

REVIEW OF GAS-LIQUID CHROMATOGRAPHY

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During the last few years gas chromatography has become established as a rapid, efficient, and relatively simple technique for the separation and analysis of mixtures of volatile substances. The present review is intended to survey critically the large amount of published work on theoretical principles, apparatus, techniques, and applications, and to give a comprehensive bibliography on all aspects of gas-liquid chromatography.

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DEFINITIONS AND HISTORICAL

The recommendations of the Hydrocarbon Research Group of the Institute of Petroleum [580] will be followed in this review. The term "gas chromatography" will be used for all those chromatographic techniques in which a mobile gas phase carries the substances to be separated through a stationary phase packed into a suitable container. When the stationary phase is a solid adsorbent, the method is Gas-Solid Chromatography (G.S.C.); when the stationary phase is an absorbent liquid supported by inert material, the method is Gas-Liquid Chromatography (G.L.C.).

The first gas chromatographic experiments were carried out by selective adsorption on, or desorption from, solid adsorbents such as active charcoal. This basic method is of long standing, for RAMSAY [500] used it in 1905 to separate mixtures of gases and vapours. CLAESSEON [101] has given a detailed bibliography of the literature up to 1944 and JANAK [328] has recently reviewed G.S.C. in detail.

Following the theoretical suggestion of MARTIN AND SYNGE [412], the method of G.L.C. was introduced by JAMES AND MARTIN [314] in 1952. This made possible the separation and estimation of small amounts of volatile substances with a very wide range of boiling points, and thus gave a great impetus to many fields of research.

SECTION I. PRINCIPLES INVOLVED IN SEPARATIONS BY G.C.

Methods of operating columns

In G.C. elution analysis, frontal analysis, and displacement development can be used. For elution analysis the mixture of substances to be separated is placed at the inlet of a column of suitable granular material and is passed through the column by a carrier-gas. The components eventually leave the column in the gas stream and their concentrations are recorded as a function of the time, or of the volume of carrier-gas, by a detecting instrument. Separation of the components is achieved by repeated equilibration between the mobile gas phase and the stationary phase. Gas-solid equilibria are involved when the stationary phase is an adsorbent, and gas-liquid equilibria when it is a liquid supported on an inert granular medium. Almost any degree of separation can be achieved by varying the nature of the stationary phase and the length and temperature of the column.

In frontal analysis the mixture to be separated is carried continuously on to a column of an adsorbent and at a constant concentration in the carrier-gas. The component which is least strongly adsorbed leaves the column first and each succeeding component leaves the column mixed with a small amount of each of the preceding components.

With displacement development the mixture to be separated is adsorbed upon a column of adsorbent. A constant concentration of a substance which is more strongly adsorbed than any of the components of the mixture is then passed through the column in the carrier-gas. Each component forms a band of constant concentration

on the column and emerges from the column substantially pure except for a small overlap fraction between each band.

Although frontal analysis and displacement development formed the basis of G.S.C. prior to the introduction of G.L.C., they have now been largely replaced by elution analysis. They are not used for analytical separations in G.L.C. (although frontal analysis has been used [61, 62] to study the symmetry of peaks) and CLAESSEN [101] should be referred to for a detailed treatment of these two methods. The possibility of a form of frontal analysis or displacement development occurring during elution analysis in G.L.C. cannot be neglected, particularly where the sample enters the first section of the column, and where components of a mixture may be present at relatively high concentrations in the stationary phase. The components may then behave non-ideally and tend either to displace one another from solution, or to associate with one another and remain in solution.

Principles governing the elution of substances through G.L. columns

Distinction between column efficiency and solvent efficiency

The overall efficiency of separation of a pair of solutes in a column can be divided into two contributions, (i) the column efficiency, and (ii) the solvent efficiency. The column efficiency is concerned with the spread of an initially compact zone of material as it passes through the column, and can conveniently be described by the height of a theoretical plate (HETP). The HETP is primarily a function of the column design and operating conditions, and to a lesser extent, of the natures of the solute and solvent (*i.e.* of the solvent efficiency). The solvent efficiency, or separation factor, can be expressed as the ratio of the times for two peak maxima to travel through a column, and is characterized by the respective distribution coefficients of the solutes. It is thus a function of the column temperature and of the natures of the solutes and of the solvent.

Theories have been developed to account for the rate of movement, and the characteristic shape, of zones of solutes in chromatographic columns. These theories are classified below and their application to G.L.C. first shown for a single solute. The solvent efficiency will be considered in detail later under principles governing the separation of mixtures of solutes.

Classification of theories of chromatography and their application to G.L.C.

The simplified theories of chromatography can be classified according to (i) the type of distribution isotherm that the solutes obey, and (ii) the ideality or non-ideality of the conditions. With "linear" chromatography the distribution coefficient (*i.e.* the amount of solute per unit volume of stationary liquid phase/the amount of solute per unit volume of mobile phase) is independent of the concentration of the solute, and with "non-linear" chromatography it is dependent on the concentration of the solute. In

"ideal" chromatography the flow of the mobile phase is considered uniform, the column is uniformly packed, equilibrium between the two phases is instantaneous, and longitudinal diffusion of solute molecules (or other processes having the same effect) does not occur. In "non-ideal" chromatography these assumptions cannot be made.

The four possible types are illustrated schematically in Fig. 1 (after MARTIN [405]).

1. *Linear ideal chromatography* has been dealt with in the classical treatment of WILSON [602]. The shape of the band remains unchanged during elution, mixtures

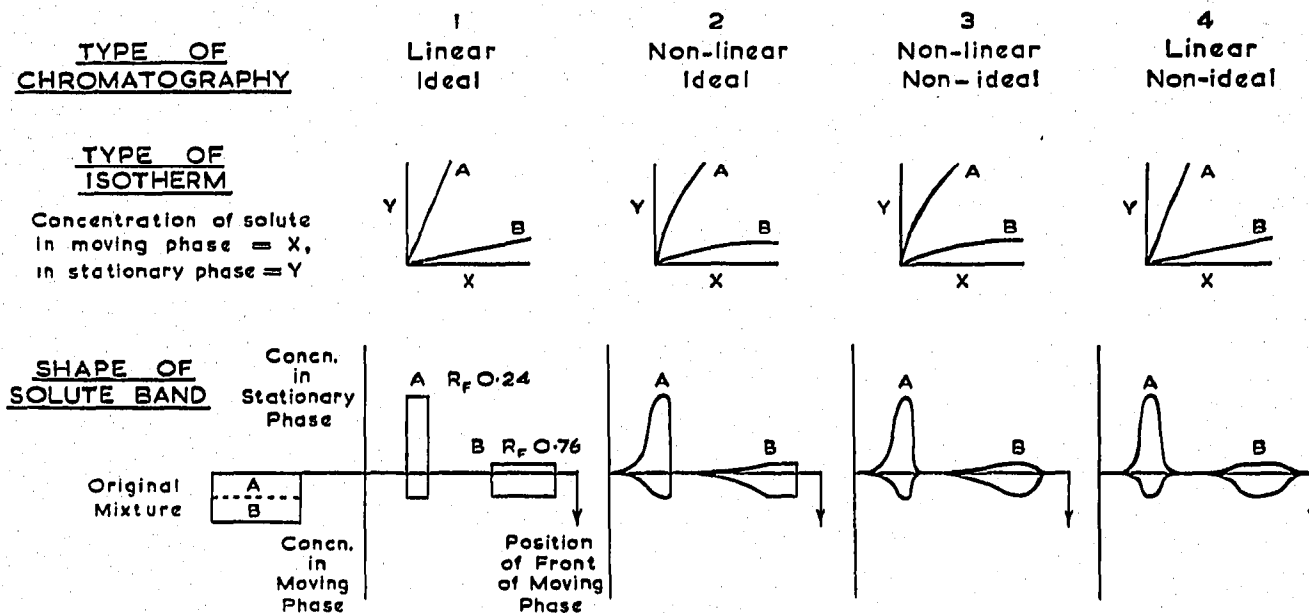


Fig. 1. Classification of types of chromatography (after MARTIN).

of solutes behave independently, and the requirements for individual bands to be separated can be calculated by simple mathematics.

2. *Non-linear ideal chromatography* was first treated by WILSON [602], and later by DE VAULT [150] for a single solute, but solutes can affect the behaviour of each other and rigorous treatment is not possible [353].

3. *Non-linear non-ideal chromatography* has been discussed by KLINKENBERG AND SJENITZER [363], but since G.S.C. is the main type of chromatography concerned and the mathematical treatment becomes very involved, it will not be considered further.

4. *Linear non-ideal chromatography* is of particular importance for the treatment of liquid-liquid and gas-liquid partition chromatography, since the assumption of a linear isotherm is usually a good approximation. The theory has been dealt with in two ways:

(i) By the "plate" theory [217, 412, 415], in which the column is regarded as a discontinuous medium analogous to a distillation column, and in which a finite volume of solution is equilibrated successively with a number of theoretical plates of solvent.

(ii) By the "rate" theory [141, 210, 219, 353, 375], in which the column is

regarded as a continuous medium in which mass transfer and diffusion phenomena are taken into account.

The shape of elution curves is given by a binomial distribution for the discontinuous theoretical plate treatment and by a Poisson distribution for the continuous treatment. Although for a sufficiently large number of equilibrations both distributions approximate to Gaussian curves, KLINKENBERG AND SJENITZER [363] have shown that their widths are different. The mechanism of the widening of a band in chromatography has been examined in terms of the "rate" theory by VAN DEEMTER *et al.* [141], who extended the theory developed by GLUECKAUF [219] and other workers. KEULEMANS [353, 357] has recently reviewed the combination of "rate" and "plate" theories, which together give a qualitative and quantitative understanding of the numerous parameters operating in G.L.C.

The three principal contributions to the broadening of a band are:

- (i) eddy diffusion due to packing,
- (ii) molecular diffusion,
- (iii) resistance to mass transfer.

From these a basic equation can be derived [141, 357] for H , the height equivalent to a theoretical plate, in a gas-liquid column:

$$H = \underbrace{2\lambda d_p}_{\text{eddy diffusion}} + \underbrace{\frac{2\gamma D_{\text{gas}}}{u}}_{\text{molecular diffusion}} + \underbrace{\frac{8}{\pi^2} \cdot \frac{k'}{(1+k')^2} \frac{d_f^2}{D_{\text{liq.}}} \cdot u}_{\text{resistance to mass transfer}}$$

where

- λ and γ = constants,
- d_p = the particle diameter,
- D_{gas} = the gas diffusivity,
- u = the linear gas velocity,
- k' = $k(F_{\text{liq.}}/F_{\text{gas}})$,
- k = the distribution coefficient,
- $F_{\text{liq.}}$ and F_{gas} = the volume fractions of liquid and gas in the column,
- d_f = the liquid film thickness,
- $D_{\text{liq.}}$ = the diffusivity in the liquid phase.

