Gas Chromatography

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(Chapter 2 and 3 in The essence of chromatography)

Introduction

A. General Information

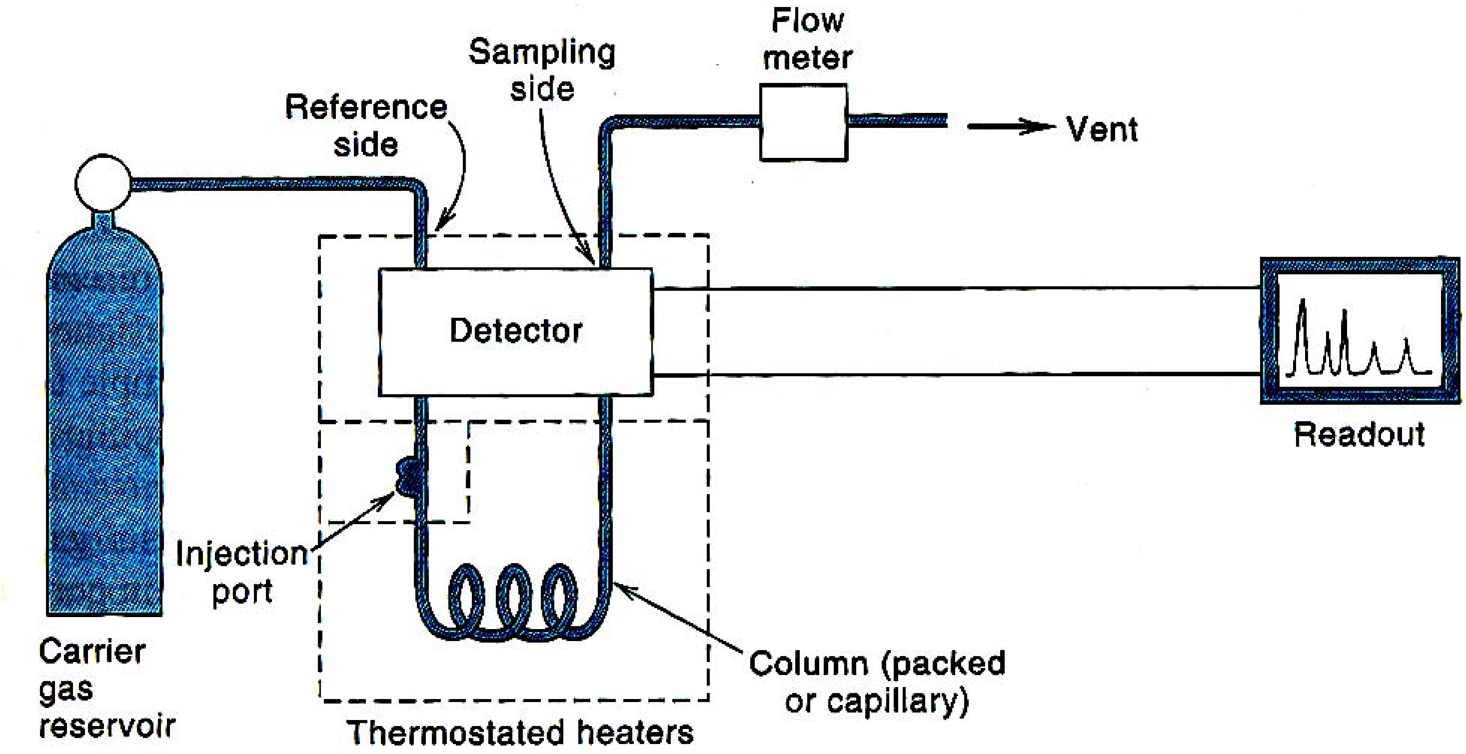
1. First used in 1951, GC is currently one of the most popular method for separating and analyzing compounds. This is due to its high resolution, low limits of detection, high speed, high accuracy and high reproducibility.

