up so that material coming into contact with it might be vaporized. The technique should ensure minimization of discrimination caused by selective fractionation from the syringe needle. Published results seem to confirm that the technique gives highly precise quantitative results.

Conclusion

For many years the introduction of sample into the column represented the weak point for accurate quantitative analysis by capillary columns. In the last few years this has largely been remedied and good quantitation can be achieved by the use of one of the range of commercially available injectors. However, it was pointed out by Deans a number of years ago that the only completely reliable method of sample introduction was in the vapour phase, i.e. handling all samples as gases. While this might be true, it is something of a council of perfection and it is likely that syringe injection through a septum will be with us for the foreseeable future.

See also: **II/Chromatography: Gas:** Column Technology; Historical Development. **III/Gas Analysis:** Gas Chromatography.

Further Reading

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Theory of Gas Chromatography

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Introduction

Gas chromatography (GC) involves the separation of the components of a mixture by virtue of differences in the equilibrium distribution of the components between two phases; the gaseous (mobile) phase moves in a definite direction, while the other phase is stationary (stationary phase).

Stationary Phase

In gas–liquid chromatography (GLC) the stationary phase is a liquid coated onto a solid support, which may or may not contribute to the separation process, or onto the walls of an open tube. The liquid may also be chemically bonded to the solid or capillary tube (bonded phase) or immobilized on it, e.g. by *in situ* polymerization (cross-linking) after coating (immobilized phase). In gas–solid chromatography (GSC) the stationary phase is an active solid (e.g. silica, alumina or a polymer). Gas chromatography is always carried out within a tube and the combination of stationary phase and tube is referred to as the column (column chromatography). The stationary phase (liquid + support) may fill the whole inside volume of the tube (packed column) or be concentrated along the inside wall of the tube, leaving an unrestricted path for the mobile phase in the middle of the tube (open-tubular or capillary column).

In open-tubular columns, the liquid stationary phase can be coated onto the essentially unmodified smooth inner wall of the tube (wall-coated open-tubular (WCOT) column). The inner wall may be made porous by etching the surface by chemical means or by depositing porous particles on the wall from a suspension, the porous layer acting as the stationary phase or as a support for a liquid (porous-layer open-tubular (PLOT) column); or the porous layer may consist of support particles deposited from suspension (support-coated open-tubular (SCOT) column). The term capillary column denotes a column (packed or open-tubular) having a small diameter.

With a solid stationary phase, separation is based mainly on adsorption affinities between the sample molecules and the surface of the active solid (adsorption chromatography). With a liquid stationary phase separation depends on the solubilities of the sample molecules (partition chromatography). In keeping with other partition processes, the sample molecules are often referred to as the solute and the stationary phase as the solvent. This terminology is acceptable in gas chromatography, but can cause confusion in liquid chromatography.

Mobile Phase

In GC at normal pressures (1–2 atm; $1–2 \times 10^5$ Pa) the mobile phase (usually called the carrier gas) plays little, if any, part in the separation, but only serves to carry the sample molecules through the column.

The time taken by a sample in passing through the column (the total elution/retention time, t_R) is a function of the carrier gas velocity, and the volume of carrier gas required to elute the component from the column, the total retention volume (V_R), is given by:

$$V_R = F \times t_R$$

where F is the volume flow rate of carrier gas measured at the column outlet at ambient temperature (T_a) and ambient pressure (p_a). If a water-containing flow meter (e.g. the soap bubble flow meter) is used, the measured flow rate must be corrected to dry gas conditions to give the mobile phase flow rate at ambient temperature (F_a):

$$F_a = F(1 - p_w/p_a)$$

where p_w is the partial pressure of water vapour at ambient temperature.

The mobile phase flow rate (F_c) at the column temperature (T_c, Kelvin) is:

$$F_c = F_a(T_c/T_a)$$

To achieve a flow rate through the column, the inlet pressure (p_i) of carrier gas must be greater than the outlet pressure (p_o), the difference being the pressure drop (Δp).