This equation is of the form $H = A + B/u + Cu$, where A , B , and C are constants referring to (i), (ii), and (iii) respectively. This is a hyperbola with a minimum H at a certain value of u at which the column is operating most efficiently (see Fig. 2). However, owing to the compressibility of the gas-phase, u is not constant over the length of the column, hence only a small section can operate at maximum efficiency. The influence of the parameters of the equation on the efficiency of separation has been discussed by KEULEMANS [353, 357], and others [140, 141, 394]. The conclusions which have been drawn are of considerable practical interest and are included later under the influence of various factors on the column efficiency.

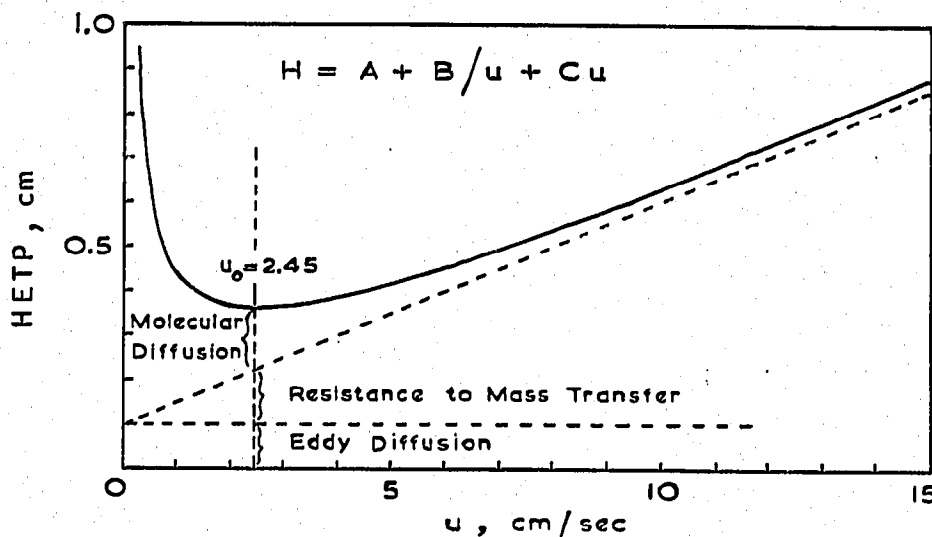


Fig. 2. Plot of HETP against calculated linear gas velocity (after KEULEMANS).

The calculation of the number of theoretical plates

Two methods were originally described [314] for the calculation of the number of theoretical plates in a gas-liquid column. Since then equations for the calculation of plate numbers from recorded chromatograms of elution peaks have been given by a number of workers [64, 395]. These equations give slightly different values and in order to provide a useful practical comparison of column efficiency, the following procedure has been recommended [580]. Tangents are drawn to the elution peak at the points of inflection. The plate number is given by $16(x/y)^2$, where y is the length of the base-line cut by the two tangents, and x is the length from the start of the elution (including the dead-volume of the apparatus) to the middle of the base-line section y .

The effect of various factors on the column efficiency (Table I)

TABLE I

Factor	Effect on column efficiency (E)	References
Flowrate of carrier-gas	Maximum E for a given value of linear velocity (see Fig. 2).	47, 65, 226, 353, 598, 612
Nature of carrier-gas	E greater for gases of low diffusivity and high molecular weight: $E \propto 1/\sqrt{\text{density}}$.	24, 151
Pressure of carrier-gas	E greater at (i) relatively high pressures and (ii) low ratio of inlet to outlet pressure.	65, 353
Density of packing of column	E constant above a certain density (~ 0.2 g/ml).	58, 146, 151, 334 353, 357
Particle size of support	Shallow maximum E at ~ 0.1 mm diameter particles.	
Amount of solvent	Optimum at $\sim 15-20\%$ w/w for normal columns (see later for very high efficiency columns operated at high inlet pressure).	
Length of column	E increases with length but is not usually directly proportional.	65, 598

TABLE I (Continued)

Factor	Effect on column efficiency (E)	References
Temperature	Complex dependence of HETP on T , e.g.: $HETP = A + B(T) + C(T^{-1})$, which is a hyperbola with a minimum H at 24° C.	151
Sample size	E increases as size decreases.	24, 141, 486, 488
Retention volume of solute	E increases with retention volume and the empirical equation holds: $\log(\text{no. of plates}) = \text{const.} + \frac{1}{2} \log(\text{retention volume})$.	395, 471, 488
Conditions of sample introduction	(i) Gaseous samples give highest E if introduced in high concentration as a "plug".	353, 492
	(ii) Liquid samples introduced by a syringe give highest E if needle touches column packing; unless this occurs E depends on the temperature of injection.	486
	(iii) Liquid samples introduced in glass bulbs (or by special methods) require careful control to obtain the highest E .	353, 416

Recent developments in the construction of very high efficiency columns

SCOTT AND CHESHIRE [99, 528-530] have recently re-examined the optimum conditions for the construction of very high efficiency columns. They conclude that efficiencies of the order of 900 plates per foot of column can be achieved with narrow columns containing 2.5-5% w/w of liquid phase on close-mesh (100-120 or 120-160) firebrick and operated at high inlet pressure (up to 150 lb./sq.in.) but at a low ratio of inlet to outlet pressure. The latter condition is obtained by placing a very narrow constriction at the end of the column so that the main pressure drop is across the constriction and not across the last section of the column. An example quoted for a 3.6 mm diameter column 9' 6" long containing 2.5% of liquid phase on 100-120 mesh firebrick operated at $p_{\text{inlet}}/p_{\text{outlet}} = 2.1$, gave plate numbers from 15,000 to 18,000 for retention times from 30-60 minutes. A mixture which was resolved into 25 components on a "normal" 1500 plate column could be resolved into 50 components on the 15,000 plate column. It is notable that, at the maximum inlet pressure that the apparatus normally withstands, the HETP was still decreasing markedly with increasing flowrate and it is expected that operation at still higher pressure and flowrate should lead to lower values of HETP (*i.e.* < 0.3 mm).

SCOTT predicts that 100,000 plate columns can quite feasibly be constructed based upon the above conclusions and provided that a small sample and a highly sensitive detector are used.

Principles governing the separation of mixtures of substances

The forces of interaction between solute and solvent

In the choice of a stationary phase (solvent) which will give large separation factors between the solutes to be separated, the forces of interaction between solutes and solvent are of great importance. The forces can be divided into four types [359]:

References p. 32/43.

(i) Dispersion, London, or non-polar, forces arising from synchronized variations in the instantaneous dipoles of two interacting species; these are present in all cases, and are the only sources of attraction energy between two non-polar substances.

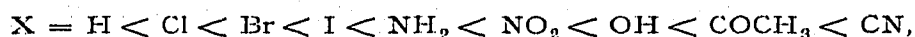
(ii) Induced dipole, or Debye, forces resulting from the interaction between a permanent dipole in one molecule and the induced dipole in a neighbouring molecule; these forces are usually relatively small.

(iii) Orientation, or Keesom, forces resulting from the interaction between two permanent dipoles, the association energy depending upon both the sizes and positions of the dipoles. (The "hydrogen-bond", *i.e.* the relatively strong interaction between negatively charged atoms and positively charged hydrogen in groups such as OH, NH, and FH, is a particularly important type of orientation force and is of considerable practical use in G.L.C.)

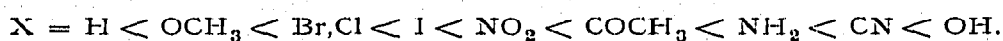
(iv) Specific interaction forces, and chemical bonding, *e.g.* complex formation between solutes and metal ions, or loose adduct formation between solutes and solvents.

These forces of interaction between solutes and solvents govern the relative volatilities of the solutes and therefore the separation achieved. With a non-polar solvent, non-polar solutes will tend to be separated approximately in the order of their boiling points since the forces of interaction (dispersion forces) between solutes and solvent will be similar to the forces between the solute molecules themselves. Polar solutes will be eluted from a non-polar solvent more rapidly than non-polar solutes of a similar boiling point, as they will have lost the strong dipole-dipole association energy which is present in their own liquid [471]. As the polarity of the solvent is increased the polar solutes will be retarded to a greater extent. Solvents of different polarities have been used by a number of workers [63, 316, 359, 395, 570] to effect the separation of mixtures of solutes such as aliphatic, naphthenic, olefinic, and aromatic hydrocarbons. Olefin selectivity increases in a series of solvents of increasing polarity [359], *e.g.* hydrocarbon oil-dinonyl phthalate-dibutyl phthalate-ethyl acetate-dimethylformamide.

By comparing the behaviour of solutes in two or more solvents it is often possible to determine (i) the chemical type and (ii) the position of the solutes in their homologous series. JAMES AND MARTIN [316] examined the behaviour of a series of aliphatic compounds, $C_5H_{11}-X$, and found that the elution sequence in an aromatic solvent, benzyldiphenyl, is (increasing interaction):



while in liquid paraffin or a poly-ether the sequence is:



The authors stress the usefulness of these sequences, as well as the regular behaviour within homologous series, for the determination of unknown substances.

The retardation of polar solutes can be made very large if H-bonding can take place. A clear illustration of this effect is provided in the early work of JAMES AND MARTIN [313] on the separation of primary, secondary, and tertiary amines using as

solvents liquid paraffin, and Lubrol MO (which contains a poly-ethylene oxide structure). The Lubrol MO retards primary and secondary amines due to H-bonding, but does not retard tertiary amines. Comparison of the behaviour of mixtures of amines on these two solvents allows the chemical types of the amines to be identified.

Specific interaction forces probably partly account for the strong retardation of aromatic hydrocarbons by aromatic solvents, e.g. the 1:1 picric acid-fluorene addition compound has been recommended [359, 595-6] as a solvent with very high selectivity towards aromatic solutes. A solution of silver nitrate in glycol or other solvents has been shown [37, 63, 113, 212, 391, 473] to retard unsaturated hydrocarbons which interact specifically with the silver ion to form weak complexes. Metal salts of fatty acids have recently been proposed as solvents with a high selectivity towards amines [473, 475], and amino-acid esters [33]. These open up a new field in which use can be made of the interaction forces between solutes and metal ions or complexes.

