CE 428

GAS CHROMATOGRAPHY FOR ANALYZING REACTION PRODUCTS

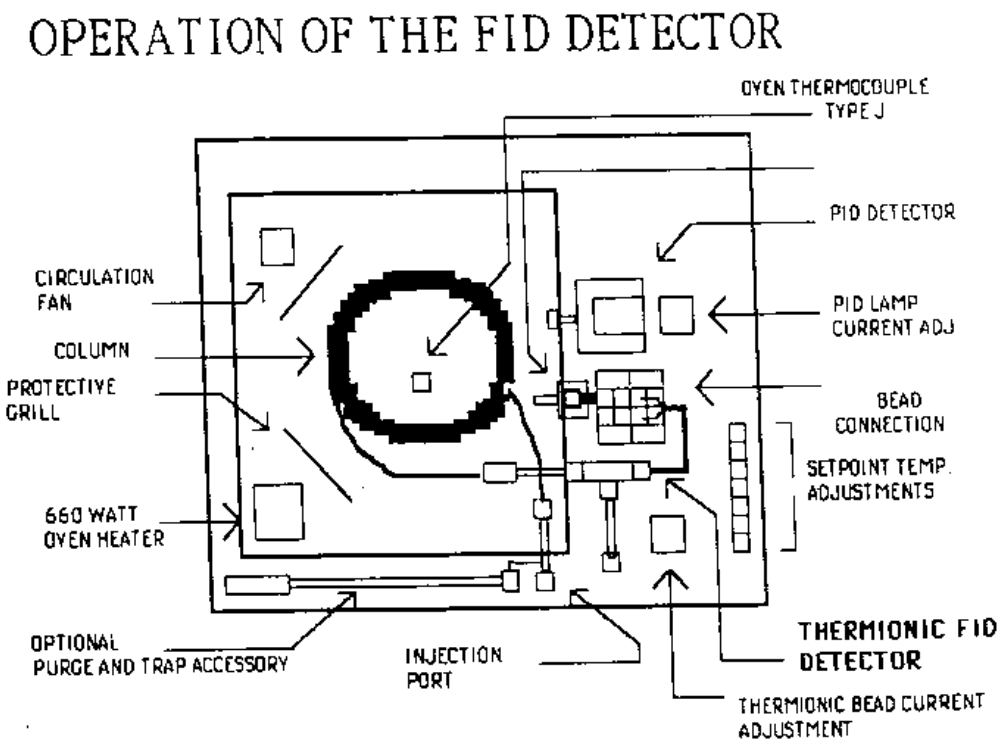
I. Introduction

Chromatography, like extraction, is based on molecular affinities. In all chromatographic methods (gas-solid, gas-liquid, liquid-solid), the mixture is introduced into a two-phase system, and each component of the mixture is "partitioned" between the phases. Unlike extraction, a similar process, in chromatography one phase is made to move physically while the other is held in a fixed position. The result is that the molecules are "carried along" with the mobile phase at different speeds according to their relative affinities to the fixed phase. Furthermore, chromatography usually provides a method of separation with a very large number of equivalent theoretical plates.

There are three important methods of chromatography. These are: (a) liquid (LC), (b) thin layer (TLC), and (c) gas (GC) chromatography. In GC, the sample is distributed between a moving gaseous phase and a stationary solid phase (often coated with a thin layer of non-volatile liquid). GC is the most commonly used tool for the qualitative and quantitative analysis of chemical mixtures occuring in the product streams from chemical reactors.

II. Chromatograph

Figure 1 is a schematic diagram of the SRI 8610 G.C. used in this experiment. The G.C. uses a thermionic flame ionization detector (FID). The injection port, column, and detector are heated by thermostatted ovens.



The column is a long, coiled tube, typically 1/8" or 1/4", packed with finely granular solid (the "column packing"). The packing may be a high area, chemically inert, diatomaceous earth with a thin coating of some non-volatile liquid, or it may be a high area (porous) solid organic polymer. Since the separation of a gas mixture depends critically on the column, you should always know what packing is being used, as well as the dimensions and temperature of the column.