Gases are compressible fluids, and in order to correct for this flow rate measurements a correction, the mobile phase compressibility correction factor (j), has to be used. Thus:

$$j = \frac{3[(p_i/p_o)^2 - 1]}{2[(p_i/p_o)^3 - 1]}$$

It is easiest to measure the volume flow of the carrier gas through the column, but for many purposes the linear flow rate ($\bar{u}$) is required. The linear velocity across the average cross-section of the chromatographic column can be calculated from the flow rate at column temperature (F_c), the cross-sectional area of the column (A_c) and the interparticle porosity (ε):

$$\bar{u} = F_c/(\varepsilon A_c)$$

where the interparticle porosity is the interparticle volume of a packed column per unit area. For an open-tubular column this term is equal to 1.

Since the flow rate at column temperature (F_c) is measured at the outlet, in GC the carrier gas velocity at column outlet (u_o) is frequently employed. Correcting this term for gas compressibility gives the average linear carrier gas velocity ($\bar{u}$) $= u_o j$.

In practice, the average linear carrier gas velocity is calculated by dividing the column length (L) by the retention time (t_M) of an unretained peak, i.e. one that moves at the same velocity as the mobile phase:

$$\bar{u} = L/t_M$$

Methods of Chromatography

In most analytical applications of GC the mobile phase is continuously passed through the column and the sample is fed (or injected) into the system as a finite plug. This process is known as *elution chromatography*. If the conditions for the analysis are optimized the sample components can be separated completely from each other. If the sample is fed continuously onto the column with no added mobile phase, the process is known as *frontal analysis*. Only the first component to emerge from the column may be obtained pure, the other components being contaminated with earlier emerging components. A third technique, used occasionally in liquid chromatography (LC) but rarely in GC, is *displacement development*, which uses a strongly sorbed mobile phase to push (or displace) the components off the column. Each component can be obtained pure, but there is overlap between adjacent components placing a detector at the end of the column, which responds to some property of the sample molecules, produces a trace (the chromatogram) that is a plot of detector response against time.

The General Elution Problem

A typical chromatogram for the separation of a mixture of components is shown in **Figure 1**. This illustrates the characteristics of chromatography, often referred to as the 'general elution problem'. The properties illustrated by the chromatogram, which must be explained by any theory of chromatography, are:

- the components of the mixture elute from the column at different times (retention);
- peak widths increase with retention time (peak shape and broadening);
- the separation of pairs of peaks is not constant (column resolution).

Chromatographic Retention

Retention parameters are measured in terms of chart distances or times, mobile phase volumes or retention factors (k) (previously called capacity factors, k'). With a constant recorder speed, chart distances are directly proportional to times. Likewise if the flow rate is constant, the volumes are proportional to times, e.g. t_R (time) is analagous to V_R (volume). In GC with a compressible carrier gas, V_M, V_R and V'_R represent volumes under column outlet pressure.

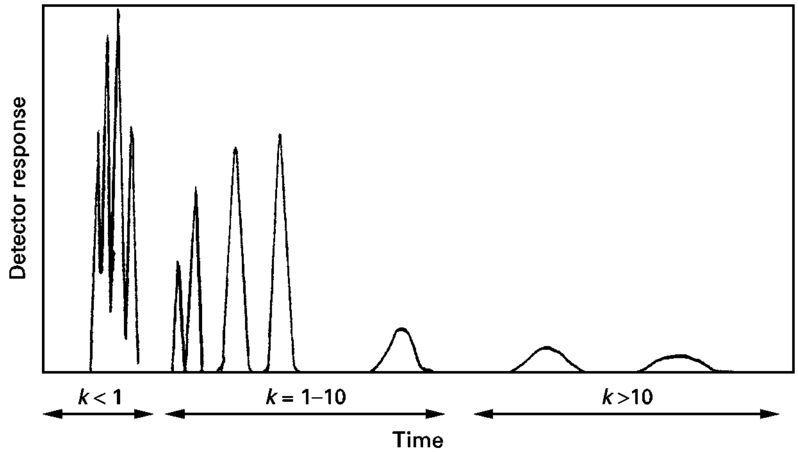

Figure 1 The general elution problem.

If F_c is used in their calculation these correspond to volumes at column temperature.

When a mixture is chromatographed, the time taken for a component to be eluted from the column, the (total) retention time (t_R), is measured from the moment of injection to the appearance of the peak maximum. This, together with the width of the peak measured at the baseline (w) or at half peak height (w_h), and the elution of an 'unretained peak', are important parameters in chromatography. These are illustrated in **Figure 2**, which represents the separation of a two-component mixture.