Classification of solute and solvent type

Although the existing theories of solutions do not allow the separation of given solutes by a given solvent to be predicted in more than a few simple cases, a qualitative scheme of classification has been put forward [353]. Five classes of substances are defined in order of decreasing cohesive energy, and a solute will be retained more strongly by a solvent as the classes to which they belong are closer together. However, the classification does not explicitly take into account the effects of mutual polarizability, nor does it allow for the effect of forces, such as those of the chemical bond, which may lead to strong retention of particular solutes by certain solvents.

(I) The molecules form a three-dimensional network of hydrogen bonds. Examples are: water, poly-alcohols, amino-alcohols, oxy-acids, polyphenols, di- and tri-carboxylic acids.

(II) The molecules possess active hydrogen atoms as well as electronegative atoms with free pairs of electrons (O,N,F). Examples: alcohols, fatty acids, phenols, primary and secondary amines, oximes, nitro-compounds and nitriles with α -H atoms.

(III) The molecules possess electronegative atoms but no active hydrogen. Examples: ethers, ketones, aldehydes, esters, tertiary amines, nitro-compounds and nitriles without α -H atoms.

(IV) The molecules possess active H-atoms and negligible dipoles only. Examples: CHCl_3 , CH_2Cl_2 , CH_3CHCl_2 , $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Cl}$, etc., aromatic and olefinic hydrocarbons.

(V) Molecules without functional groups, such as saturated hydrocarbons, carbon disulfide, tetrachloromethane, etc.

The effect of temperature on the solvent efficiency

Since the separation of solutes depends upon the distribution of molecules between the gas and liquid phases, corrected retention volumes (V_R^0 , the volume of mobile phase required to elute the maximum of a peak and corrected for dead-volume of column, pressure-drop across column [580], and measured at the column temperature)

vary with the temperature according to a Clapeyron-Clausius equation. For small variations of temperature

$$\frac{d \ln V_R^0}{T} = \frac{\Delta H_S}{RT^2} + K$$

where

ΔH_S = the heat of solution of the solute in the solvent,

K = a constant for different solutes in a given solvent.

The heat of solution is negative (*i.e.* heat evolved) and because of the increasing solute-solvent interaction usually increases numerically with the retention volume.

If V_1 and V_2 are the retention volumes of solutes S_1 and S_2 ($V_2 > V_1$), the separation factor (V_2/V_1) will decrease as the temperature is raised since

$$\frac{d \ln V_2/V_1}{dT} = \frac{\Delta H_2 - \Delta H_1}{RT^2}$$

In a plot of $\log V$ against $1/T$ approximately straight lines are obtained (indicating that this type of equation is obeyed) and the lines for V_1, V_2, V_3 , etc. tend to be closer together at high temperatures than at low temperatures (hence smaller separation factor). As a general rule therefore, better separation factors are obtained by operating at low temperatures.

The presentation and correlation of G.C. data

Gas-chromatographic data have been presented in many forms, *e.g.* as retention times, or volumes, relative to various arbitrary standard solutes, and as absolute retention times, or volumes. The committee appointed to investigate the presentation of data has recommended [11, 580] that one of the following should be given (for definitions see below):

(i) *The specific retention volume (V_g) or the partition coefficient (k)* for at least two temperatures (if only two then as far apart as possible). The value of V_g or k may be given relative to a standard solute, particularly if this gives a straighter relationship between $\log V_g$ and $1/T$.

(ii) An equation relating V_g , or k , and temperature, for example

$$\log V_g = \frac{\Delta H_S}{2.3 RT} + D,$$

or an Antoine equation,

$$\log V_g = \frac{A}{t + B} + C,$$

where

V_g = the retention volume fully corrected for pressure-ratio across the column, dead-volume of apparatus, sample size, and weight of solvent,

k = the weight of solute per ml solvent \div weight of solute per ml of gas phase,

ΔH_S = the heat of solution,

T and t = the temperature in $^{\circ}\text{A}$ and $^{\circ}\text{C}$ respectively,

A, B, C and D = constants determined to fit the equations.

Examples of these methods of presentation are given by YOUNG [613] and AMBROSE [10]. The use of punched cards has been described [547, 603] for the storage and reporting of G.C. data, and this will probably become widely used.

The committee has recommended [580] standard solutes and solvents (see p. 20) and further considers that it is important to include in published work the following: the nature of the support, the nature and weight of the solvent, the sample size (if not corrected for), inlet and outlet pressures, the method of flow-measurement, the accuracy of temperature control, the type of detector, and the density of the solvent (if known) since this enables V_g and k to be interconverted.

Several empirical methods have been used for correlating gas-chromatographic data for solutes in homologous series, and for solutes of similar structure, with other physical data. Straight lines are usually obtained for plots of the log retention volume (or relative retention volume) in a given solvent against:

- (i) The number of carbon atoms in the molecule [314, 351, 353, 501],
- (ii) The boiling point of the pure solute [180, 235],
- (iii) The log of the vapour pressure of the pure solute [283, 284, 496],
- (iv) The inverse of the solvent temperature [353, 395, 489],
- (v) The log of the retention volume (or relative retention volume) in a second solvent [476]; alternatively a non-log plot can be used [305, 319].

Data in the above form can be used for the qualitative analysis of quite complex mixtures (plots iv and v), for the determination of thermodynamic properties, e.g. heats of solution (plot iv, see later for details), and for the determination of retention volumes of solutes (a) for which no standards are available (extrapolation of type i plots) or (b) at temperatures other than the measured ones (type iv plots).

HERINGTON in his thermodynamic treatment [281] of G.L.C. as an example of extractive distillation, deduced the fundamental relation for a pair of solutes in a homologous series:

$$\log V_{21} = \log (p_1^0/p_2^0) + \log (\gamma_{13}^0/\gamma_{23}^0)$$

where

- V_{21} = the retention volume of solute 2 divided by that of solute 1,
- p_1^0 and p_2^0 = the vapour pressures of the pure liquids 1 and 2 at the temperature employed,
- γ_{13}^0 and γ_{23}^0 = the activity coefficients of solutes 1 and 2 at *infinite dilution* in the binary mixtures 1, 3 and 2, 3 respectively, where component 3 is the solvent.

Examination of the various terms in this equation using experimental data other than those from G.L.C. reveals the theoretical foundation for many of the empirical relations in current use, e.g., plots of types (i)-(v) above.

Activity coefficients (preferably at infinite dilution γ^0) can be relatively easily calculated from gas-chromatographic data (for details see later), and since they are much less dependent on temperature than are retention volumes or partition coefficients, they can conveniently be used for the characterization of solute-solvent systems.

TABLE

CROSS-REFERENCE OF CLASSES OF SOLUTES

The bibliography references to the original papers in which a particular class of solute has been separated

General class of solvent	Examples of solvents	Class of substance separated				
		Saturated, unsaturated, aromatic, etc., hydrocarbons <C ₁₀	Hydrocarbons >C ₁₀	Halogenated hydrocarbons	Volatile fatty acids and their esters	Alcohols
Hydrocarbons	<i>n</i> -hexadecane (C ₁₆)	353, 357, 373		505, 513	373	373
	benzylidiphenyl	149, 316, 319		316	316	316
	squalane	160, 179-181, 373, 425, 476, 492, 570, 617			570	476
	liquid paraffin	28, 113, 151, 172, 316, 490, 512, 526-7, 592-4		28, 254, 316, 488, 497, 498, 596	28, 596	316, 596
	<i>n</i> -hexatriacontane	148-9				
tri-isobutylene	30, 63, 254					
fluoro-hydrocarbons			187, 505			
Alcohols	glycerol			10, 488-9		85
	polyethylene glycols	2, 13, 57, 58, 73, 605		187	2, 333-4, 596	2, 52, 58, 137, 333, 596
Ethers	Lubrol MO	318				
Esters	dinonyl phthalate	28, 51, 65, 73, 85, 123, 129, 249, 353, 359, 435, 501-2, 596		10, 36, 186-7, 249, 250, 254, 486, 488-9, 511, 519, 576	28, 487, 501, 511, 596	1, 28, 123, 486, 501, 596
	didecyl phthalate	160, 201, 230, 364, 476, 492, 556		160, 258		160, 258, 476, 492
	other alkyl phthalates	280, 326, 359, 374, 390, 455, 496, 518, 544, 556		187, 238, 465, 488		353
	tricresyl phosphate	83, 241, 379, 523, 566		241, 254, 255, 566	379, 395, 418	379, 395, 523
	tritoly phosphate	10, 259, 395		259	10, 325, 395	10, 259, 395, 469
	fluorene picrate	595-6				
Silicone and other oils and greases	silicone 702 or 703	10, 249, 250, 395, 473		10, 187, 250, 488-9	10, 325, 395	10, 395, 473
	silicone 550, etc.	150, 440, 469, 538, 595-6, 614	596, 614	188, 231, 254, 366, 417, 488	16-19, 304, 313-4, 334, 343, 418, 469	469, 614
	silicone high vac. grease	51, 429	3, 127	187, 429	3, 38, 117-119, 127, 159, 297, 545, 566	118, 119, 159, 351
	Apiezon L	528	3, 527		3, 38	
Apiezon M or others	99, 158	336	187	158, 351, 378, 590		
Metal salts	AgNO ₃ /glycol, etc.	37, 63, 106, 113, 212, 391, 473	106			
	metal stearates, caproates, etc.	473				473
Miscellaneous	polythene		127		38, 127, 351	
	sugars					
	dimethylformamide	113, 353, 356, 359, 440, 518, 568, 605				
	dimethylsulpholane	113, 182, 201, 277, 353, 364, 558				
	zeolites and alkyl-ammonium bentonites	31, 327, 592-4, 597		327		31
nitrobenzene	518		202			

It is not important for the presentation of results whether γ^0 or k^0 (the value of k at infinite dilution) is used, since γ^0 can be calculated from p^0 and k^0 and vice versa. However, γ^0 is particularly useful for discussing solute-solvent interaction and for correlating the structures of solutes and solvents with their chromatographic behaviour. PIERROTTI and co-workers [476, 492] have developed a method (PIERROTTI'S "Building Block" Method) for correlating activity coefficients with the structures of the solute and the solvent. They have determined activity coefficients prevailing in a large variety of binary mixtures, so chosen that variations within homologous series of both solutes and solvents could be studied systematically. Although much of this work has involved solvents of volatilities too high to be of direct interest for G.L.C., certain regularities in behaviour are applicable to the understanding, and prediction, of the behaviour in practical G.L.C. systems (for example, see the discussion by KEULEMANS [353]).