2. GC can be applied to the separation of any compound that is either naturally volatile (i.e. readily goes into the gas phase) or can be converted to a volatile derivative.

3. GC is widely used in the separation of a number of organic and inorganic compounds, Examples of its applications are shown below:

   a. Petroleum product testing.
   b. Food testing and analysis
   c. Drug identification and analysis
   d. Environmental testing
   e. Characterization of natural and synthetic polymers

B. Instrumentation:



1. The basic system consist of the following: A gas source (with pressure and flow regulators); an injector; a column (with an oven for temperature control); a detector; and a computer or recorder for data acquisition.

2. Advanced systems may contain an auto-injector, two or more columns and multiple detectors.

3. Extra-column band-Broadening

a. Extra-column band-broadening refers to broadening of solute peaks that occurs at any place in the system other than the column.

b. Band-broadening due to extra-column source is especially important for chromatographic system with small volumes or high efficiencies (small H). (e.g., Capillary GC column)

c. Plate height contributions due to extra-column band broadening can arise from any of the following areas:

(1). Injector
(2). Detector
(3). Connection tubing
(4). Other system components

$$H_{ec} = H_{inj} + H_{det} + H_{con} + H_{other}$$

$$\sigma^2_{ec} = \sigma^2_{inj} + \sigma^2_{det} + \sigma^2_{con} + \sigma^2_{other}$$

d. Injector Band-broadening

$$\sigma_{inj}^2 = V_{inj}^2/K$$

Where, V_{inj} is the injector volume, and K is a constant with values between 1-12 depending on the characteristics of the injector.

$$H_{inj} = \sigma_{inj}^2/L$$

e. Detector Band-broadening

$$\sigma_{det}^2 = V_{det}^2/12$$

Where, V_{det} is the injector volume.

$$H_{det} = \sigma_{det}^2/L$$

f. Connection tubing Band-broadening

$\sigma_{con}^2 = u\, r^2 l/24D_m$, r= radius of connection tubing, D = diffusion coefficient of solute in the mobile phase, u=linear velocity of the mobile phase, l = length of tubing

$$H_{con} = \sigma_{con}^2/L$$

g. Band-broadening due to ther system components:

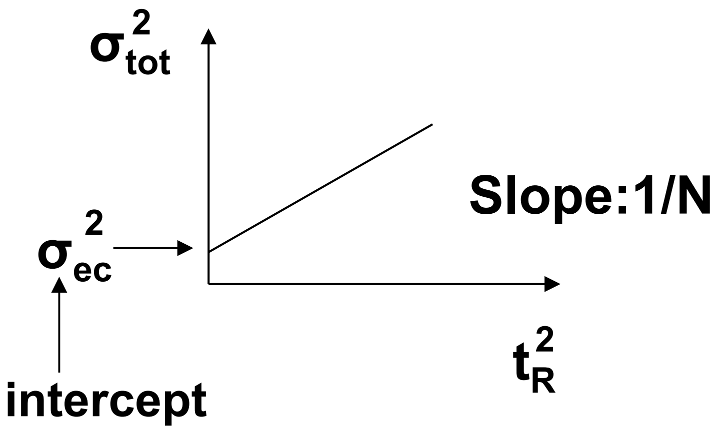
(1). Occurs due to other system components as connecting tee and mixers, post-column reactors, pre-columns, switching valves, etc.

(2). These can generally be minimized by simply using low volume components.

h. Experimental determination of extra-column band-broadening

$$\sigma_{tot}^2 = \sigma_{col}^2 + \sigma_{ec}^2$$

$$N = \left(\frac{t_R}{\sigma_{col}}\right)^2$$



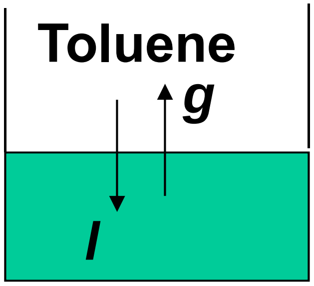
C. Solute retention mechanisms and Mobile phase:

1.Retention mechanisms:

GC differs from other chromatographic methods in that a solute's retention is determined mostly by its vapor pressure and volatility, which are in turn controlled by the solute's interaction with stationary phase. This results from the fact that the gaseous mobile phase has a much lower density and chance for interacting with solute than the solid or liquid that makes up the stationary phase.