The injector is a metal block of high heat capacity. A liquid sample is injected by a microsyringe (to 10 μl) through a teflon septum into the injector block, where it is vaporized, mixed with carrier gas, and carried into the column. For a gaseous sample, a complex gas sampling valve of 0.5-5 ml capacity is usually used. A gas-tight syringe may also be used for injection of gas samples through the septum.

Caution: Microsyringes are very subject to damage if used roughly. Obtain instruction on their proper use beforehand. Groups making corkscrews out of syringe needles will be invited to contribute $60 for the purchase of a new syringe.

The Thermionic FID detector is located on the right side of the column oven. It is called a Thermionic FID because of the thermionic bead mounted in the detector. The main component in this type of detector is an electrically-heated thermionic emission source in the form of a bead or cylinder which is usually composed of an alkali-metal compound impregnating a glass or ceramic matrix. In the detector, the thermionic source is positioned so that sample compounds may impinge upon its surface, and any ionization produced is measured by an adjacent collector electrode.

Figure 2 shows a typical chromatogram for a single compound. Compounds are characterized qualitatively by the retention time and quantitatively by the peak area. Retention time is the time from injection to the emergence of the top of the peak. For a given column and specified set of conditions, retention time is a constant that can usually be used for quantitative analysis.

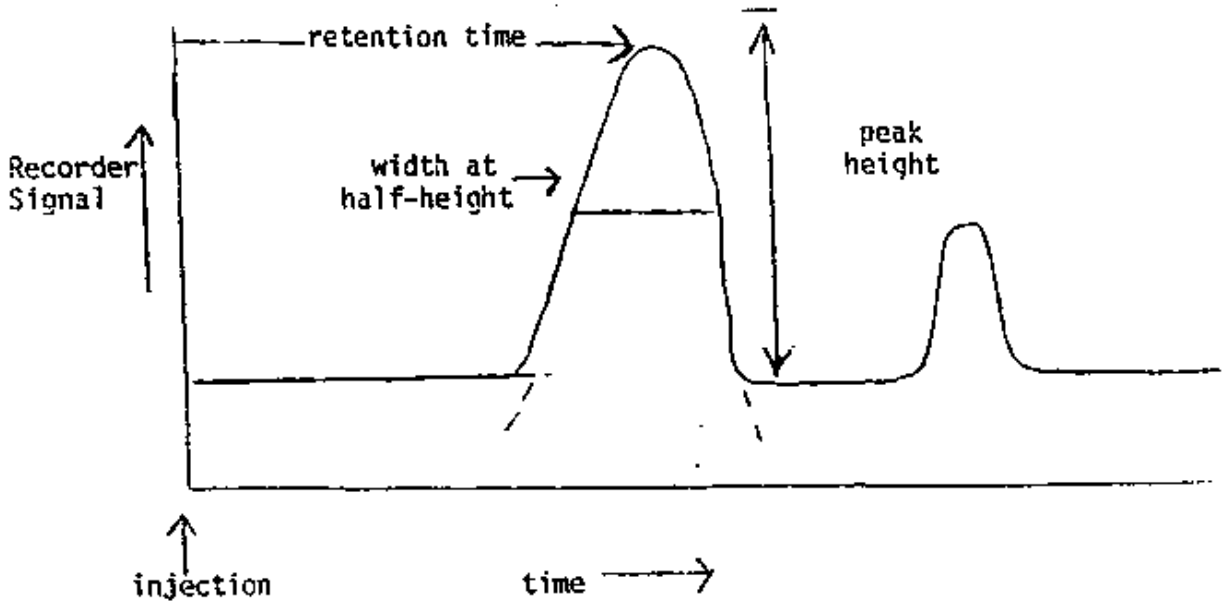


Fig. 2

Note: A given chromatographic peak is sometimes not symmetrical, unfortunately, and sometimes shows severe "tailing."