I

SEPARATED BY A NUMBER OF SOLVENTS

by a particular solvent are given at the intersection of the respective horizontal and vertical columns.

Class of substance separated										
Ketones	Aldehydes	Ethers	Sulphur-containing compounds	Nitro-compounds and organic nitrates, etc.	Amines and amino-acid derivs.	Boron, silicon or deuterium compounds	Essential oils, terpenes, etc.	Pyridine bases	Phenols and derivs.	H ₂ O
373 316 476, 570	373		149		307					
316		570	512, 527 149		301, 307, 319	346(B)		74, 313		596
2, 52, 57, 137, 596		52	137		313			74, 76, 445 74, 76		445 2, 52, 596
					301, 307, 319			313		
64, 85, 123, 429, 486, 501, 596, 613	85, 123, 501	64, 65, 501, 558	546	75, 249, 250, 487				74, 76		1, 123
160, 258, 476	160					604(D)				
			557	490					344-5	
379 259	379 259	259, 469	7, 523		395	346(B) 346(B)	384			
473, 488	294	473			473 319		167, 384	74, 76, 313		
351	159				33, 34		508			
158, 508		95	270, 566				289, 290, 508		270, 297 95	
473		473			33, 34, 473, 475					
									329	
		558								
						202(Si)				

Analytical applications of G.L.C.

A very wide range of substances have now been examined by G.L.C. and examples of the solvents used to separate various classes of substances are illustrated in Table II. In principle all components of mixtures which can be separated (and usually qualitatively analysed) can also be quantitatively analysed by the application of methods suitable to the detector employed, and which are reviewed in Section II.

References to the application of G.L.C. to the complete or partial analysis of some complex mixtures are given below.

Organic fluoro-compounds [21, 185-7, 221, 238, 465, 513-5, 519, 541, 553, 559, 563].

Combustion products of internal combustion engines [88, 148, 182, 195, 272, 295].

Essential oils [41-2, 49, 66, 87, 167, 288-291, 300, 387, 446-8, 468, 508, 552, 569, 588, 609].

References p. 32/43.

- Components of tars [72, 234-5, 297-8, 344-5] and tar heavy oils [175].
Naphthalene hydrogenation products [544].
Trace analysis at parts per million level [40, 56, 126-7, 272, 589].
Solvents for plastics and lacquers [126, 259, 260, 372, 378, 596].
Determination of steroid side-chains [111].
Monitoring of distillates from fractional distillation columns [221, 438, 487].
Halogen and interhalogen compounds [184].
Flavours in fruit, vegetables, and other foodstuffs [96, 110, 127, 161-4, 189, 262, 292, 300, 333, 380, 437, 506, 539, 540, 551, 588].
Components of tobacco smoke [460, 464, 498, 532, 534].
Products of Fischer-Tropsch reactions [129].
Products of reaction-kinetics studies [84-5, 104, 123, 170-2, 209, 348, 366, 422-5, 490].
Separation of *o*-, *m*- and *p*-nitrotoluenes [451], and *m*- and *p*-xylene [200, 374, 458].
Volatile fatty acids (and their esters) in natural products [16-19, 24, 38, 109, 115, 117-120, 266-9, 274-5, 296, 311-7, 320-2, 343, 351, 385, 386, 392, 418-420, 453-4, 462, 485, 498, 536-7, 572, 581, 590].
Polymer degradation products [135] and impurities [126, 560, 587, 606].
Insecticides and antioxidants [3, 332].
Radiolysis products of organic compounds [83, 152-3, 165, 188, 195, 230, 507, 600].

*The determination of activity coefficients and heats and entropies
of solution by G.L.C.*

A number of recent papers [12, 14, 284, 353, 373, 395, 492, 593] have shown the usefulness of G.L.C. in the study of the thermodynamics of systems involving volatile solutes and involatile solvents. Activity coefficients and free energies of solution are derived from retention volumes at a given temperature; heats of solution are derived from the temperature dependence of the retention volume; and entropies of solution can be derived from the combination of heats and free energies of solution. KEULEMANS [353] reviewed the methods for the calculation of γ^0 , the activity coefficient at infinite dilution, from symmetrical and asymmetrical elution curves and tabulated values of γ^0 for a number of hydrocarbons and oxygenated compounds. However, the data were not regarded as highly accurate since they were derived from incidental analyses carried out for other purposes. A greater accuracy can be achieved in specially designed experiments, for example, the work of KWANTES AND RIJNDERS [373]. These authors also measured values of γ^0 for polar solutes in non-polar solvents by using fine metal helices as the inert support, and extended the method to solvents of relatively high volatility by presaturating the carrier-gas with solvent vapour. In this way, the value of γ^0 for a normal hydrocarbon in its next higher homologue was determined with fair accuracy.

The determination of the activity coefficient at infinite dilution, γ^0

The value of γ^0 is usually obtained in the form of γ_p^0 or γ_f^0 from the equations:

$$\gamma_p^0 = \frac{N_{llq} RT}{k \cdot p^0} \quad \text{or} \quad \gamma_f^0 = \frac{N_{llq} RT}{k \cdot f^0}$$

where

p^0 and f^0 = the vapour pressure and fugacity respectively of the solute at temperature $T^\circ\text{A}$,

N_{llq} = the number of moles of solvent per unit volume at temperature T ,

k = the partition coefficient derived from:

$$V_R^0 = V_{\text{gas}} + k V_{llq}$$

where

V_R^0 = the retention volume corrected to the column temperature and average column pressure,

V_{gas} and V_{llq} = the volumetric gas and liquid hold-up of the column respectively at the temperature T .

The requirements for the accurate evaluation of γ^0 are:

(i) A very small sample size, or extrapolation of V_R^0 to zero size from a range of small samples.

(ii) Accurate measurement of retention time, dead-volume of apparatus, temperature and pressure of flowmeter, inlet and outlet pressures at the column, and column temperature.

(iii) Relatively long columns (3-6 m recommended [353] to reduce the effects of non-ideality in the first part of the column).

TABLE III
VALUES OF γ_p^0 FOR HALOGENATED HYDROCARBONS

Solute	Solvent						
	Silicone 702				Dinonyl phthalate		
	20.2°C*	40.1°C	77.0°C	97.9°C	39.7°C	76.8°C	97.9°C
CH ₃ Cl	0.36 (23.1)	—	0.37	—	0.45 (23.6)	0.45	—
CH ₂ Cl ₂	0.38	0.40	0.44	0.50	0.42	0.46	0.49
CHCl ₃	0.32	0.37	0.40	0.45	0.33	0.38	0.37
CCl ₄	0.45	0.50	0.50	0.58	0.71	0.71	0.71
CH ₂ ClBr	0.42	0.45	0.47	0.51	—	0.49	0.48
CH ₂ Br ₂	—	0.52	0.59	0.61	—	0.60	0.61
CHBr ₃	—	—	0.65	—	—	—	0.64
CF ₂ Cl ₂	0.75 (21.9)	0.76	0.63	—	0.91 (24.5)	0.80	—
CFCI ₃	0.56 (21.9)	0.53	0.52	—	0.80 (24.5)	0.66	—
CHFCl ₂	0.36 (23.1)	—	0.38	—	0.28 (23.6)	—	—
CHF ₂ Cl	0.76 (23.1)	—	0.71	—	0.58 (23.6)	—	—
<i>cis</i> -Dichloro-ethylene	—	—	0.42	0.51	0.38	0.42	0.42
<i>trans</i> -Dichloro-ethylene	—	—	0.46	0.53	0.52	0.58	0.60
Trichloro-ethylene	—	—	—	0.57	0.46	0.55	0.60

* Other temperatures are given in parentheses.

References p. 32/43.

(iv) Accurate determination of the mass of the solvent and the volume of the solvent at each value of T (which requires a knowledge of the coefficient of expansion), and correction or compensation for any loss of solvent due to its volatility.

(v) The molecular weight of the solvent (γ^0 values cannot therefore be accurately evaluated for solvents containing a mixture of substances in unknown proportions, or for polymers for which accurate molecular weights are not known).

Values of γ^0 which have been calculated by these methods are: aliphatic and aromatic hydrocarbon solutes in C_8 - C_{10} hydrocarbons [373], C_{16} - C_{36} hydrocarbons [353, 364, 373], 1,2,4-trichlorobenzene [373], diisodecyl phthalate [353, 364], and polyalkylene glycols [353, 364]; oxygenated solutes in *n*-hexadecane (C_{16}) [373], diisodecyl phthalate [353], and poly-alkylene glycols [353]. Values of γ^0 for several halogenated hydrocarbons in dinonyl phthalate and in silicone oil 702 have been calculated [251] (Table III) from the data of POLLARD AND HARDY [489].

The determination of the heat of solution

The apparent heat of solution (ΔH) and the excess partial heat of solution ($\Delta \bar{H}_S^E$) [492] can be derived from a plot of the logarithm of the partition coefficient (k) against the inverse of the absolute temperature:

$$\frac{d \ln k}{d \left(\frac{1}{T} \right)} = - \frac{\Delta H}{R} = - \left(\frac{\Delta H_v - RT - \Delta \bar{H}_S^E}{T} \right),$$

where

ΔH_v = the latent heat of vaporisation of the solute at its boiling point,

R = the gas constant.

Alternatively ΔH can be obtained by plotting $\log_{10} V_\theta$ against $1/T$ when [395]

$$\Delta H = -2.3R (\text{gradient}) + RT^2 d \log \rho / dT,$$

where

ρ = the density of the solvent.

Straight line plots are usually obtained over the range 20-100 °C, but when the plots are slightly curved the value of the gradient is taken at the boiling point of the solute.

Heats of solution have been obtained for (i) several hydrocarbons and oxygenated compounds in the solvents squalane and diisodecyl phthalate [492], silicone 702 and tritoyl phosphate [395], (ii) for halogenated hydrocarbons in silicone 702 and dinonyl phthalate [489], (iii) for benzene and cyclohexane in liquid paraffin [14], and (iv) for several hydrocarbons in paraffin wax, liquid paraffin, and dimethyl-dioctadecyl-ammonium bentonite [593].