The retention volume (V_M) of an unretained peak (where $V_M = F \times t_M$) is also called the gas hold-up volume or dead volume, and is equal to the volume (both inter- and intra-particle) available to the mobile phase in the column. The corrected gas hold-up volume (V_M^o) is corrected for gas compressibility where $V_M^o = V_M j$.

Injection techniques in GC, where the sample is held at the head of the column before it starts moving through the column, have necessitated the introduction of additional terms. These are the peak time/volume (t_R, V_R), where the time/volume is measured from the start of elution rather than time of injection, and the adjusted retention time/volume (t'_R/V'_R), which is the total elution time/volume minus the gas hold-up time/volume:

$$t'_R = t_R - t_M; \quad V'_R = V_R - V_M$$

The corrected retention time/volume (t_R^o/V_R^o) is the total retention time/volume corrected for carrier gas compressibility:

$$t_R^o = t_R\, j = V_R\, j/F_c = V_R^o/F_c; \quad V_R^o = V_R\, j$$

The net retention time/volume (t_N, V_N) is the adjusted retention time/volume corrected for carrier gas

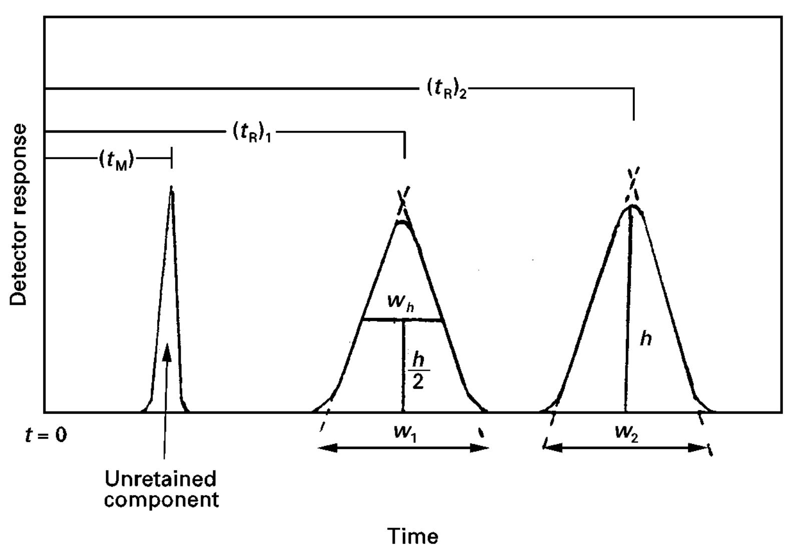

Figure 2 Separation of a two-component mixture showing retention parameters.

compressibility:

$$t_N = V'_R j/F_c = V_N/F_c; \quad V_N = V'_R j$$

The specific retention volume at column temperature θ (V_g^θ) normalizes the retention for the amount of stationary phase on the column (W_s):

$$V_g^\theta = V_N/W_s$$

Normalizing the specific retention volume to 0°C (273.15 K) gives rise to the specific retention volume at 0°C (V_g):

$$V_g = V_g^\theta \times \frac{273.15\ k}{T_c} = \frac{V_N}{W_s} \times \frac{273.15\ k}{T_c}$$

where T_c is the column temperature.

The unretained peak is given by a substance that has no affinity for the stationary phase and therefore passes through the column at the same speed as the mobile phase. A substance that shows affinity for the stationary phase moves through the column more slowly than the mobile phase and is said to be retained. The ratio of the two velocities is known as the retardation factor (R):

$$R = \frac{\text{rate of movement of retained peak}}{\text{rate of movement of mobile phase}}$$

A retained component spends time in both the mobile phase (t_M) and the stationary phase (t_S), and retention time t_R is given by:

$$t_R = t_M + t_S$$

The time spent in the stationary phase is dependent on the distribution coefficient (K_c) such that $t_S = K_c V_S$. If C_S and C_M are the concentrations of a component in the stationary phase and mobile phase, respectively, then the distribution constant is given by:

$$K_c = C_S/C_M$$

The rate of movement of a component through the column is inversely proportional to the distribution constant, i.e. a substance with a high concentration in the stationary phase (a high distribution coefficient) moves slowly through the column. Components of a mixture are, therefore, separated only if their distribution coefficients differ. Using volumes rather than times we can write:

$$V_R = V_M + K_c V_S \qquad \text{or} \qquad V'_R = K_C V_S$$

which is the fundamental equation for chromatography, neglecting the effects of nonlinearity of the sorption isotherm and band broadening.

