in the sample, since different phenols react to varying extents with 4-amino antipyrine. The GC technique quantifies each phenol individually, thus producing a more satisfactory analysis when phenols other than phenol itself are present; many p-substituted phenols, for example, give no response when the colorimetric method is used. Similarly when an infra-red technique is used to determine mineral oils it is common to measure 'oil' by the methylene-stretching

frequency at 2960 nm, but if the type of oil is unknown there are difficulties in choosing a standard with a suitable extinction coefficient unless GC is first used to characterise the oil present in the sample.

The principal advantage, therefore, of GC over most other non-chromatographic techniques is its ability to separate the organic components before quantification so that there is more certainty about what exactly is being measured.

# 8. Common Faults

## 8.1. Contamination

Contamination of all or part of the system can be derived from:
(a) the carrier gas
(b) the septum
(c) the injection port liner
(d) dirty packing material at the head of the column
(e) the samples themselves.

The carrier gas used should be of good quality e.g. white spot nitrogen passing through molecular sieve. Rogue cylinders are sometimes found and these should be discarded. The septum is normally composed of silicone rubber and will bleed siloxanes into the system. The effect can be minimised by the use of septum purge and backflushing techniques and by vacuum baking of the septum before use, but it is possible that quite distinct peaks or raised baselines in the chromatograms are derived from septum contamination. If injections of samples containing non-volatile material are made, then the column liner or the first few inches of the column will become contaminated with this material. Some compounds will pass very slowly through the column and may give rise to broad peaks in the chromatograms of a later injection. Other compounds will be retained and this may lead to a gradual broadening of the peak and sometimes to peak splitting. The samples themselves may also cause very rapid deterioration in the quality of the chromatograms if they contain excessive quantities of materials such as fats. Extracts of animal tissue can quickly produce problems unless a clean-up step is carried out prior to analysis. Electron-capture detectors are particularly prone to contamination. This manifests itself in chromatograms where, following a peak, a dip in the trace below the baseline can be seen. In extreme cases these negative excursions from the baseline can cause the trace to disappear temporarily off the bottom of the chart. When baseline excursions appear, any quantitative measurements made are invalid. In such instances it is time to check the standing currents and to clean the detector.

## 8.2. Plumbing Problems

Plumbing defects often cause leaks in the system and this in turn may cause loss of the sample or a low flow rate of carrier gas or both and hence systematic checks for leaks should be regularly made. The most common source of leaks is the septum, and this should be checked whenever it is noticed that the retention times of the eluting components are longer than expected or are varying from sample to sample. Leaks also occur at the points where the column joins the injector and the detector and these seals should also be checked, tightened or replaced as necessary.

## 8.3. Electrical Defects

Electrical or electronic defects are usually best left to the manufacturer to solve, but a common fault which develops in the laboratory is that the electrical connections to the detector are defective. These can be repaired quite readily and it is worthwhile checking these, together with the amplifier connections, if the recorder trace is unstable.

## 8.4. Column Deficiencies

Gas-chromatographic columns become less efficient with prolonged use and have eventually to be replaced. It is sometimes possible to improve the performance by repacking the first few inches of the column or by breaking off the first few coils of a capillary column. If the maximum working temperature of the stationary phase is exceeded, causing loss of the phase, the detector becomes heavily contaminated and a grossly inefficient 'saw-toothed' chromatogram results.

The manufacturers of chromatographs always produce a handbook which contains information about troubleshooting and it is worthwhile referring to these schedules for less obvious faults.

## 9 Future Trends in GC

The future areas for developments in GC seem to be in increased automation, the use of inert capillary columns rather than packed columns, increased sophistication in injectors, and the development of better detectors.

The most obvious current trend in GC is towards making the analyses simpler and faster. Microprocessors are already being used to take over some of the controls of the chromatograph and microprocessor-controlled computing integrators are in common use to measure retention times and to calculate results relative to internal or external standards. Automatic injection from sample vials is also common, and a number of systems employing automatic injection, chromatographic separation, automatic peak sensing, and calculating and printing of the results have been described for analyses commonly performed in water industry laboratories[50,64]. A computer can also be used in conjunction with a number of chromatographs. This might be more economical than the use of several separate computing integrators. Data logging and/or data reduction by computer can also assist in the quality control of water treatment processes by recording and comparing changes which occur in GC profiles obtained from samples over a period of time.

As well as the trend towards simplifying the chromatographer's job by automation there is also a tendency to use more efficient columns to minimise interference and to carry out subtle separations. Glass or fused silica capillary columns are being increasingly used, usually the wall-coated open tubular type, and fused silica columns where the stationary phase is chemically bonded on to the walls of the tube have recently been developed. Capillary columns require special injection procedures and these are now available commercially, offering split and splitless injection. More recently 'on-column' injectors for glass and fused silica capillary columns have been described and constructed[65-68] and these septumless injectors which are commercially available, may become the best and most common type for use with capillary columns.

New detectors which show enhanced selectivity or sensitivity for various types of organic compound are likely to be developed in the future. An interesting innovation is the photo-ionisation detector where the material emerging from the column is subjected to UV radiation with a known energy. The photons emitted by the UV lamp (~10 eV) have sufficient energy to ionise many organic compounds but not the carrier gas. The ions produced are accelerated towards a collecting electrode where the current, proportional to the concentration of the eluting component, is measured.

Another detector which might be developed could consist of a number of metal oxide-silicon field effect transistors (MOSFET) in which some organic compounds emerging from the GC could be incorporated temporarily into transistor or diode structures, resulting in a change of conductivity which could be measured. Whilst these 'electronic nose' devices are still in their infancy and no practical GC detector has yet been constructed, their inherent potential sensitivity might form the basis for commercial development.

GC can also be interfaced with other equipment such as a fluorimeter[67] an infra-red spectrophotometer or a mass spectrometer. A capillary column GC interfaced to a high-resolution mass spectormeter probably offers the analyst the maximum chance of separating and identifying the components present in environmental samples.
Reviews of recent developments appear biennially in Analytical Chemistry[70].

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