The determination of the entropy of solution

The entropy of solution (ΔS) of a solute in a solvent at temperature ($T^\circ A$) can be calculated from the heat of solution (ΔH) and the free-energy of solution (ΔG) by the relation

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

The value of ΔG has been calculated from the retention volume or partition coefficient at a given temperature by the equation [14]

$$\Delta G = -RT \ln k_B$$

in which k_B is Bunsen's partition coefficient defined by $k_B = 273k/T$.

WHITE AND COWAN [593] obtained entropies of solution analogously, but using the chemical potential of the solute ($\Delta\mu_n$) at a definite mole fraction, e.g. $n = 0.1 M$, calculated from the vapour pressure of the solute exerted above a $0.1 M$ solution under ideal conditions.

Values of the entropy of solution have been calculated from gas-chromatographic data for only a few systems: (i) for benzene — 13.2 e.u., and cyclohexane — 9.5 e.u. in polyethylene glycol cresyl ether [14], (ii) for homologous series in silicone 702 and in tritolyl phosphate [471]; in silicone 702 the addition of 3 carbon atoms along a series resulted in an average change of 1 kcal/mole in ΔG at 70° C, and 3 entropy units in ΔS ; in tritolyl phosphate an average change of 2 kcal/mole in ΔG and 6 e.u. in ΔS respectively were found, and (iii) for benzene, toluene, *o*-xylene, hexane, cyclohexane, and heptane in liquid paraffin [593]; values of $-\Delta\mu_n$ and $-\Delta S_n$ from 1.44–1.80 kcal/mole and 15.1–16.9 cal/mole deg. respectively were obtained (n referring to a $0.1 M$ fraction).

SECTION II. APPARATUS AND TECHNIQUES FOR G.L.C.

This section deals with apparatus for analytical and preparative gas-liquid chromatography and the techniques for quantitative analysis. For elution analysis one requires a supply of a suitable carrier-gas at a constant flowrate, a sample-introduction system, a column containing a stationary phase, and a detector.

Apparatus

The mobile phase

The gases most frequently used for the mobile phase are nitrogen, hydrogen, helium, and carbon dioxide. High molecular weight gases lead to better separation in the gas-liquid column because of the reduced axial diffusion of the solutes, but the choice of mobile phase is also intimately connected with the detector. Hydrogen and helium have lower densities and higher thermal conductivities than nitrogen and both increase the sensitivity of detecting systems using these properties and also simplify the quantitative interpretation of chromatograms. However the efficiency of separation has been shown to be lower for hydrogen than for nitrogen [353, 357]. Carbon dioxide has been used with considerable success [113, 326–31, 353, 502] but the detection method (see later) limits the solutes which can be separated to those which do not condense at room temperature and which are not attacked by alkali.

The column efficiency depends upon the linear gas velocity which is not uniform along the column. There is an optimum velocity for a given set of operating conditions, but usually the gas flowrate is not a highly critical parameter. The volumetric gas

rate used depends upon the column diameter, among other factors, and flowrates for 6 mm diameter columns range from about 10-400 ml/min. A value of about 100 ml/min is usually satisfactory for this diameter of column, but for columns of greater diameter the flowrate should be increased in proportion to the square of the diameter, in order to maintain approximately the same linear rate.

The flowrate can be controlled with either a simple manometer [314, 323] or a well constructed needle valve, and measured by a number of methods, e.g. capillary, U-tube, and moving-bubble flowmeters, and rotameters. The latter are useful for indicating the flowrate but are not recommended [353, 580] for accurate measurements in the calculation of retention volumes.

The required flowrate is obtained by applying a pressure difference between the column inlet and outlet. Frequently either the inlet or outlet are at atmospheric pressure, but sometimes both pressures are controlled. Very long columns can be used for difficult separations without too excessive a pressure drop across the column provided that they are packed with a coarse supporting material (30-60 BSS mesh). Operation of columns at reduced pressure does not appear to offer any very great advantages [353], and usually leads to less efficient separation. Some gain in detector sensitivity is to be expected from operation of certain detectors at low outlet pressure but thermal conductivity detectors in particular become more pressure-sensitive at low pressure.

The sample and sample-introduction systems

The sample to be analysed may be introduced into the apparatus as a gas, a liquid, or a solid dissolved in a suitable solvent. Volumes introduced can vary from 0.1 ml to 1 μ l for liquids and up to 20 ml N.T.P. for gases on a 4-6 mm diameter analytical column. Introduction of liquids with a micrometer syringe and hypodermic needle through a self-sealing rubber cap has become a standard technique, and many improvements of Ray's original method [501-2] have been suggested [91, 119, 571]. The introduction of reproducible amounts of liquids in glass capillaries through large bore metal valves is used in some recent commercial equipment [566-7]. For good resolution the whole of the sample should be introduced as rapidly as possible. This is best achieved by injection of the sample directly on to the column packing or on a glass-wool plug maintained at the column temperature. Alternatively a separate heater can be used at the inlet point to provide rapid vaporization [63, 187, 250, 486, 566] and the effect of the temperature of the heater on the column efficiency and retention volume has been studied [250, 254, 486]. Special methods for the introduction of samples from biological materials are required, e.g. liberation of free fatty acids and bases from their salts [54, 314, 418].

Gas samples can be injected directly with a hypodermic syringe [502] but by-pass gas pipettes or mercury burettes are more generally used [248, 256, 353, 568]. By-pass systems are particularly useful for periodic analysis of gas-streams [26, 276, 616] and can be adapted to automatic control. Greaseless systems are of particular importance since the majority of gases and vapours are soluble in greases and can cause severe

cross-contamination, especially if trace components are to be analysed. Special lubricants for taps have been used [113, 238] to overcome this problem. Many techniques used for the introduction of samples into mass spectrometers or vacuum systems can be applied to gas chromatography systems [6, 133, 433, 521].

The chromatographic column

Various materials have been used to contain the stationary phase, *e.g.* glass, copper, polythene, and stainless steel, and in many different shapes, *e.g.* straight, coiled, and U-shaped. Typical analytical columns are of the order of 4–6 mm internal diameter and 3–10 foot long. For longer columns, coiling can lead to a considerable reduction in the size of thermostat and the slight loss of efficiency can be tolerated. Columns of larger diameter have been used for the routine separation of larger samples, *e.g.* 3 cm diameter for up to 10 g samples [186, 361].

The column is usually maintained at a constant temperature by a vapour-jacket or a thermostatted oil- or air-bath. Accurate control of temperature is necessary for good reproducibility of retention volumes and accurate quantitative analysis. Vapour jackets are very convenient but the temperature is dependent upon the atmospheric pressure and for long term constancy a thermostat is better. In order to obtain a range of temperature with only one vapour jacket, the pressure above the liquid can be controlled with a manostat, but variable temperature air-baths are becoming widely used [23, 353].

Details have been given of columns operated under "programmed" heating, *i.e.* with the temperature increasing with time [124, 171, 231, 240–1, 246, 255, 523]. This method has advantages for the rapid separation of mixtures of substances having a wide range of boiling points, but a major difficulty is the maintenance of a constant base-line in the detector. Multiple columns in series with take-off points for the slower moving substances have also been used to decrease the analysis time [70, 103, 134, 201, 238, 255, 391, 432, 455, 538, 568, 617].

The stationary phase

(i) *The solid support.* Carefully prepared kieselguhr (Celite) has been used by many workers, and details of its preparation and purification have been given [314, 471]. More recently, a coarser form of kieselguhr, ground furnace-brick, has been recommended and the optimum particle size found to be 30–80 BSS mesh [141, 353, 357]. The advantages of the latter are that it is free-flowing and easy to pack into columns, and it has a low pressure-resistance so that long columns can be used without an excessive pressure-drop. The kieselguhr is often not completely inert and its weak adsorption leads to elution peaks with slight tails. This has been partly prevented for fatty acids by treatment with a solution of dilute phosphoric acid [314] or for bases by treatment with methanolic sodium hydroxide [319]. The treatment may saturate a small number of very active sites in a similar way to the reduction of tailing on active charcoal by the addition of a small amount of an involatile liquid, *e.g.* squalane [180–1], or the de-activation of clay by treatment with glycerin in adsorption chromatography

[128]. The latter experiments with glycerinated clay may have been the first G.L.C. separations, although it was not realized at the time.

The method of mixing the liquid phase and the support can influence the separation efficiency of the column and the recommended method is to dissolve the liquid phase in a volatile solvent, to slurry the mixture with the support, and to evaporate the solvent with continual stirring.

Many other types of support have been used with varying success. Silicone rubber vulcanized and ground to a suitable size has been used for the separation of fluorocarbons [186] and can be used either alone as a dry column packing, or mixed with a conventional liquid phase. Glass powder has been used successfully by several workers [123, 394] but samples of some types of glass can give very inefficient separations compared to kieselguhr [488] and the resultant glass-liquid mixture is often difficult to pack. It was concluded [488] that for high-efficiency columns a porous support is preferable to a non-porous one. Stainless steel [545] or copper [373] helices give a very low pressure drop [545] and negligible interaction even with highly polar solutes [373], but the efficiency is low. Sodium chloride crystals have been used [118-9] at high temperature in preference to Celite in order to obtain a lower resistance to flow. Zeolites have been used as supports for liquid phases [326] in addition to their use as a solid adsorbent [31, 326, 592-4, 597]. Another, and perhaps novel, support reported is carborundum [557].

Capillary tubes coated internally with an involatile liquid (*without a porous packing*) have recently been shown to give good resolution and rapid separations, but require a very small sample and a very sensitive detector [158, 228-9]. The potentialities of this development are very great and in the future very high efficiencies are to be expected, e.g. a 250-ft. 0.010 in. internal diameter copper capillary coated with approximately 60 mg of squalane separated a 2 μ g sample of 9-isomeric C7-paraffins in 50 minutes with an efficiency of 106,000 theoretical plates [143].

(*ii*) *The liquid component of the column packing.* Ideal requirements for the liquid phase are that it should be relatively involatile and stable at the temperature of operation, it should have a low molecular weight and low viscosity, and that it should be readily available in high purity. As many of these requirements are directly opposed to each other, some compromise is effected in practice. Although the selection of a suitable liquid phase for a given separation has often been empirical, considerable attention is now being given to this problem (see p. 7).

The following liquid phases have been recommended [580] for the intercomparison of solutes and for the presentation of retention volumes of new substances (useful temperature range given in brackets):

<i>n</i> -hexadecane (20-50° C)	dinonyl phthalate (20-100° C)
squalane (20-150° C)	dimethylformamide (-20- +20° C)
benzylidiphenyl (80-150° C)	diglycerol (20-100° C)

As a standard, a mixture of 20 parts by weight of liquid phase to 80 parts by weight of Celite 545 support should be used [580]. The above liquids are now being prepared in high purity commercially for special use in gas chromatography.

