Chem 112-2010

Gas Chromatography

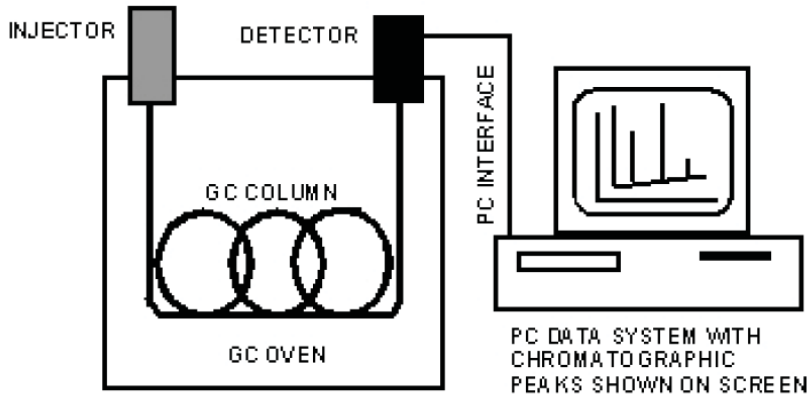
The purpose of this experiment is to determine the composition of solutions that contain a mixture of different alcohols. The analysis is performed using gas chromatography.

Introduction

The term ***chromatography*** applies to the separation of chemical constituents in a sample so they can be either detected or utilized individually. ***Gas chromatography*** (GC) is a method of separating "volatile" compounds (those with a high-vapor pressure or a relatively low boiling point) so that they may be detected individually in complex mixtures. Compounds are separated based on differences in their vapor pressures and their attraction to solid materials inside the instrument (a gas chromatograph or GC). Because the vapor pressure of a given compound is a function of the intermolecular forces between molecules, GC takes advantage of differences in at least one of the properties of matter discussed in lectures and in the text.

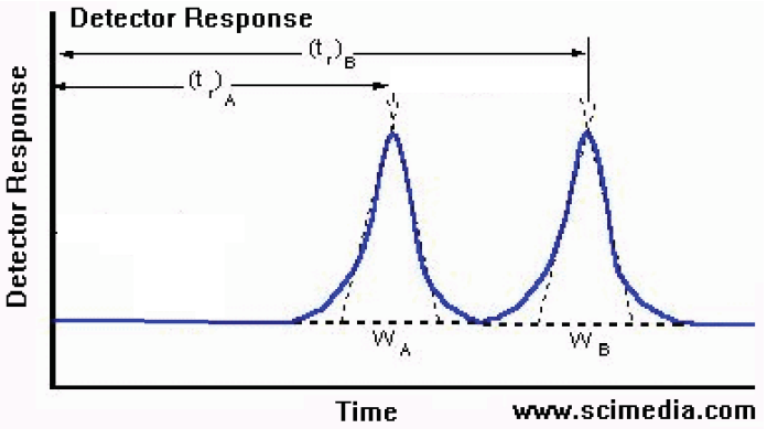
In GC, the sample is injected into the instrument using a small syringe. The sample is swept into the instrument using a ***carrier gas*** (usually He) where the sample is separated into its individual chemical components, called ***analytes.*** Separation is achieved by both attraction to the ***stationary phase*** (the coating on the inside of the column) and differences in vapor pressure. Because vapor pressure varies with temperature, the temperature of the instrument is often adjusted during the chromatographic run. A detector, which is designed to "sense" analyte molecules as they exit the GC, is at the end of the column.

We will be using a ***thermal conductivity detector*** (TCD). That measures changes in the properties of the carrier gas. The changes are due to the presence of the separated analyte molecules in the carrier gas stream. Because the analyte molecules bind differently to the stationary phase, they travel through the GC column at different rates. That is, they have different ***retention times*** on the column. As an analyte appears in the detector, its presence is signaled by a peak. Thus, a ***gas chromatogram*** consists of a series of peaks, one for each of the components of the sample. The chromatogram is displayed on a chart recorder or computer screen.



SCHEMATIC OF A GAS CHROMATOGRAPHY SYSTEM

An example of a chromatogram is shown below for a mixture of two compounds, A and B.



The position of a peak on the x-axis is a measure of retention time and is a function of the structure of the compound. They are labeled on the chromatogram above as $(t_r)_A$ and $(t_r)_B$ for the two components, A and B. The area under the peak is a function of that compound's concentration in the sample. The area of the peak is measured by assuming the peak has a triangular shape, with the base measured by extrapolating the sides of the peak to the baseline (shown above as W_A and W_B). The area is then ½ x height x width at the base.