Usually the area of the peak is proportional to the concentration of the corresponding component in the effluent. However, at high concentrations, this linear relationship may not be followed. Furthermore, the response factor (peak area per unit concentration) is different for different classes of compounds. Therefore, a calibration curve is needed for accurate quantitative analysis.

III. Optimum Operation

1. Theoretical Consideration:

Column efficiency is usually described by the number of theoretical plates, i.e. the number of equilibrium stages. One simple method involves measurement of retention time (RT) and peak width for a single recorded peak as shown in Figure 3. For symmetrical peaks the number of theoretical plates (TP) is calculated from

$$TP = 16(RT/\Delta t)^2 \qquad (1)$$

The HETP (height of an equivalent plate) is calculated by dividing the column length by the total number of plates; or by the Van Deemter equation:

$$HETP = A + B/v = Cv \qquad (2)$$

where v is the carrier gas linear flow rate, and A, B, and C are factors related to eddy diffusion, gas diffusion and mass transfer, respectively.

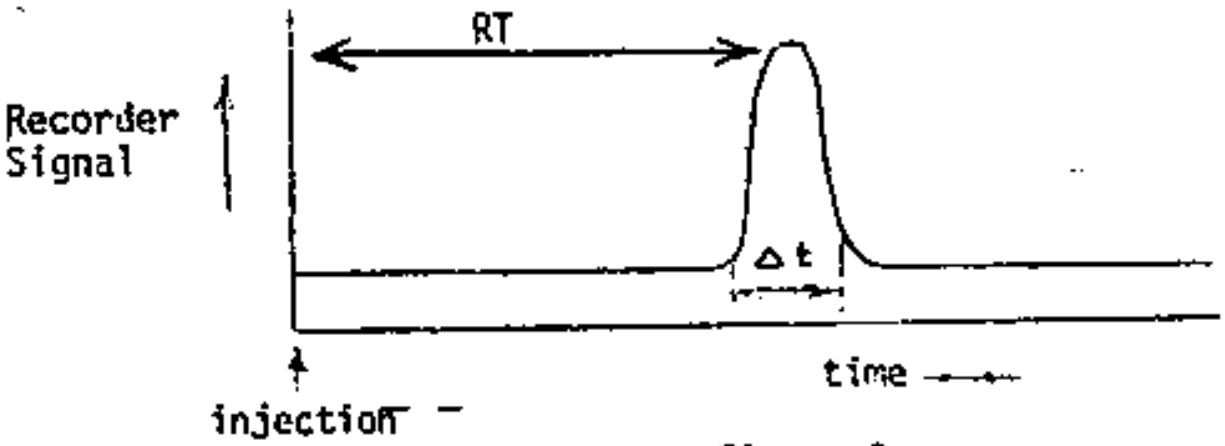


Figure 3.

2. Column Temperature:

Higher column temperature results in shorter retention time but usually in poor resolution. Too low a temperature will result in retention time too long to be practical. Generally, increasing the column temperature by 30°C decreases most retention times by about 50%. Peaks of very long retention time are highly diluted with carrier gas and thus give very broad, low peaks, which decreases the accuracy of the analysis. There is usually a temperature that is low enough for adequate separation but high enough to allow the chromatographic analysis to be completed in a reasonable length of time. If the difference in retention time for various constituents is too great, the mixture can be chromatographed at two or more different temperatures or with a programmed column temperature.

3. Injector Temperature:

A typical plot of the number of TP vs. injector temperature is shown in Figure 4. Above the boiling point of the sample, the efficiency is not greatly increased by further increase in the injector temperature. A general rule is to set the injector temperature about 20°C higher than the boiling point of the highest-boiling component of the sample, provided the sample is thermally stable.