Since, in general, migration of the solute through the chromatographic column depends upon the equilibrium distribution of the solute between the stationary and mobile phases, retention is controlled by those factors that affect the distribution. In GLC, the distribution is essentially that for a two-component system; the sample (or solute) and the stationary phase (or solvent) (or the adsorbate and adsorbent respectively in gas–solid chromatography). The distribution then is a result of the molecular forces between the sample and the stationary phase and the effect of temperature and pressure on these interactions, although at the pressures normally used in GC the effect of pressure is negligible. All such forces are electrostatic in origin and are based on Coulomb's laws of attraction and repulsion between charges. The major forces involve those between charged ions (e.g. in ion chromatography), i.e. dipole–dipole interactions, dipole-induced dipole interactions, dispersion forces and hydrogen bonding forces. Dispersion forces are present in all atoms and molecules, but the other interactions depend on structural features in the molecule, i.e. ions (e.g. Cl^-), polar functional groups (e.g. C–Cl, C–OH) and polarizable groups (e.g. aromatic and conjugated molecules).

In this case of GLC, assuming that the concentration of the sample (or solute) molecules in the mobile (gas) phase is very small, as is the case if small volume sample injections are made, then the solution of solute in the stationary phase may give rise to an 'ideal solution', and the vapour pressure (p) of the solute above the solution is given by Raoult's law:

$$p = p^o x$$

where p^o is the vapour pressure of the pure liquid solute and x is the mole fraction of the solute in solution. To correct for the 'nonideality' of real solutions, Raoult's law must be written:

$$p = \gamma p^o x$$

where γ is the activity coefficient at infinite dilution. The distribution coefficient (K) for the sample in the stationary phase is given by:

$$K = \frac{RT_c}{M_s \gamma p^o}$$

where T_c is the column temperature and M_s the molecular weight of the stationary phase. For two solute molecules (1, 2) with distribution coefficients K_1 and K_2, activity coefficients γ_1 and γ_2 and vapour pressures p_1^o and p_2^o, we can write:

$$\frac{K_1}{K_2} = \frac{\gamma_2}{\gamma_1}\frac{p_2^o}{p_1^o}$$

For solutions that approximate to ideal behaviour, $\gamma \sim 1$ and the separation depends on differences in the vapour pressures; this is the case with nonpolar solutes in a nonpolar stationary phase. The existence of polar interactions between the solute and stationary phase molecules introduces nonideality into the system and $\gamma \neq 1$. This can be made use of to provide a separation. A good example is the separation of benzene (C_6H_6) and cyclohexane (C_6H_{12}), which have boiling points of 353.2 and 353.8 K, respectively. In a nonpolar stationary phase the predominant molecular interactions, between benzene or cyclohexane and the stationary phase, will be dispersion forces, and the activity coefficients for both solutes are ~ 1. Because the difference in the vapour pressures is small, little separation is observed and the solutes are eluted from the stationary phase in order of their boiling points, i.e. benzene is eluted before cyclohexane. If a polar stationary phase is used, cyclohexane, because of its saturated nature, still only exhibits dispersion interactions and $\gamma \sim 1$. However the π electrons in benzene cause it to undergo dipole-induced dipole interactions, leading to a decrease in γ and an increase in its distribution coefficient. Hence in a polar stationary phase benzene is eluted some time after cyclohexane.

The relationship between retention and molecular structure has long been used in GC as an aid to the assignment of chromatographic peaks. Many homologous series of compounds show a linear relationship between log (retention) and boiling point or carbon number. Since different solute types (e.g. *n*-alkanes, *n*-alkyl alcohols, *n*-alkyl esters) give different linear relationships with different slopes, these plots can be used to assign a chromatographic peak to a particular class of compound and to determine its carbon number and boiling point. These relationships have also been used to provide data in the form of a Retention Index as an aid to peak identification. However, with the widespread use of mass spectrometer detectors these techniques are used less than formerly.