The percent composition of each component in an *unknown* sample is determined using the area under its peak in the chromatogram of that unknown mixture and that component's ***response factor.*** A response factor is a conversion factor between the area under the curve for a component and its percent abundance in the mixture. The response factor is determined by comparing the area under the peak to the percent abundance of a component for a solution of *known* composition. Because the solution you use to determine this for each of the four compounds is composed of 25% of each compound ,

$$\text{response factor} = \frac{25\%}{\text{area under peak}}$$

Different compounds affect the detector differently, so each compound has its own unique response factor.

Once you have the response factors and retention times for the four compounds, you can analyze your unknown samples. The percent composition of any component in an *unknown* mixture is determined by multiplying the peak area for the unknown mixture by the response factor for that component.

$$[\text{analyte}]_{\text{sample}} = \text{area}_{\text{sample}} \times \frac{\text{response factor percent}}{\text{response factor cm}^3}$$

Be sure to identify which compound each peak represents by matching its retention time to the knowns.

To review: You tell which compounds are in a sample by when they are detected and how much is present by the area under the peak. You measure retention times and response factors using known solutions, and then use that information to analyze unknown solutions.

Samples to Analyze:

Four compounds are involved in this experiment: pentanol, hexanol, heptanol, and octanol.

Known Samples are provided of pure pentanol, hexanol and octanol and a mixture of 25% each of pentanol, hexanol, heptanol and octanol.

A variety of unknown samples that contain mixtures of these four compounds.

Procedure:

Your instructor will assist you with the operation of the GC.

1. Your instructor will provide you with three *Unknown Samples*, which are mixtures of the four possible alcohols. You will also receive three *Pure Solutions,* each containing one of the possible compounds (pentanol, hexanol and octanol).

2. Inject 10 μL of *Standard* into the "B" injector on the right of the GC.

3. Inject each of the three *Pure Solutions* into the GC. Inject 5 μL volumes for these known samples that contain just one compound. Collect the chromatograms on the chart paper. At the start of each run, mark on the chart paper where the run started. The chart paper moves at a rate of 1 cm/minute. At the end of each run, label the chromatogram with the sample name, injection volume, and other parameters.

> You should now know what the retention time is for each of the your alcohols. By comparing the three *Pure Solution* chromatograms with the chromatogram of the *Standard*, you can identify the peaks. The peak for heptanol will be the one in your *Standard* that does not correspond to any of the three *Pure Solution* peaks!

4. Analyze the three *Unknown Samples* by injecting 10 μL of each into the GC. Your *Unknown Samples* may contain one, two, or three of the compounds.

Calculations and Report

The purpose of the experiment is to determine the composition of the unknown solutions. Those compositions make up the conclusion of your report. Things you need to do:

1. Determine the retention times of the four compounds. Those for pentanol, hexanol and octanol can be determined directly from the chromatograms performed on their pure samples. Use the chromatogram of all four compounds to identify the peak for heptanol and determine its retention time.

2. Using the chromatogram that contained all four compounds, calculate a response factor for each compound by comparing its percent composition to the area under its peak. The units of the response factor are percent/cm%.

3. Make a table of retention times and response factors for the four compounds.

4. For each unknown sample:
   a. identify which compounds are present.
   b. use the area under each peak to determine the percent composition for each compound present.
   c. Make a table listing the compounds present. For each compound present, list the area under the peak and the calculated percent composition.

Gas Chromatography REPORT FORM

Known Compounds

Compound	Retention Time, min	Area, cm^3	Response Factor, $\%/cm^3$
Pentanol			
Hexanol			
Heptanol			
Octanol			

Unknown #____

Component	Retention time	Compound Name	Area, cm^3	Percent Composition
Component 1				
Component 2				
Component 3				

Unknown #____

Component	Retention time	Compound Name	Area, cm^3	Percent Composition
Component 1				
Component 2				
Component 3				

Unknown #____

Component	Retention time	Compound Name	Area, cm^3	Percent Composition
Component 1				
Component 2				
Component 3				

Post-Lab Questions:

1. Two different common methods of separating compounds using a column depend on boiling point and on molecular size. In columns depending on boiling point, the compound with the lowest boiling point spends the most time in the gas phase, where it can move. The lowest boiling compound therefore moves down the column fastest. In the method using molecular size, called size-exclusion chromatography, smaller molecules get "stuck" in pores in the column whereas larger molecules can't fit and float on by. Therefore, the larger molecules move down the column faster. To answer this, you need the structures and boiling points of the four compounds.

Which of these two is more likely to be used in this experiment?

2. Examine your data and explain any facets- if there are any- that you see.