Gas Chromatography

Gas chromatography is a technique used for separation of volatile substances, or substances that can be made volatile, from one another in a gaseous mixture at high temperatures. A sample containing the materials to be separated is injected into the gas chromatograph. A mobile phase (carrier gas) moves through a column that contains a wall coated or granular solid coated stationary phase. As the carrier gas flows through the column, the components of the sample come in contact with the stationary phase. The different components of the sample have different affinities for the stationary phase, which results in differential migration of solutes, thus leading to separation

Martin and James introduced this separation technique in 1952, which is the latest of the major chromatograhpic techniques. However, by 1965 over 18000 publications in gas chromatography (GC) were available in the literature. This is because optimized instrumentation was feasible. Gas chromatography is good only for volatile compounds or those, which can be made volatile by suitable derivatization methods or pyrolysis. Thus, about 20% of chemicals available can be analyzed directly by GC.

Gas chromatography can be used for both qualitative and quantitative analysis. Comparison of retention times can be used to identify materials in the sample by comparing retention times of peaks in a sample to retention times for standards. The same limitations for qualitative analysis discussed in Chapter 26 also apply for separations in GC. Quantitative analysis is accomplished by measurement of either peak height or peak area

Gas - Solid Chromatography (GSC)

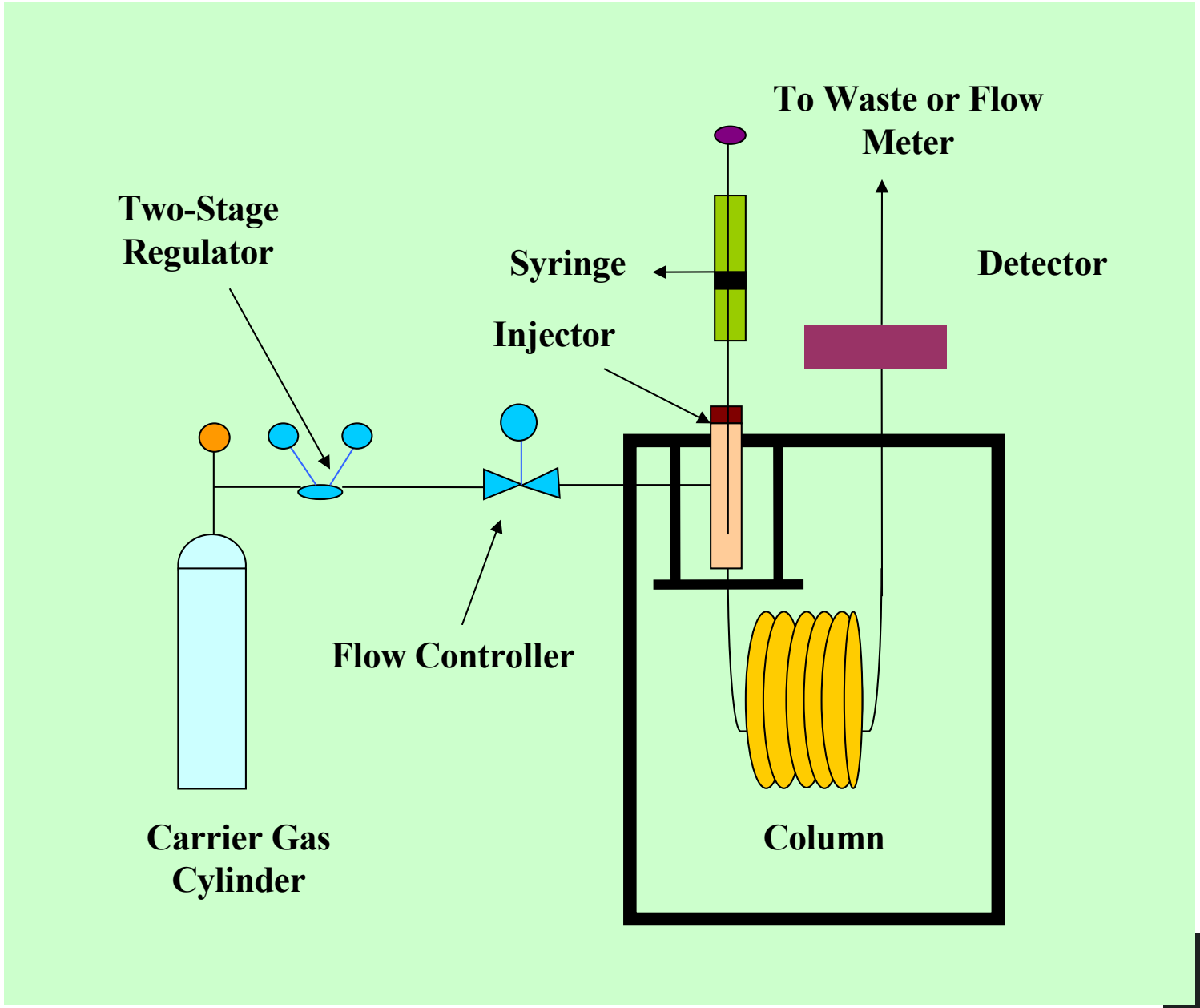
The stationary phase, in this case, is a solid like silica or alumina. It is the affinity of solutes towards adsorption onto the stationary phase which determines, in part, the retention time. The mobile phase is, of course, a suitable carrier gas. This gas chromatographic technique is most useful for the separation and analysis of gases like CH_4, CO_2, CO, ... etc. The use of GSC in practice is considered marginal when compared to gas liquid chromatography.

