CHAPTER II

THEORY

2.1 Gas chromatography (11, 12)

Gas chromatography is a technique for the separation of volatile substances. The basic principle for gas chromatographic separation is the distribution of a sample between two phases; the stationary bed with large surface area and the moblie gas phase which percolates through the stationary bed. Depending upon the physical state of the stationary phase, gas chromatography can be divided into two types, i.e. gas-solid chromatography (GSC) for solid stationary phase and gas-liquid chromatography (GLC) for liquid stationary phase.

In gas-solid chromatography, the separation depends upon the adsorptive properties of the column packing to separate samples, primarily gases. In gas-liquid chromatography, the liquid is coated as a thin uniform film on a solid support, so the separation depends on the partition of the sample in and out of this liquid film.

The time that the substances take to pass through the column to the detector is called the "retention time". The separation efficiency or the resolution of the chromatographic separation is governed by the column efficiency and the solvent efficiency which are shortly described as follows:

a. column efficiency: Column efficiency is measured by the number of the theoretical plates which, in turn, can be easily evaluated from the chromatogram

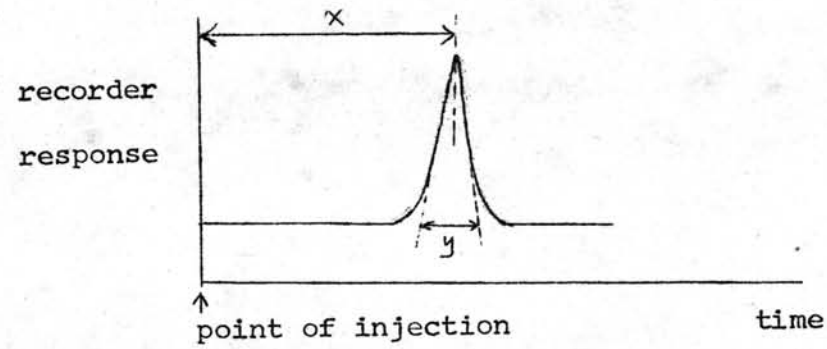

Figure 2.1 Calculation of theoretical plates from a chromatogram

The number of theoretical plates, N, is given by $16(x/y)^2$, where "y" is the length of the baseline cut by the two tangents, and "x" is the distance from injection to peak maximum. For the comparison of efficiency between columns of different lengths, the height equivalent to a theoretical plates, HETP, is evaluated. This is related to N by :

$$HETP = L/N \qquad \ldots\ldots\ldots(1)$$

Where L is the length of a chromatographic column, usually in centimeters.

The rate theory developed by van Deemter et.al. is one of the most frequently applied theories to account for the shape of elution curves from chromatographic columns. According to this theory, the three principal contributions to the broadening of a band are :

i) Multipath effect or eddy diffusion (A term)

ii) Molecular diffusion (B term)

iii) Resistance to mass transfer (gas and liquid, C term)

The basic van Deemter equation for the height equivalent to a theoretical plate in a gas-liquid column is :

$$HETP = A + \frac{B}{\mu} + C \cdot \mu \qquad \text{.....(2)}$$

When μ is the linear gas velocity through the column which is measured by

$$\mu = \frac{\text{length of column, cm}}{\text{retention time of air, seconds}} \qquad \text{.....(3)}$$

To minimize the A term, one should use small particles of uniform size consistent with low pressure drop and small diameter column. The packing technique should give a high packing density without crushing the particles. The molecular diffusion term (B term) is proportional to the solute diffusity in the carrier gas which can be reduced by increasing the density of the gas, either by increasing the pressure or the molecular weight of the gas. To minimize the C term, a thin uniform of a low viscosity liquid should be used. The flow rate must be low enough and distribution coefficient high enough to favor equilibrium between the liquid and gas phase.

