Chem 321 Lecture 22 - Gas Chromatography

11/14/13

Student Learning Objectives

Gas chromatography has been one of the most widely used methods of separation in the analytical chemistry laboratory for many decades. It can be used to separate many different types of substances and requires relatively simple and inexpensive equipment. The only requirement is that the analytes be volatile.

The basic components of a gas chromatography are shown in Figure 15.1

.

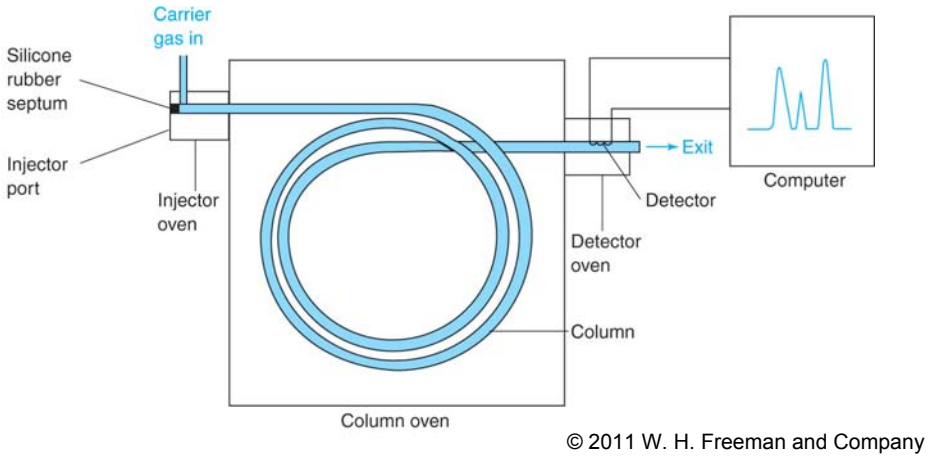

Figure 15.1 Schematic diagram of a gas chromatograph

The mobile phase is a chemically inert carrier gas that is conveniently supplied by a high-pressure gas cylinder. The particular choice of carrier gas depends on which detector is used to monitor the components eluting from the column (**eluate**). Nitrogen is the carrier gas in our experiment. Since the mobile phase is a gas, there is basically little interaction between the components of the sample and the mobile phase. The sole purpose of the mobile phase is to carry the components through the column.

Liquid samples are introduced onto the column by injection through a silicone rubber septum into a heated zone that provides rapid vaporization of the sample. Consequently, the temperature of the injection port is usually set well above the boiling point of the highest boiling component in the sample. This ensures that the sample is introduced onto the column quickly and in as small a band as possible, thereby lessening band broadening and improving the separations.

The choice of stationary phase in gas chromatography is critical to a satisfactory separation. Two types of GC columns are generally available: packed or capillary. **Packed columns** typically consist of a metal tube about 3 m long with an inside diameter of 2-4 mm filled with small particles of an inert support that are coated with the

liquid stationary phase. Gas chromatography is sometimes referred to as gas-liquid chromatography, or GLC, because the stationary phase is a often a liquid. **Capillary**, or **open tubular, columns** have no packing and have an inside diameter of usually only 0.10-0.52 mm. The inner walls are coated with the liquid stationary phase. Since there is no packing to resist the flow of the mobile phase, capillary columns may be much longer, typically 15-100 m. Because there is no packing in capillary columns they have a smaller plate height and since capillary columns are so much longer, they have many more plates overall and hence can separate components much better. Capillary columns cannot handle large samples because they contain much less stationary phase than is found in packed columns. This means that a more sensitive detector must be used with capillary columns.

Since our gas chromatography experiment involves the separation of a mixture of nonpolar alkanes, a nonpolar stationary phase is used. The stationary phase for our packed columns is dimethyl silicone (a polymer consisting of $-(CH_3)_2Si-O-$ units). This high boiling liquid is mechanically deposited onto the inner wall of the capillary column. Separation of the components occurs because the alkanes dissolve in this nonpolar stationary phase and then get carried along with the mobile phase based on their vapor pressure. The elution order is the same as the order of increasing boiling point; octane followed by nonane followed by decane. The column length is 30 meters.

Gas chromatography columns are generally housed in an oven so that column temperature can be carefully controlled. Column temperature will affect the vapor pressure of the analytes and the diffusion of the analytes while passing through the column.

Check for Understanding 15.1 **Solution**

1. How should the retention time for octane change if the column temperature is increased from 80 °C to 100 °C? Explain.

If a simple mixture is being separated, it may be possible to keep the temperature constant during the entire run. Such separation conditions are referred to as **isothermal**. However, more complicated mixtures may not separate efficiently, or at all, at constant temperature. A very powerful approach to improving the separation efficiency in gas chromatography is **temperature programming**. This involves changing the temperature during the run, usually ramping the temperature from some lower initial value to higher levels as the separation proceeds. In our experiment it is

possible to separate octane and nonane from each other and the ethanol solvent using a constant temperature of 60 °C. However, the boiling point of the internal standard decane is almost 50 °C higher than that of any of the other components and consequently it elutes only very slowly at a temperature of 60 °C.