When liquid phases are operated at high temperature, *e.g.* $> 100^{\circ}\text{C}$ for many liquids, a number of problems are encountered including the loss of liquid phase by vaporization and by decomposition [3, 23, 90, 93, 119, 190, 246, 270, 351, 566-7]. The development of stable liquid phases of low volatility is of great importance because of the opportunity of extending gas chromatography to the separation of organic and inorganic materials of low volatility. A number of stationary phases have already been used successfully for long periods at up to 300°C and these include silicone greases, apiezon greases, silicone elastomers, silicone-gum, and polythene. Many other materials have been examined and found to be less satisfactory; for examples, refer to those rejected by KEPPLER and co-workers [351].

The detector

A large number of types of vapour detector have been used for the detection and recording of the separations achieved by the chromatographic column. The detectors can be divided into two main divisions, (A) integral detectors and (B) differential detectors. An integral detector measures some function of the total quantity of vapour which has passed through it, while a differential detector measures some function of the vapour concentration. The latter can in principle be converted into an integral detector by an electronic or mechanical integrator.

The ideal requirements for a detector are: high sensitivity to the presence of a component in the carrier-gas; rapid response; linear response; independence of operating variables such as pressure and flowrate of gas; good base-line stability; simplicity of construction and auxiliary equipment; robustness; low-cost. BOER [53] compared eight types of differential detector on the basis of many of the above requirements and concluded that thermal conductivity detection and β -ray ionization detection appeared to be, at that time, the two systems most suitable for a wide range of applications in routine laboratories. However, the detectors in widespread use are (a) thermal conductivity, (b) gas-density balance, (c) hydrogen flame, and (d) direct measurement of gas-volume after absorption of the carrier-gas. Methods not considered by BOER, or which have appeared since then, are based on interferometry, measurement of dielectric constant, velocity of sound, or ionization potential at low pressure.

A. Integral detectors

(a) *Measurement of volume or pressure.* JANAK and co-workers [330] used carbon dioxide as the mobile-gas to carry the separated components of mixtures from the column into a nitrometer containing a concentrated solution of potassium hydroxide. The carbon dioxide was absorbed and the residual gases measured in a burette. The method is limited to gases and vapours which do not condense at room temperature and which are not attacked by alkali. Much valuable work has been done with this simple type of apparatus and automatic recording models have recently been developed [327, 377, 535]. VAN DE CRAATS [113] also described recording integral detectors based on the measurement of the volume, or of the pressure in a constant volume

chamber. A convenient method of purification of CO_2 for this detector is given by KEULEMANS [353].

(b) *Direct titration.* JAMES AND MARTIN [313-4] directly titrated volatile fatty acids and bases by passing the gas stream from the column through a titration cell, and gave details of automatic and manually operated micro-burettes. A number of modifications of the original methods have since been described [418]. BLOM [50, 51] has described a simple and inexpensive method based on combustion of the vapours over copper oxide. The CO_2 formed is titrated in a glass apparatus with pyridine as solvent and sodium methylate in pyridine-methanol as titrant. This has been applied to 1-10 mg mixtures of a wide variety of organic substances including nitrogen-, sulphur- and halogen-derivatives.

(c) *Other methods.* Mercaptans have been estimated [557] by iodine oxidation in a redox half-cell by passing the vapours through the column with nitrogen and absorbing them in a solution of iodine in potassium iodide/70% alcohol which formed a redox half-element. In a 100 μg mixture each component could be quantitatively determined to 0.03-0.04 μmole . With a small excess of iodine over mercaptan the sensitivity was as high as 10^{-9} mole/mV output. However, tertiary mercaptans cannot be oxidized by this method.

For the analysis of fatty acids BOER has described [54, 55] a coulometric titrator coupled to a recorder, and also an electrolytic conductivity cell. The latter is simple and only requires a thermostatted titration vessel containing dilute sodium hydroxide, a conductivity cell, and a slightly modified electronic recorder. It can be adapted to other detecting systems such as bases with sulphuric acids, or ketones with hydroxylamine chloro-hydrate [44, 54]. LIBERTI has also described [381-6] two methods involving coulometric titration, one for components with an active chemical group, e.g. acid or base, and the other for general application.

In the first method the vapours are absorbed in a cell containing a suitable indicator and are titrated with a generating electrode connected to a coulometer in which the current can be controlled by a photo-electric relay.

In the second method oxygen is used as carrier-gas and a small furnace at the exit of the column burns each component to CO_2 . The oxygen and CO_2 bubble through barium chloride solution in a cell containing a Pt-wire which acts as an oxygen-electrode and shows the presence of each component. Coulometrically generated hydroxyl-ions bring back the potential to its initial value.

JANAK and co-workers [331] have determined halogens polarographically by eluting them from a silica-gel column and following the increase in the Ti(IV) wave after absorption of the halogens in a Ti(III) solution. NEDOROST [449] has given details of a polarographic cell for continuous gas analysis.

B. Differential detectors

(a) *Thermal conductivity.* The measurement of thermal conductivity has been used for many years for the analysis of simple mixtures of gases, and details of the general design and operation of thermal conductivity cells (or katharometers) are given by

DAYNES [138], WEAVER [585], and MINTER AND BURDY [434]. The principle of the detector is that if a constant flow of gas passes over a fine wire heated by a constant electric current the rate of loss of heat by the wire is constant. A change in composition of the gas stream will cause a change in heat loss and thus a change in resistance. In practice two wires and two streams are generally used, one stream from the chromatographic column and one from a source of gas of constant composition. The wires are connected in a Wheatstone bridge circuit and any change of bridge output, due to a change of wire resistance, is amplified and recorded.

Thermal conductivity cells have found widespread use in gas chromatography because of their simplicity, low cost, general applicability and comparatively high sensitivity. They were used in 1936 by EUCKEN AND KNICK [471] to detect gases removed from a column of adsorbent and were also used by many of the early workers in G.S.C. and G.L.C.

A variety of metal-block, and glass, cells with straight and coiled platinum and tungsten wires have been described [8, 57, 59, 60, 63, 75, 101, 117-8, 130, 138, 159, 178, 184, 190, 194, 213, 236, 241, 257, 309, 351, 358, 390, 402, 429, 430, 434, 459, 477, 483, 501, 516, 522, 525, 543, 555, 567, 596, 608]. Optimum operating conditions and sensitivity have been studied by many workers and have recently been discussed in detail by KEULEMANS [353].

The general conclusions from studies of the sensitivity and stability of cells operated with various carrier-gases are that a higher sensitivity can be obtained with hydrogen and helium than with nitrogen, but in most cases this leads to lower stability. The use of hydrogen or helium instead of nitrogen can have definite advantages for quantitative analysis since the thermal conductivity of volatile materials is then less dependent upon the type of molecule and the amount of calibration can be reduced. The sensitivity can be increased for small amounts of impurities by combustion of the vapours to (i) CO_2 [236, 272, 450], (ii) methane [618-9], or (iii) hydrogen [236] which are subsequently detected. The behaviour of the thermal conductivity cell depends considerably upon the temperature of the wire and of the walls of the cell. Incorrect choice of wire temperature can lead to loss of sensitivity and even complete insensitivity to particular substances, *e.g.* non-polar molecules [257]. The inclusion of the katharometer in the column heating chamber is not recommended if maximum sensitivity and resolution are desired. Independent heating is advisable if it is necessary to avoid condensation in the cell.

Thermal conductivity cells for continuous operation at high temperature, *e.g.* up to 350°C , have been developed [23, 38, 117-9, 127, 130, 190, 194, 351, 566-7] and some design implications of high temperature operation have been discussed [130, 351]. The problems are largely those of choosing suitable materials to withstand temperatures of 300°C and upwards, particularly for electrical insulation and gas seals. A comparison of copper, stainless steel, and glass cells [351] showed that metal cells could be used for temperatures up to 250°C , and glass cells up to 300°C . With a 0.67 mm diameter glass cell and a $20\ \mu$ diameter wire operated at 8 V, a minimum amount of $0.5\ \mu\text{g}$ of methyl caproate could be detected as a peak eluted from a column

in nitrogen. A compact and simple detector (up to 500° C) has been described using 'glow plugs' as elements in a diffusion type cell [192-4].

Thermistors are becoming more widely used in place of metal wires and advantages claimed are low dead-volume, and short response time [27, 40, 78, 124, 131-2, 258, 277, 346, 455, 459, 564-8, 570]. Satisfactory thermistor detectors are now operating in many laboratories and more detailed work is available on stability, sensitivity and optimum operating conditions [40, 112, 583]. DAVIS AND HOWARD [131, 132] described a detector which was stable for long periods and had a low noise level provided that the flowrate of gas, and the temperature of column and detector, were kept constant, and that the whole system was allowed to reach thermal equilibrium before samples were eluted. They found that the magnitude and the direction of the signal varied with the distance of the detector from the exit of the column, and proposed that the heat capacity of the gas was measured by a detector in close proximity to the column exit, whereas the thermal conductivity of the gas was measured by a detector at a distance from the column exit. The development of thermistors to work at high temperature with high stability and sensitivity may be difficult due to the resistance-temperature curve falling sharply with increasing temperature. BISHOP [48] has compared a number of commercial thermistors and has shown that the curve relating sensitivity and operating current passes through a maximum (see also ref. [112]). When operated in this region the thermistor detector has a comparable sensitivity to the "wire" thermal conductivity cell. Care must be taken that the thermistor element is not reduced at high temperatures when hydrogen is used as carrier-gas.

(b) *Gas-density balance.* CLAESSEON [101] in 1946 measured the density of the gas from a chromatographic column by means of a liquid manometer connected to two 6'-long columns of gas, one containing the effluent gas and the other a standard gas.

MARTIN AND JAMES later developed an instrument based on the same principle but having extremely high sensitivity [411]. The instrument, called a gas-density balance, consists of a metal block bored with a series of tubes which are connected together in a manner analogous to a Wheatstone bridge to compensate pressure differences due to the flow of gas. The pressure difference set up between two of the tubes is then a function of the gas-density only, and the density of the effluent gas from the chromatographic column is compared to the density of the carrier-gas from a "dummy" column. Any difference in density causes a flow of gas in a cross-channel in the metal block. This channel contains a flow-detector consisting of an electrically heated filament close to two connected thermojunctions and a flow of gas alters the temperature of these thermojunctions. The thermoelectric output is amplified and recorded, and for small density differences the recorder deflection is linearly related to the density difference of the two gas streams.