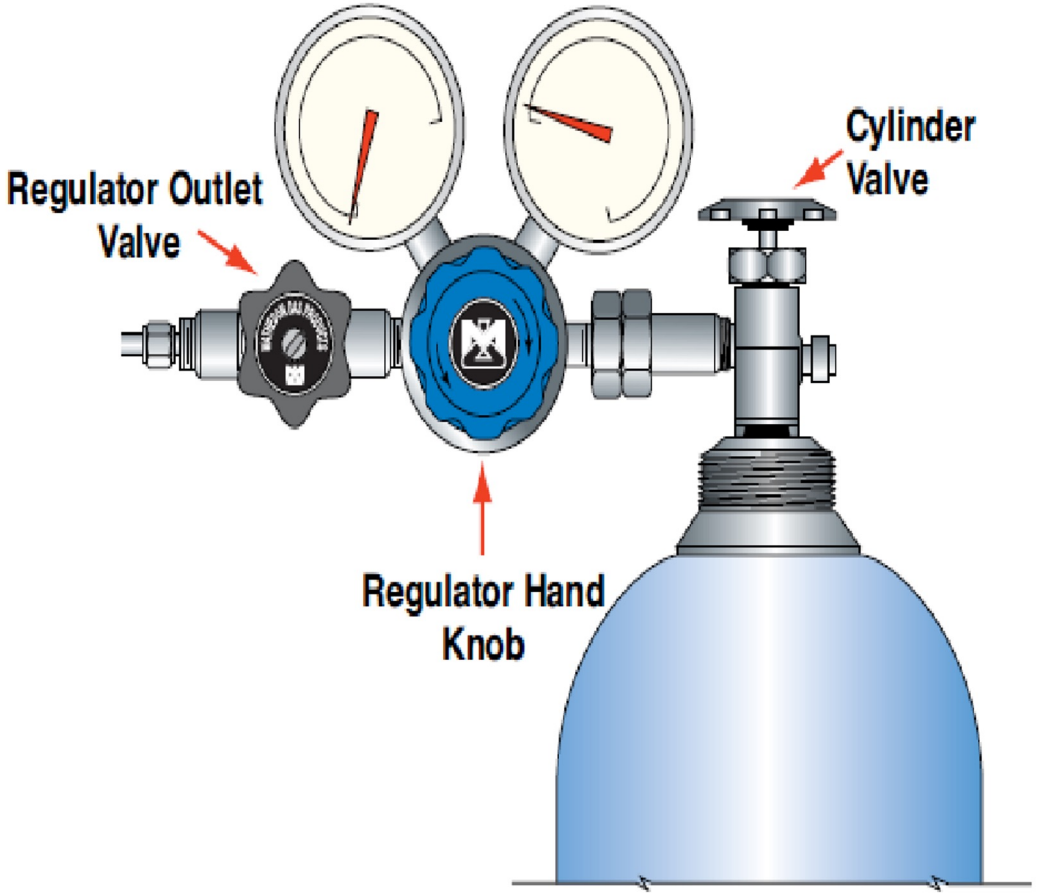
Gas - Liquid Chromatography (GLC)