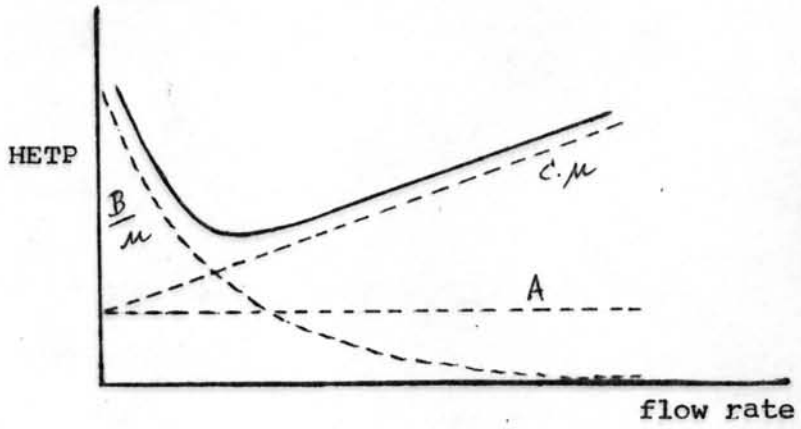

Figure 2.2 van Deemter plot

From the van Deemter plot which is given in Figure 2.2, the minimum HETP gives the optimum flow rate for the best column efficiency. In practice, operating at flow rate slightly higher than optimum will decrease the analysis time and not materially affect the HETP.

b. Solvent efficiency: Substances having the same vapor pressure can be easily separated by appropriate selection of the liquid phase. The partition coefficient, k, which determines the separation efficiency, is given by

$$k = \frac{\text{the amount of solute per unit volumn of liquid phase}}{\text{the amount of solute per unit volumn of gas phase}} \quad \ldots(4)$$

The value of k is high when most of substance is retained in the liquid phase. This means that the substance moves slowly down the column and only a small fraction will be in the carrier gas at any given time. Thus, separation between two compounds is possible if their partition coefficients are

different. The partition coefficient decreases with increasing temperature of the column since the fraction of the solute in the gas phase increases, with increasing temperature. This results in decrease in separation since it is the liquid phase which performs the separation, Low temperatures mean more liquid phase interaction, more separation, and longer analysis time. As a minimum, the solute should spend 50% of the time in the liquid phase, so that the retention time exceeds twice the retention time of air.

The liquid phase chosen depends on the composition of the sample. For an efficient separation, the liquid phase should be similar in chemical structure to the components of the mixture, for example hydrocarbon compounds are best separated with a hydrocarbon solvent

2.1.1 Basic gas chromatographic system

The basic parts of a gas chromatograph are shown in the schematic diagram of Figure 2.3

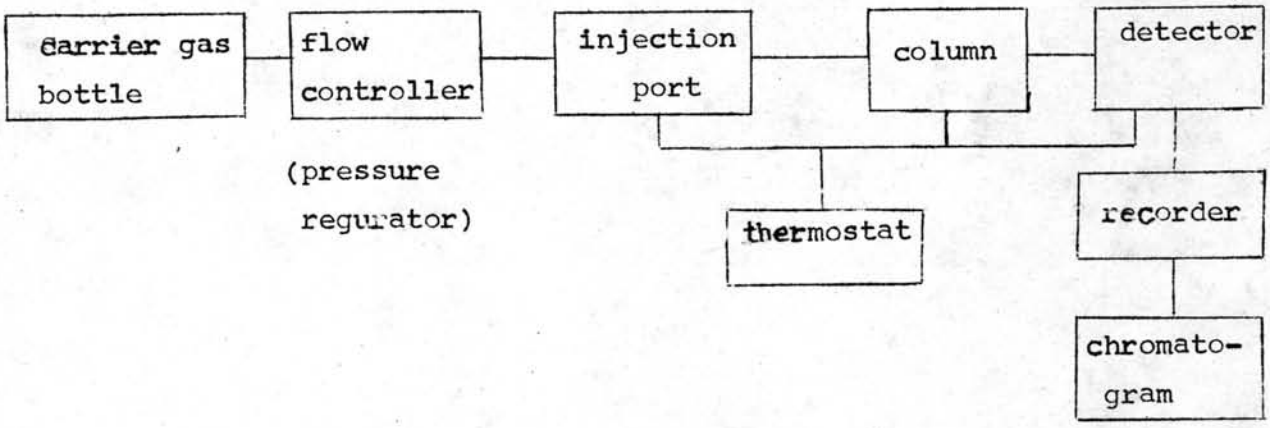

Figure 2.3 Schematic diagram of a gas chromatographic system.