In adsorption chromatography the stationary phase volume is replaced by the surface area (A_S) of the stationary phase, and the distribution coefficient is replaced by the adsorption coefficient (K_A). In GC both V_R and V_M have to be corrected for gas compressibility.

An alternative expression (the retention factor, k) for the distribution of a sample component is in terms of the relative number of moles (n) of a component in the stationary and mobile phases, such that:

$$k = n_S/n_M = K_c(V_S/V_M)$$

The ratio V_S/V_M is the phase ratio. Early literature will refer to the retention factor as the capacity ratio (k').

Since a sample molecule only migrates through the column when it is in the mobile phase, the retardation factor (R) may be written:

$$R = \frac{\text{amount of solute in the mobile phase}}{\text{amount of solute in mobile + stationary phases}}$$

or:

$$R = n_M/(n_M + n_S) = 1/(1 + k)$$

Substituting the retention factor into the equation:

$$V_R = V_M + K_C V_S$$

gives:

$$V_R = V_M(1 + k)$$

or using retention times:

$$t_R = t_M(1 + k)$$

and on rearrangement:

$$k = (t_R - t_M)/t_M$$

This last expression is widely used as a simple way of expressing retention from values easily measured from the chromatogram, and without the need to measure flow rates. Since:

$$t_M = L/\bar{u}_M$$

we can write:

$$t_R = \frac{L}{\bar{u}}(1 + k)$$

Hence the retention time is directly proportional to the column length and inversely proportional to the linear flow rate of the mobile phase.

Peak Shape and Broadening

The variation of solute concentration in the stationary phase with solute concentration in the mobile phase, at constant temperature, is known as the sorption isotherm. Simple chromatographic theory assumes a linear isotherm relationship, i.e. the distribution coefficient is constant. Under these conditions the retention time is independent of sample concentration and the peak moves with a constant speed. Given a peak profile with plug-shape distribution on injection, this plug shape should be maintained as the peak passes through the column to emerge at the exit. However, because of longitudinal diffusion in the direction of flow, the peak takes on a Gaussian distribution. If the isotherm relationship is nonlinear (e.g. Langmuirian or anti-Langmuirian), the distribution coefficient is not constant but varies with solute concentration and there is a distribution of solute molecule velocities across the peak that is described as tailing or fronting. This relationship between isotherm shape and peak shape is illustrated in **Figure 3**.

The width of a chromatographic peak is a function of the column efficiency, expressed as the plate number (N), calculated from the following equations depending on the value used for the peak width (see Figure 2):

$$N = (V_{\mathrm{R}}/\sigma)^2 = (t_{\mathrm{R}}/\sigma)^2 = 16(t_{\mathrm{R}}/w_{\mathrm{b}})^2 = 5.545(t_{\mathrm{R}}/w_{\mathrm{h}})^2$$

where σ is the standard deviation of the Gaussian peak.

The column length divided by the plate number gives the plate height or height equivalent to one theoretical plate (H) and normalizes the plate number for column length:

$$H = L/N$$

The concept of 'plates' in chromatographic theory (the plate theory) is by analogy with the distillation process and represents the notional length of the column in which the solute molecules reach a distribution equilibrium. Thus a large number of theoretical plates corresponds to an efficient column.

Consideration of the chromatographic process as controlled by equilibrium gives a satisfactory explanation of chromatographic retention in term of the distribution coefficients. However when considering band broadening a different approach is required, known as the rate theory of chromatography. This was first applied by van Deemter, Klinkenberg and Zuiderweg to packed columns, but has been extended and modified to include open-tubular columns.

As the solute band passes through the column the bandwidth increases and the solute is diluted by the mobile phase. Although the process of fluid flow is complex, three main contributions to band broadening (i.e. to the variance (σ^2) of the Gaussian peak) may be recognized in GC: the multipath effect, A (formerly called eddy diffusion); molecular diffusion, B; and mass transfer, C. These contributions have been combined by van Deemter and co-workers in the van Deemter equation, which expresses the broadening of a band in terms of the plate height, H, and the average linear velocity ($\bar{u}$) of the mobile phase:

$$H = A + B/\bar{u} + C_{\mathrm{s}}\bar{u}$$

A plot of H versus $\bar{u}$ is shown in **Figure 4**. The relationship highlights the importance of using the correct flow rate for minimum H values (maximum