MUNDAY AND PRIMAVESI [444] have constructed an electrical analogue of the system to evaluate the performance, and have compared a copper-block gas-density balance with a balance constructed from copper tubing of the same internal dimensions as the tubes in the solid block. The response curves of the two models were very

similar, the solid block model having slightly greater sensitivity and lower background noise. The balances gave a response which was linear with the density difference over the range of practical importance, and the authors discussed the reasons for non-linearity at higher density differences. HAWKES has given details [270] of the construction of a gas-density balance for operation at temperatures up to 300° C, but sensitivity decreases as the temperature is raised, e.g. the sensitivity at 56° C is 20% less than at 20° C. An instrument constructed of Monel tubing has been described [184] for the analysis of corrosive and highly reactive gases. Many other applications have been reported [38, 149, 234, 296, 302, 309] and the gas-density balance has been used to determine the molecular weight of solutes to $\pm 4\%$ [388].

(c) *Hydrogen flame detector.* This detector was introduced in 1955 by SCOTT [526] and has since been studied in detail by a number of workers [127, 183, 279, 527, 605]. Hydrogen or a mixture containing hydrogen is generally used as the carrier-gas and is burnt at a small jet at the exit of the column. The temperature of the flame is measured by a thermocouple (for flame temperature contours see PRIMAVESI [495]) and the area of a peak on the recorded chromatogram, corrected for the heat of combustion of the substance, is proportional to the weight of substance present. The detector has the advantages of simplicity, low dead-volume, and low cost, and can be applied to gas chromatography at high temperature. SCOTT used hydrogen and nitrogen-hydrogen mixtures as carrier-gases and found a linear relationship between peak height and weight of substance present, but the sensitivity decreased as the retention volume increased. A single straight-line plot was obtained for peak area against sample weight for a number of hydrocarbons. HARRISON [254] found that pure hydrogen is not a suitable carrier-gas for the elution of methane but that 75:25 or 70:30 hydrogen-nitrogen mixtures are satisfactory. WIRTH [605] has reported the accuracy and reproducibility of quantitative results and compared the response of oxygen, water, and oxygenated and chlorinated compounds with the response of hydrocarbons. He used nitrogen carrier-gas and mixed it with hydrogen (from a dummy column) at the column exit. HENDERSON AND KNOX [279] found that the temperature rise of the thermocouple during the combustion of any band is directly proportional to the rate of liberation of heat, and obtained a linear relationship between the peak area per mole and the molar heat of combustion for twenty-four substances.

GRANT AND VAUGHAN have described [233, 235] a micro-flame, or emissivity, detector which measures the luminosity of the flame rather than its temperature. The hydrogen gas from the column is carburetted with benzene or mixed with coal-gas before burning in the detector. The detector is at least as sensitive as the katharometer and possesses several advantages. It is of simple construction and is particularly suitable for use at high temperatures. Also the response depends largely on the nature of the eluted solutes, hence by comparison of the responses of the emissivity detector with those of a katharometer, a classification scheme can be evolved.

MCWILLIAM AND DEWAR have recently described [427-8] an ionization detector using a hydrogen-flame. This is claimed to have extremely high sensitivity (e.g.

$S = 1 \cdot 10^9$ mV.ml/mg [53, 160] with a background of 0.1 mV and compares favourably with other types of ionization detector (see later). In its simplest form, a small platinum loop or brass gauze forms the negative electrode and is supported from 5–10 mm above the jet from which the nitrogen–hydrogen mixture is burnt. A potential of from 0–200 V can be applied between the earthed jet and the negative electrode and the output taken across a high resistor between the jet and earth. A similar instrument has been described by HARLEY *et al.* [252].

(d) *Ionization detectors.* The measurement of the ionization current in a gas has been used for analytical purposes by a number of workers. A method based on ionization by β -rays from a radioactive source was developed for gas analysis [491] and later applied to detection in gas chromatography [53, 139]. The advantages of this system are that it is very sensitive; calibration is virtually unnecessary since the differential ionization current may be predicted from the ionization cross-sections of the component molecules; the cell is simple to construct and is adaptable to high temperature; and it is inherently insensitive to changes in flowrate of carrier-gas (N_2 or H_2). Disadvantages are that the auxiliary equipment is more elaborate and costly than, for example, the thermal conductivity method, and precautions are necessary in handling the radioactive source. A sensitive and stable detector has been described using argon as the carrier-gas and a β -radioactive source [398], but to reduce or prevent radioactive handling problems, a number of other methods have been considered. The simplest and most effective is that based on a spark discharge operating at atmospheric pressure [399].

HARLEY AND PRETORIUS [253] introduced a detector in which the potential difference was measured across two electrodes in a high-voltage (900 V) discharge tube through which a part of the carrier-gas passed at a few mm pressure. Less than 10^{-11} mole of a hydrocarbon could be detected and a similar figure has been given by PITKETHLY [479, 480] who recommends modified small neon indicator lamps, or aged iron electrodes from neon lamps.

RYCE AND BRYCE [522, 524] have developed a sensitive low-voltage ionization detector. A small fraction of the helium gas stream from the column passes through a leak into a modified commercial ionization gauge operated at ~ 18 V which is not sufficient to produce ions when helium alone is flowing through. Solutes from the column have ionization potentials below 18 V and give rise to a plate current which is amplified and recorded. The sensitivity claimed is 200 times that of the thermal conductivity method and compares with that of the high-voltage detector. The detector is insensitive to changes in ambient temperature, pressure, and flowrate of the main gas stream of which only a small fraction ($< 0.5\%$) is used.

(e) *Radioactivity detectors.* GLUECKAUF, BARKER AND KITT [220] followed the separation of gases by measurement of radioactivity and this is the most sensitive method if the materials to be detected are radioactive. EVANS AND WILLARD [188] have recently demonstrated the detection of amounts of the order of 10^{-15} g of $CH_3^{80}Br$ or 10^{-13} g of $CH_3^{82}Br$, the sensitivity being inversely proportional to the half-life of the respective radioactive isotope, ^{80}Br (18 min), ^{82}Br (36 h). These authors

used a Geiger counter, or a sodium iodide scintillation counter coupled to a photomultiplier, amplifier, ratemeter, and recorder, and separated substances from columns operated at up to 200° C. These results indicate that gas chromatography is as effective with materials at "trace"-levels as at macro-levels. KOKES and co-workers [369] also describe the use of a Geiger counter to detect radioactive components separated from catalytic reactor mixtures. Apparatus for the detection of tritium and ¹⁴C-labelled compounds by their weak β -radioactivity has been described [4, 79, 231, 400, 441, 507, 610].

(f) *Surface potential detector.* GRIFFITHS, JAMES AND PHILLIPS [241-2] introduced a detector based on the measurement of the e.m.f. set up over a vibrating condenser formed by two metal plates, one of which is coated with a suitable surface film (e.g. stearic acid). The detector gives a high sensitivity with polar vapours and the sensitivity increases with molecular weight, but it has a slow and non-linear response. However, it has been successfully applied to displacement analysis in G.S.C.

(g) *Other detectors.* MARTIN AND SMART [404], LIBERTI and co-workers [389], and others [200, 272, 531] have applied infra-red analysers to gas chromatography. Organic vapours are passed in the carrier-gas over heated copper oxide and converted to carbon dioxide. With an infra-red analyser sensitive to carbon dioxide a high sensitivity (proportional to the number of carbon atoms in the molecule) is obtained, provided that combustion is complete. The method is then limited to carbon compounds and a considerable disadvantage is the destruction of the chromatographed material. MARTIN AND SMART suggested that for infra-red absorbing vapours a detector sensitive to all the vapours present would suffice but then the sensitivity would not be high, and would vary with the vapour. However, LIBERTI [389] has reported that hydrocarbons can be analysed satisfactorily without combustion by measuring the absorption at the C-H band frequency, 3330 cm⁻¹.

GRIFFITHS and co-workers [241] investigated methods of detection based upon the measurement of (i) the specific heat of the effluent-gas, (ii) the latent heat of adsorption of vapours, (iii) changes in the dielectric constant of a section of the column as the vapours passed through, and (iv) the flow impedance of the carrier-gas. Only (ii) and (iii) have received any recent application. A simple and robust detector of changes in dielectric constant has been designed [578] for use with routine preparative columns, but has high enough sensitivity for many analytical applications.

DUDENBOSTEL AND PRIESTLEY have reported [173] a detector based on the measurement, by thermocouples, of the differential heats of adsorption and vaporization as the carrier-gas passes through a small bed of an adsorbent at the end of the chromatographic column. The detector is sensitive to low concentrations of hydrocarbons in air and was applied in a continuous process-plant to the analysis of propane in propylene. PRIESTLEY reported [580, p. 165] an improvement whereby a thermocouple inserted directly into the end of the column gives a signal which is proportional to the amount of a component passing the thermocouple.

The measurement of sound velocity has been suggested [310] as a method of detection but the present difficulty is the large volume of sample required to give a

sensitive and reliable response. Gas interferometers have been used [577, 614] in gas-solid chromatography but such instruments have never come into general use.

Additional apparatus

The collection of fractions is important not only for the application, if necessary, of further methods of analysis to resolve complex mixtures, but also for the isolation of substances in high purity, and for the measurement of their physical properties. Details of apparatus and methods are given under preparative gas chromatography. The measurement of physical properties can easily be achieved on very small amounts of substances, e.g. by mass-spectrometry, but larger amounts are usually required for infra-red [39, 165, 207, 447] or ultra-violet spectrometry [401]. However, micro-cells requiring only 0.002 ml of liquid are now available with commercial infra-red spectrometers. JAMES AND PHILLIPS [324] have described a simple micro-Schliermacher apparatus for the determination of boiling points to 0.1° C on 0.02 ml of liquid. LITTLEWOOD [393] has developed an effusimeter for the determination of molecular weights of boron and silicon hydrides to 5% on samples of 10–100 μg . LIBERTI and co-workers [388] have measured molecular weights with an accuracy of about 4% by eluting the mixture of an unknown and known substance in two different carrier-gases of very different molecular weight. From the ratios of peak areas in each gas the molecular weight of the unknown can be calculated.