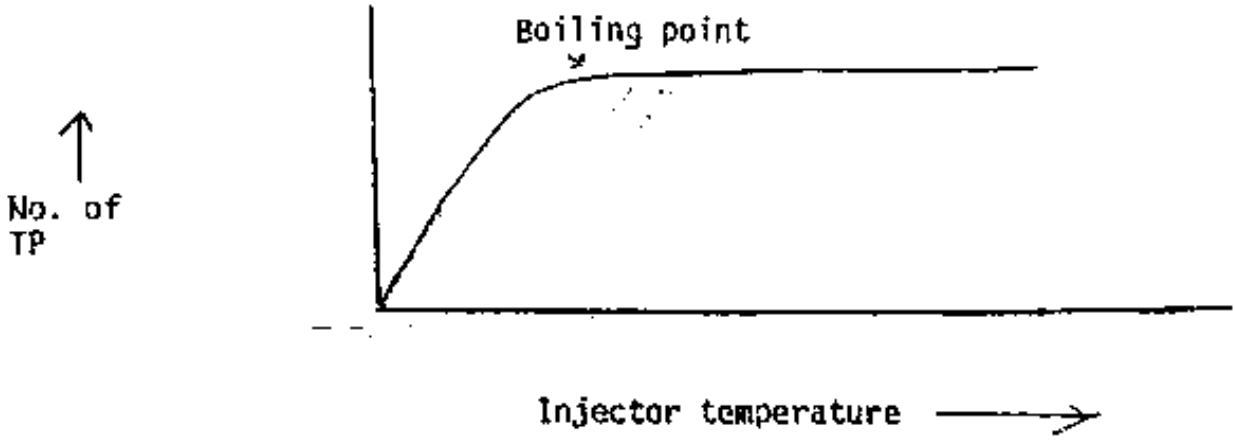


Fig. 4

4. Carrier Gas and Carrier Gas Flow Rate:

The most commonly used carrier gases are He and N_2. Sometimes H_2, Ar, or occasionally CO_2 are used. The faster the flow rate, the shorter the retention time but the broader the peaks become. Figure 5 shows the efficiency of the column (expressed as HETP) vs. flow rate. That flow rate is optimum which gives the lowest HETP.

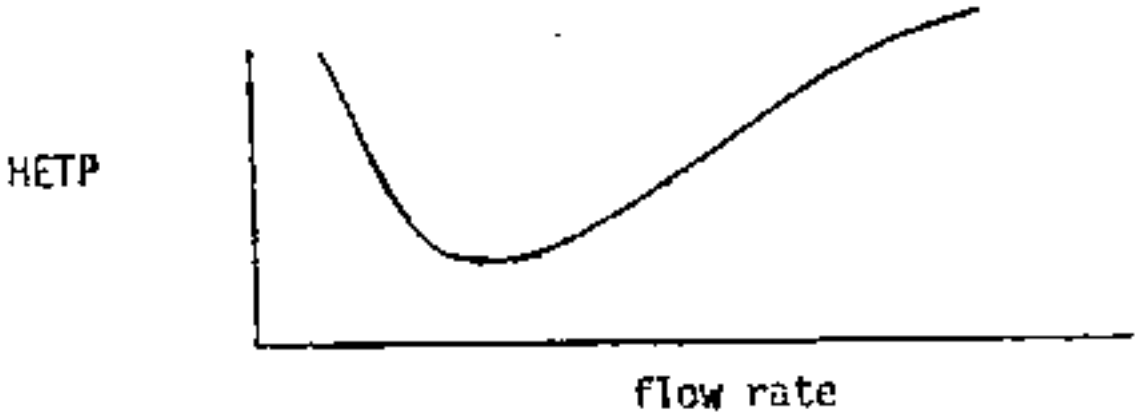


Fig. 5

IV. Typical Reference Books

- Littlewood, *Gas Chromatography*, 2nd Ed., 1970, Academic Press.
- Kaiser, *Gas Phase Chromatography*, Vol. 1, 1963, Butterworths.
- Szepeny, *Gas Chromatography*, 1970, Iliffe Books Ltd.