The stationary phase is a liquid with very low volatility while the mobile phase is a suitable carrier gas. GLC is the most widely used technique for separation of volatile species. The presence of a wide variety of stationary phases with contrasting selectivities and easy column preparation add to the assets of GLC or simply GC.

Instrumentation

It may be wise to introduce instrumental components before proceeding further in theoretical background. This will help clarify many points, which may, otherwise, seem vague. It should also be noted that a detector will require special gas cylinders depending on the detector type utilized. The column temperature controller is simply an oven, the temperature of which can be varied or programmed


To Waste or Flow Meter
Two-Stage Regulator
Syringe
Detector
Injector
Flow Controller
Carrier Gas Cylinder
Column


Regulator Outlet
Valve
Cylinder
Valve
Regulator Hand
Knob

Three temperature zones can be identified:

1. Injector temperature, T_I, where T_I should allow flash vaporization of all sample components.
2. Column temperature, T_c, which is adjusted as the average boiling points of sample components.
3. Detector Temperature, T_D, which should exclude any possible condensation inside the detector.

Generally, an intuitive equation can be used to adjust all three zones depending on the average boiling point of the sample components. This equation is formulated as:

$$T_I = T_D = T_c + 50\ ^oC$$

The Carrier Gas

Unlike liquid chromatography where wide varieties of mobile phase compositions are possible, mobile phases in gas chromatography are very limited. Only slight changes between carrier gases can be identified which places real limitations to chromatographic enhancement by change or modification of carrier gases

A carrier gas should have the following properties:

1. Highly pure (> 99.9%)
2. Inert so that no reaction with stationary phase or instrumental components can take place, especially at high temperatures.
3. A higher density (larger viscosity) carrier gas is preferred.
4. Compatible with the detector since some detectors require the use of a specific carrier gas.
5. A cheap and available carrier gas is an advantage.

Longitudinal Diffusion Term

This is an important factor contributing to band broadening which is a function of the diffusivity of the solute in the gaseous mobile phase as well as the molecular diffusion of the carrier gas itself.

$$H_L = K D_M / V$$

Where; D_M is the diffusion coefficient of solute in the carrier gas. This term can be minimized when mobile phases of low diffusion, i.e. high density, are used in conjunction with higher flow rates.

The same van Deemter equation as in LC can be written for GC where:

$$H = A + B/V + CV$$

The optimum carrier gas velocity is given by the derivative of van Deemter equation

$$V_{opt} = \{ B/C \}^{1/2}$$

However, the obtained velocity is much greater than that obtained in LC.

The carrier gas pressure ranges from 10-50 psi. Higher pressures potentially increase compression possibility while very low pressures result in large band broadening due to diffusion. Depending on the column dimensions, flow rates from 1-150 mL/min are reported. Conventional analytical columns (1/8”) usually use flow rates in the range from 20-50 mL/min while capillary columns use flow rates from 1-5 mL/min depending on the dimensions and nature of column. In most cases, a selection between helium and nitrogen is made as these two gases are the most versatile and common carrier gases in GC.