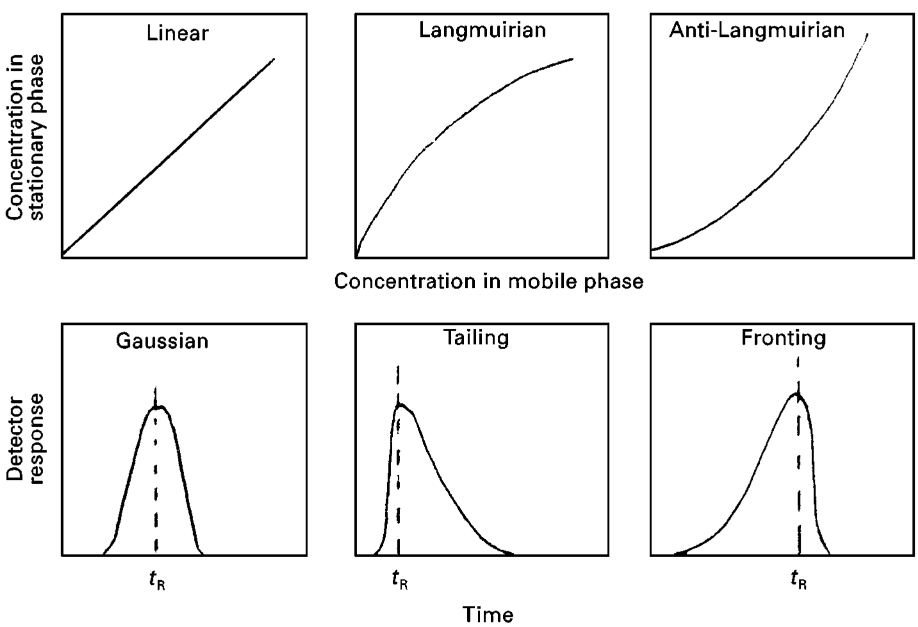

Figure 3 Isotherm shape and its effect on peak shape and retention times.

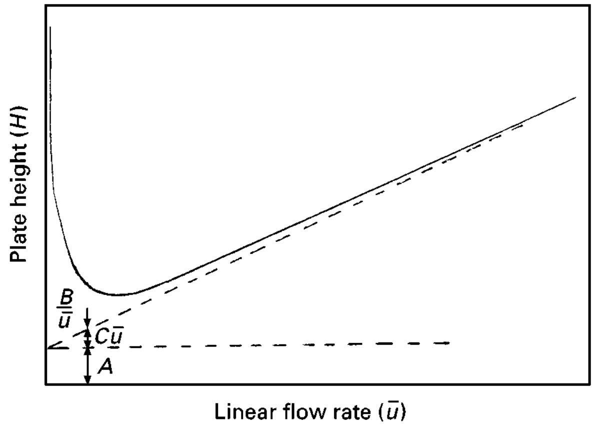

Figure 4 The 'van Deemter' plot and determination of the constants A, B and C_s.

N values) and allows values of A, B and C_s to be calculated as shown.

The multipath effect Molecules flowing through a packed bed of stationary phase will take paths of different lengths, resulting in a small difference in retention times. This has the effect of broadening the band by an amount dependent on the particle diameter (d_p), such that:

$$A = 2\lambda d_p$$

The packing constant (λ) is an empirical term depending on the shape (spherical or irregular) of the packing material and the packing efficiency, and reaches a minimum value $\cong 0.5$. For open-tubular column there is no 'A' term.

Longitudinal molecular diffusion Solute molecules diffuse in a longitudinal direction (i.e. along the column axis) according to Fick's law of diffusion. The amount of band spreading is directly proportional to the coefficient of diffusion (D_M) of the solute molecules in the mobile phase, and inversely proportional to the mobile phase flow rate. An obstruction factor (ψ) is introduced to account for the restricted diffusion in a packed bed. Hence:

$$B = 2\psi D_M/\bar{u}$$

Mass transfer In GC the only form of mass transfer that is significant involves the movement of the solute molecules in and out of the stationary phase (stationary phase mass transfer, C_s). At the head of the column the solute is distributed between the stationary and mobile phases according to the value of the distribution coefficient. As the band moves down the column, solute at the leading edge of the band is continually meeting new stationary phase into which it dissolves. To maintain the equilibrium, solute will move from the trailing edge of the band, out of the stationary phase back into the mobile phase. Because this process is not instantaneous, the band is broadened. A fast-moving mobile phase sweeps the zone more rapidly through the column and accentuates the band broadening, as does a greater film thickness (d_f) of stationary phase. A higher rate of solute diffusion in the stationary phase (D_S) will decrease the band broadening, so that:

$$C_s = q \times \frac{k d_f^2 \bar{u}}{(1+k)^2 D_S}$$

where q is a configuration factor depending on the nature of the stationary phase. In adsorption chromatography the C_s term is expressed in terms of the adsorption/desorption kinetics of the solute molecules on the stationary phase.

van Deemter type plots using different carrier gases show that although nitrogen gives slightly lower H values, this is only achieved at relatively low flow rates ($\sim 15\ \mathrm{cm\,s^{-1}}$), and as the flow rate increases the value of H increases rapidly. Hydrogen has a much flatter curve and is best for fast analysis with high flow rates (above $30\ \mathrm{cm\,s^{-1}}$). Because of the inherent safety problems from hydrogen, helium is a good compromise and is used in most coupled techniques (e.g. gas chromatography–mass spectrometry, GC-MS).

A modernized version of the van Deemter equation includes the multipath term (A) in a more generalized term covering mass transfer in the mobile phase (C_M):

$$H = B/\bar{u} + C_S\bar{u} + C_M\bar{u}$$

where:

$$C_M = f(d_p^2, \bar{u})/D_M$$

Open-tubular columns are often evaluated by comparing the theoretical maximum number of plates with that of the actual calculated number of plates, where:

$$H(\min) = r_o \frac{1 + 6k + 11k^2}{3(1+k)^2}$$

and r_o is the column radius.

Extra-column band broadening So far we have only considered band broadening processes within the chromatographic column itself, but in assessing the overall performance of the system the instrument as a whole is important. Thus the injection system, detector and connecting tubing all contribute to the overall analysis. The objective for the injection is to vaporize the sample onto the column in as narrow a plug as possible; slow vaporization or the existence of zones unswept by mobile phase in the injector will lead to both band broadening and peak tailing. Large dead volumes in the detector can lead to remixing of components and deterioration of the separation as well as dilution of the sample peaks, thus reducing detection limits. Generally the design of gas chromatographs eliminates the need for long lengths of connecting tubing, often a major problem in liquid chromatographs.

Column Resolution

Chromatographic separation is only achieved when there is a difference in the distribution coefficients of two components, i.e. the molecular interactions (dispersion forces, dipole interactions and hydrogen bonding forces) between the sample molecules and the stationary phase are sufficiently different. More fundamentally it is the free energies of distribution $\Delta(\Delta G^{\ominus})$ of the components of a mixture that must differ. It can be shown that:

$$\Delta(\Delta G^{\ominus}) = -RT \ln \alpha = -RT \ln [(K_c)_2/K_c)_1]$$

A stationary phase that produces a large degree of separation is said to have a high selectivity. The separation of two components (1 and 2) is expressed by the relative retention (α):

$$\alpha = t'_{R(2)}/t'_{R(1)} = V'_{R(2)}/V'_{R(1)} = k_{(2)}/k_{(1)} = K_{C(2)}/K_{C(1)}$$

If one of the pair is a standard substance, the symbol used for relative retention is 'r'.

Having achieved a separation it is necessary to prevent remixing of the components. The ability to achieve this is a function of the column efficiency, as measured by the plate number. The combined effects of stationary phase selectivity and column efficiency is expressed in the peak resolution (R_s) of the column. (see Figure 2):

$$R_s = \frac{(t_R)_2 - (t_R)_1}{\frac{1}{2}(w_1 + w_2)}$$

A value of $R_s = 1.5$ is normally considered to represent baseline separation for Gaussian shaped peaks. To achieve the maximum peak resolution, both high selectivity and column efficiency (giving narrow bands) are required.

Increased resolution can always be achieved by an increase in column length since the peak separation (Δt_R) is proportional to the distance of migration down the column, but peak width is only proportional to the square root of the migration distance. The penalty for this, however, is longer retention times and an increased inlet pressure of mobile phase.