Gas-Liquid GC

Solute: Toluene



H_2 as the mobile phase →

(i.e. stationary phase: dimethylsiloxane, a polymer) →

Gas-liquid equilibrium

100 °C

Capacity factor k is strongly depended on Temperature.

2. Thus the main purpose of gas in GC is simply move solutes along the column, the mobile phase in this technique is often simply called the carrier gas.

3. Common carrier gases used in GC includes Ar, N_2 He, H_2, O_2, CO_2, and H_2O (steam).

CO_2 and steam could affect the retention of solutes

4. Although the gas used mobile phase does not greatly affect solute retention, the choice of which gas to use is important in affecting the system in other ways. Factors considered in choosing a mobile phase for GC include:

a. The efficiency of the chromatography.
b. The stability of the column and solutes
c. The response of the detector
d. Possible risks or hazards in using the gas.
e. Expense and availability.

5. The mobile phase used in GC is usually supplied by a standard commercial gas cylinder, with a two-stage regulator for control of the gas pressure (usually 40-100 psi). By controlling this pressure, the rate of gases flow though the column is also controlled.

6. The mobile phase used in GC should be a high purity gas (>99.995% pure) or should be purified prior to use. The contamination of the system by these impurities can giving rise to a possible loss in sensitivity and resolution.

7. To get a good separation, the GC may required special control devices that maintain a constant flow of the mobile phase as the temperature or pressure of the system is varied. This may be particularly important in systems where a drift in the baseline of the detector may occur due to flow-rate changes, such as in open tubular column GC and in temperature-programmed GC. Flow control is also important in producing highly reproducible column efficiencies and resolutions.

8. In plate height equations, such as the van Deemter equation, it is the average linear velocity of mobile phase in the system that is used in calculations. However, experimentally it is the linear velocity at the outlet of the system which is actually measured. To calulate the average linear velocity from the outlet linear velocity, following relationship is used:

$$u_{avg} = j\ u_0$$

$$j = \frac{3}{2} \frac{(P_i/P_0)^2-1}{(P_i/P_0)^3-1}$$

Where: j = correction factor
P_i=inlet pressure
P_0 = outlet pressure
u_{avg} = Average linear velocity
u_0 = linear velocity at column outlet

9. The linear velocity at the outlet of the column is usually measured by using simple bubble flowmeter. To obtain the tru average linear velocity of the carrier gas in the column, the column temperature and vapor pressure of the water in the bubble flowmeter must be considered.

$$u_{avg} = j\, u_0\, (T_c/T_0)\, [(P_o - P_w)/P_o]$$

Where: T_c = column temperature
T_0 = outlet temperature
P_w = vapor pressure of water at T_0

10. The average column flow-rate (F_{avg}) can be similarly calculated

$$F_{avg} = j\, F_0\, (T_c/T_0)\, [(P_o - P_w)/P_o]$$

Question: **In a GC system, a solute with a retention time t_R = 12.61 min; t_M = 0.23 min; carrier gas Flow rate at outlet measured by a bubble flowmeter: F_0 = 21.78 mL/min; Column temperature T_c = 121 ^oC (394.2 K); outlet temperature T_0 = 23 ^oC (296.2 K); ambient pressure P_0=754.5 mm Hg; column head pressure P_G = 62.9 mm Hg; P_w=21.068 mm Hg. Calculate the retention volume of this solute and void volume of the system.**