The sample, liquid or gas, is introduced into the gas chromatographic system through a heated chamber (injection port). The carrier gas carries the sample through the column where the components in the sample are separated in bands according to their distribution coefficients. These component bands leave the column in the gas stream and are recorded as a function of time by a detector. The detector indicates the presence and measures the amount of components in the column effluent.

An electron capture detector (ECD) is used in the pre - sent work. The radioactive source, usually nickel - 63 or tritium, ionizes the carrier gas to give a stream of slow electrons. These electrons migrate to the anode under a fixed voltage and produce a steady current. If a sample containing electron absorbing molecules such as alkyl halides, conjugated carbonyls, nitriles and organometals is introduced, these molecules will capture the slow electrons and the current will be reduced. The loss of current is a measure of the amount of compounds.

2.1.2 Gas chromatography in qualitative and quantitative analyses

In qualitative analysis, the retention time is the principal characteristic of the sample and the liquid phase at a given temperature

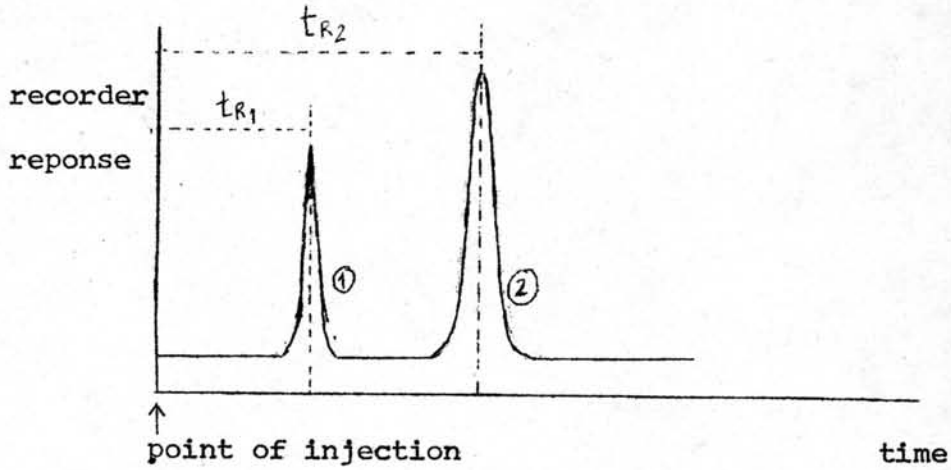

Figure 2.4 Chromatogram showing the retention time (t_R)

Several compounds may have identical or close retention times, but each compound has only one retention time. The retention time is not influenced by the presence of other components. In quantitative analysis, the area under peak of the chromatogram is proportional to the concentration. This can be used to determine the concentration of each component. The peak height can replace the peak area if the base width is narrow (11).

2.1.3 Temperature effect

There are three important parts in the chromatographic system in which the temperature must be controlled, i.e, the injection port, the column and the detector. The injection port is kept at a relatively high temperature consistent with the thermal stability of the sample, usually about 50°C above the boiling points of the components. The detector must be hot

enough to avoid condensation of the sample, water or by-products formed in the ionization process. Finally, the column tempera - ture is an important factor for the determination of retention time and resolution. The column temperature should be high enough so that the analysis is accomplished in a reasonable time, and low enough that the desired separation is achieved.

2.2 Solvent extraction

Extraction is a separation process in which a solute is distributed between two immiscible solvents. The extraction efficiency is given by :

$$K_D = C_1/C_2 \quad \text{.....(5)}$$

where K_D is the distribution coefficient or the partition coefficient

C_1 is the concentration of solute in the solvent in numerator part

C_2 is the concentration of solute in the solvent in denominator part

If the distribution coefficient is very large ($>$ 1000) a single extraction in a separating funnel will probably remove all of the solute from one phase to another. However, it can be shown that for a given amount of extracting solvent, it is more effective to divide it into several small portions and use each portion successively rather than a single extraction with all of the solvent at one time.