The Purnell equation shows how peak resolution is related to the retention factor (k), the plate number (N) and the relative retention (α):

$$R_s = \frac{\sqrt{N_2}}{4} \times \frac{(\alpha - 1)}{\alpha} \times \frac{k_2}{1 + k_2}$$

where the subscript 2 refers to the second peak.

Conditions for obtaining maximum values of the plate number have already been discussed. The relative retention is mainly governed by the nature of the stationary phase, since in GC at normal pressures, only molecular interactions between the solute molecules and the stationary phase are involved. These interactions are maximized in the concept of 'like has an affinity for like'. Thus, for a sample that contains predominantly nonpolar species a nonpolar stationary phase will optimize the dispersion forces and, since polar interactions will be absent, solutes will elute according to their volatility with the most volatile (lowest boiling point) components eluting first. For polar samples a polar stationary phase is used to maximize both dipole–dipole interactions and dipole-induced dipole interactions. Because the effect of volatility is still present, it is much more difficult to predict elution behaviour in this latter case. Most naturally occurring mixtures contain species spanning a range of polarities, and in this case it is still better to use a polar stationary phase. At least a partial separation can be achieved with α values as low as 1.05, but values in the range 1.5–3.0 are preferable and above α values ~ 5.0 little additional resolution is achieved. Peak resolution increases rapidly with increasing k values, but at values >10 the term $k_2/(1 + k_2) \to 1$ and the term plays no further part in the resolution. The use of k values <1 gives very short retention times and poor resolution, so that the optimum range for k is between 1 and 10. The retention equation $t_R = L/\bar{u}(1 + k)$ shows that retention times are a function of both the mobile phase velocity ($\bar{u}$) and the retention factor.

In GC, k values are controlled by temperature. The van't Hoff equation describes the change in equilibrium constant with temperature and if the phase ratio (V_S/V_M) is independent of temperature we can also write for the retention factor:

$$\frac{\mathrm{d} \ln k}{\mathrm{d}T} = \frac{\Delta H}{RT^2}$$

where ΔH is the enthalpy of solution (or adsorption) from the mobile phase to the stationary phase.

Figure 1 for the general elution problem also shows values of k for different zones of the chromatogram. With low k values ($k < 1$) the peaks are eluted too rapidly and there is no time for separation. With high k values ($k > 10$) elution times are long, the peaks are broad and the peaks are overresolved. This problem can be corrected using the technique of temperature programming. Assuming that this chromatogram was obtained isothermally at 100°C it would be possible to choose a lower starting temperature (say 50°C) and then raise the temperature to say 150°C over a given period of time. This would have the effect of increasing the k values for the early peaks and decreasing the k values for the later peaks, the object being to get all peaks in the optimum region $1 < k < 10$. Modern computer-controlled gas chromatographs have the facility to use isothermal periods and linear and nonlinear temperature programs with multiple ramps to giver better control over k values.

The retention equation also indicates that a similar effect could be achieved using the analagous technique of flow-programming and changing the carrier gas flow rate. However, increase in carrier gas flow rate gives an approximately linear effect whereas temperature programming has a logarithmic effect. In spite of this, flow programming finds a use in the separation of labile and temperature-sensitive samples where high temperatures are to be avoided.

A satisfactory separation is achieved when all three terms in the Purnell equation are optimized.

Future Developments

The theory of gas chromatography is well established and it is unlikely that there will be any significant new developments. A greater understanding of the interactions involving new stationary phases (e.g. chiral phases), and the preparation of stationary phases with better temperature stability would lead to an extension of its application. Developments in instrumentation with new coupled techniques is also a possibility. The most likely area for further development is in the area of data handling and instrument control using the newer breed of computers.

See also: **II/Chromatography: Gas:** Column Technology; Gas–Solid Gas Chromatography; Historical Development.

Further Reading

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CHROMATOGRAPHY: LIQUID/Electron Spin Resonance Detectors in Liquid Chromatography

See **II/CHROMATOGRAPHY: LIQUID/Detectors: Electron Spin Resonance**

CHROMATOGRAPHY: LIQUID/ Chiral Separations in Liquid Chromatography: Mechanisms

See **II/CHROMATOGRAPHY: LIQUID/Mechanisms: Chiral**