Check for Understanding 15.2 **Solution**

1. What is the problem with using a higher constant temperature, say 120 °C, for the separation of the mixture containing decane?

For your separation of the solvent and the alkane analytes the initial column temperature is 100 °C. At this temperature there is good separation and rapid elution of the solvent, octane and nonane. As these components are eluted, the temperature is ramped at 40 °C/min to a final temperature of 150 °C. This increases the vapor pressure of the decane dissolved in the stationary phase, causing it to spend more time in the mobile phase and to elute much faster. For very complex samples the temperature may be ramped in more than one step to optimize the separation.

In our experiment material eluting from the column will be detected by a **flame ionization detector (FID)**. This detector (Fig. 15.2) consists of a small hydrogen flame through which the sample passes as it elutes from the column. As the eluate burns in the flame, any compounds containing oxidizable carbon atoms (e.g., organic compounds such as hydrocarbons) produce cations that are collected by an electrode positioned by the flame. This flow of ions constitutes the detector signal and is proportional to the number of oxidizable carbons in the separated compound as well as the amount of the compound present in the injected sample. Extremely low levels (pg/s) of hydrocarbons can be detected while no signal is produced by molecules such as O_2, CO_2, H_2O, N_2 and H_2S. This high sensitivity makes the FID well suited for use as a detector for capillary columns where only a small amount of sample can be separated. One drawback to the FID is that is requires three gas supplies: a carrier gas plus hydrogen and oxygen for the flame.

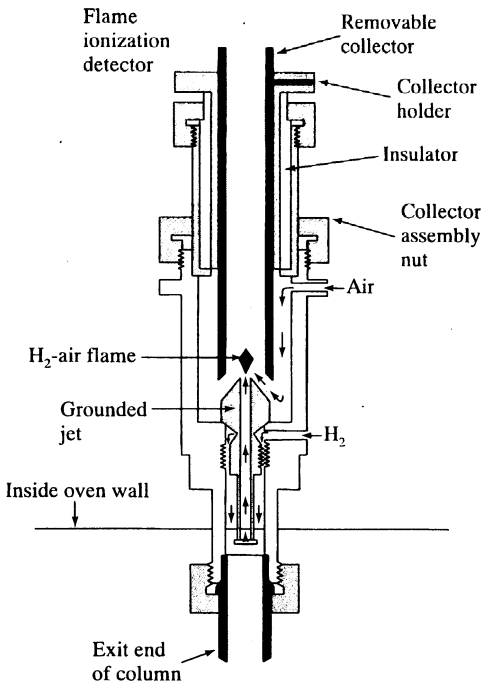

Figure 15.2 Schematic diagram of a flame ionization detector

Generally, as more sample is injected onto the column the area of the resulting chromatography peak(s) gets proportionally larger. A simple comparison of the peak areas for a standard and sample run under the same conditions provides quantitative information about an analyte. However, the syringes used for gas chromatography injections are usually not precise enough to allow for very reproducible injection volumes. Consequently, a different approach must be used for quantitative gas chromatography. In our experiment an **internal standard** is used.

To see how this approach works, consider two injections of a sample of octane that is spiked with an internal standard, decane. Assume the first injection is 1 µL and the second injection is 2 µL. You should expect that the octane peak area for the first injection is only about half as large as that for the second injection. The same should be true for the decane peak areas. Consequently, the ratio of the octane peak area to the decane peak area is the same for both injections. This normalized area (component peak area divided by internal standard peak area) serves as a quantitative measure of how much octane is present. As the concentration of octane in the sample is increased (while keeping the concentration of the internal standard fixed) the normalized area increases, regardless of how much sample is injected.

In our experiment, you will carefully spike a given volume of the standard and the unknown sample with a fixed volume of the internal standard, decane. You should calculate normalized areas for octane and nonane for each run of standard and unknown. Then average these values for the standard runs. The percent octane and percent nonane in your unknown can be determined by a simple comparison of normalized peak areas

$$\frac{\left(\frac{Component\ AREA}{Decane\ AREA}\right)_{unk}}{\left(\frac{Component\ AREA}{Decane\ AREA}\right)_{std\ avg}} = \frac{C_{unk}}{C_{std}}$$

where $(Component\ AREA/Decane\ AREA)_{unk}$ is the normalized peak area for a particular component in the unknown solution, $(Component\ AREA/Decane\ AREA)_{std}$ is the average normalized peak area for that particular component in the standard solution, and C_{unk} and C_{std} are the unknown and standard solution concentrations of that component, respectively.

Any samples that are a mixture of these alkanes must be keep tightly sealed unless a sample is being taken. Otherwise, evaporation will occur at different rates for the components and the composition of the mixture will change. Do not place your samples on top of the GC oven. Perform all runs of the standard and unknown the same day with the same chromatograph. Use the spiked standard and spiked unknown only on the day they are prepared.

Exercises for Gas Chromatography