The combination of mass spectrometry and gas chromatography can be of great value. BRADFORD and co-workers [63] described in 1955 an analysis in which a complex petroleum mixture gave sixteen chromatographic peaks with a thermal conductivity detector, each of which was collected and analysed by a mass spectrometer. Thirty-two components were finally identified in the mixture. DREW and co-workers [172, 422–6, 542] applied mass-spectrometry to the positive identification of chromatographic peaks and the analysis of mixtures having identical emergence times (particularly deuterated hydrocarbons). They also used gas chromatography to separate mixtures of hydrocarbons which have almost identical cracking-patterns so that mass-spectrometric analysis alone had not previously been possible. The combination of gas chromatography and mass-spectrometry has been reported by a number of workers [45–6, 80, 137, 169, 172, 206, 222, 224, 230, 286, 348, 380, 510, 532, 550, 551].

Commercially available apparatus

In the last few years a number of gas chromatography apparatus have become available commercially. At the present time a variety of types are marketed by a large number of manufacturers in the U.S.A. and Great Britain. The apparatus is robust and the reproducibility of quantitative analysis and sensitivity in qualitative analysis of trace materials is usually of a high order. Prices in Great Britain are of the order of £ 600–£ 1000. The most recent development is the application of gas chromatography to continuous automatic analysis of, for example, liquid and gaseous

process streams in industry [5, 26-7, 77, 173-4, 176, 191, 198-9, 271, 276-8, 368, 461, 483, 549-51, 591, 616].

Techniques

Quantitative analysis

A quantitative analysis can be obtained from measurements on the recorded chromatograms, the method depending upon the type of detector used and the nature of its response to the components passing through in the carrier-gas. In quantitative analysis with integral detectors the step heights recorded in the chromatogram directly measure the amount of substance separated, for example, in terms of volume, or pressure, of a gas, or μg equivalents of acid or base etc.

With differential detectors in which the chromatogram is a series of peaks on a chart the quantity of a substance can be related to the height of a peak or the area under a peak. The area can be measured by a mechanical or electronic integrator [125, 353, 554], a planimeter [177, 390, 489], cutting out and weighing the chart [159, 516], or by multiplying peak heights by half-widths [116]. With a small sample, the peak height is proportional to the quantity of a component [501-2] and this affords a very simple and rapid method of quantitative analysis. For detectors which have a response dependent upon the nature of the substance in the carrier-gas, calibration for each substance is usually necessary. With thermal conductivity detectors using nitrogen as carrier-gas, calibration is necessary, but with hydrogen or helium carrier-gas (which have thermal conductivities higher and very different from those of the vapours) the response is less dependent upon the type of vapour molecule. However, for the most accurate results, calibration for each substance is recommended [78, 114, 160].

In gas chromatography it is difficult to introduce quantitatively small samples of liquids and gases and to keep the operating conditions constant. These problems can be largely overcome by using either an internal standard or internal normalization.

In the *internal standard method*, a known amount of a suitable substance is added to the sample to be analysed and the peak-areas or -heights are referred to the area or height of the internal standard peak [63, 117-9, 501]. DIMBAT and co-workers [160] investigated the effect of operating variables using a reproducible by-pass sample injection system and found that the height of recorded peaks is sensitive to column temperature but not to flowrate, whereas the peak area is sensitive to flowrate but not to column temperature. They consider that control of column temperature to at least 1°C and flowrate to $\pm 1\%$ is required for quantitative analysis using peak areas. RAY [501-2] found that 1°C change in column temperature gave 2.4% error in determination of methylcyclohexane by the height relative to *n*-pentane. A 1°C change in column temperature gave only a 0.3% error for the above materials when peak areas were used [160]. The introduction of liquid samples under constant conditions is stressed by POLLARD AND HARDY [486]. They showed that the rate of change of peak height of an internal standard with temperature of injection may be significantly different from the rate of change of height of the peaks being analysed.

In the *internal normalization method* the areas of all the peaks present are added

to give a total area which is normalized to 100%. The ratios of the individual areas to this total give the weight percentage amounts directly. Calibration, or correction, factors can be applied in this and the previous method when mixtures to be analysed contain substances whose responses to the detector are not independent of the type of substance, *e.g.* correction for heats of combustion with the hydrogen-flame detector [527], and for thermal conductivities [78, 358, 430, 516, 568].

The accuracy and reproducibility of quantitative analysis varies with many factors such as the type of detector, the method of analysis used, and the control of operating conditions. The simple detectors based on volume measurement or titration are claimed to be highly accurate ($\pm 0.1\%$ for the JANAK technique) but the sensitivity of these methods is somewhat limited, *e.g.* by the difficulty of accurate measurement of very small volumes of gas. The other detectors and methods, while more versatile and sensitive, can seldom be claimed to give results to better than $\pm 1\%$ of each component, and it may not be possible to achieve this for the analysis of trace-components. However, it may sometimes be desirable to sacrifice some accuracy or reproducibility for speed of analysis. The reproducibility of particular methods of analysis has occasionally been quoted in terms of the standard deviation. DIMBAT and co-workers [160] reported standard deviations of 7–10% for methods using peak areas and a thermal conductivity detector without calibration, and 0.76% with prior calibration. POLLARD AND HARDY [489] give an average standard deviation of 1.4% for three determinations of halogenated hydrocarbons using peak heights relative to an internal standard. The difference between the amount found and the amount taken was usually under 2% for this method. PERCIVAL [465] analysed fluorinated hydrocarbons and gave 95% confidence limits for the mean of duplicates of about $\pm 0.5\%$ at the 50% level for any component. The accuracy was within the reproducibility limits. LICHTENFELS *et al.* [390] report an average error of 0.6 mole % for the analysis of an 18-component mixture of hydrocarbons by peak areas, but all the peaks were not completely resolved.

Preparative applications of G.L.C.

Gas-liquid chromatography is primarily a batchwise method of separation of mixtures and has been developed more extensively as an analytical technique than as a technique for the preparation of pure substances. Analytical scale columns can be used to isolate constituents of complex mixtures in small amounts suitable for further study, *e.g.* by mass-spectrometry, but for very complex mixtures or small amounts of impurities, larger samples are desirable.

The amount of sample which can be eluted through a gas-liquid column can be increased in proportion to the cross-sectional area of the column without seriously impairing the efficiency of separation. EVANS AND TATLOW [186–7] separated g amounts of mixtures of fluorinated hydrocarbons on columns 16 ft. long by 3 cm diameter and more recently 16 ft. by 7.5 cm diameter [185]. The latter columns are capable of routinely dealing with 10–70 g of volatile mixtures and give separations previously unobtainable by fractional distillation because of azeotrope formation and

the close similarity of boiling points. Compounds boiling 1°C apart, 3H- and 4H-nonafluoro-cyclohexene, were separated from each other. WHITHAM [595] has applied medium-scale, 830 cm (27 ft.) \times 13 mm diameter, columns to the analysis of up to 3 ml liquid samples of complex petroleum fractions. BRADFORD, HARVEY AND CHALKLEY [63, 256] in 1955 also used comparable diameter columns for separating 0.5 ml samples of liquid hydrocarbons. They overcame any decrease in separation efficiency (due to larger sample size) by eluting at a lower column temperature. ROBB AND VOFSI [511] separated 500 mg quantities of mixtures of vinyl acetate and bromotrifluoromethane on 140 cm (4 ft. 8 in.) \times 10 mm diameter columns, and obtained quantitative recoveries to 1.5 mg. Several other applications have been described [66, 71, 92, 361, 371, 551, 559, 579].

AMBROSE AND COLLERSON [9] developed an apparatus for preparative gas chromatography in which the cycle of batch operation was automatically repeated. As each substance emerged at a constant time after sample-injection a clock was used to control the cycles, and solenoid valves directed the samples to collecting traps. The authors used 100 cm \times 15 mm diameter columns and sample charges of slightly less than 1 g, but the method is applicable to any size of column. The success of the method depends upon the chromatogram remaining in phase with the clock. Constant elution times were achieved by control of column temperature, carrier-gas flowrate, and presaturation of carrier-gas with the stationary liquid phase. Developments of this type of apparatus have recently been described by a number of workers [25, 273, 287, 371].

The development of efficient collecting systems for samples eluted from gas chromatographic columns has received considerable attention, and a number of techniques have been discussed recently (see ref. [580]: *V.P.C. Symp.*, pp. 96, 209). Simple U-tube traps cooled in liquid nitrogen have been used with varying degrees of success. A relatively low pressure at the column outlet is claimed to facilitate quantitative condensation of components. Expendable traps have been developed with low hold-up volume and sintered glass packing for the recovery of very small fractions (less than 30 μg) from reaction kinetics studies [171].

The rapid cooling of mixtures of a carrier-gas and a condensable vapour often leads to loss due to the formation of fog or minute crystals. Without using filters a good recovery can be obtained by placing several cooling traps in series and heating the gas stream between the individual traps sufficiently to evaporate the floating droplets or crystals [580, p. 96]. GLUECKAUF [580, p. 97], finds that if traps are filled with cotton-wool or some other material on which droplets can collect, there is complete condensation up to the vapour pressure of the substance concerned. If the vapour pressure of the substance is too high at liquid nitrogen temperature, then a small plug of active charcoal can be used. Amounts of less than 10^{-12} g of krypton and xenon, were quantitatively retained by this method. AMBROSE [580, p. 210] reported that active charcoal retained organic materials too strongly and recommended activated alumina. An electrostatic precipitator is stated to overcome fog formation completely [25].

Under certain conditions, small 4 mm diameter gas-liquid columns can be considerably overloaded in order to prepare small samples of pure substances, *i.e.* liquid samples of the order of 0.3 ml can be eluted instead of the normal 1-10 μ l [487]. The required substance must have a sufficiently different retention volume from the impurities present. If the retention volumes of impurities and the major component are very similar, the column cannot be overloaded to the above extent, and a larger column is required. Pure ethyl nitrate and formic acid have been prepared by this method.

CONCLUSIONS

Gas chromatography has been used to separate complex mixtures of substances in amounts ranging from 10⁻¹⁵-70 g and with boiling points from -200° to +400° C. It can both qualitatively and quantitatively analyse these substances with good accuracy and in the comparatively short time of a few minutes to a few hours. The separated substances can then be recovered in a high state of purity. Not only is it an outstanding technique on its own, but it can also be used in conjunction with methods such as fractional distillation, mass-, and infra-red-spectrometry, and can achieve results which were previously not possible with existing methods. The appearance of commercial instruments designed for application to research, to the routine analysis of all types of substances, and to process-control in industry, is greatly aiding in the adoption of gas chromatography as a universal separation-process.

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