Chemistry 231 – Spring 2013
GC Experiment 1
Introduction to Gas Chromatography
Adapted from Dr. Brad Baker

Overview

This experiment is designed to introduce you to gas chromatography (GC), and the Buck Scientific 910 instrument. You will separate a mixture of straight-chain aliphatic hydrocarbons, and then examine the response of the flame ionization detector (FID) to various hydrocarbon functional groups.

Introduction

The Buck Scientific GC is a highly functional instrument, however bare bones when compared to the much more common and expensive Agilent 5890 or 6890 GC. The Buck GC is almost entirely controlled by turning 'trim-pots' that are mounted inside the chassis of the instrument with a small screwdriver. Peak Simple software monitors detector response, and controls the GC's oven temperature. It also controls the analysis time and post run functions (e.g. setting integration parameters).

A GC system is made up of 4 parts. These are: the carrier gas, the injector, the column and oven, and the detector. With the exception of the oven, you will control each part's parameters using the trim-pots mounted in the GC. You will use the Peak Simple software to control the oven temperature and to collect the FID's output. More details on the Buck GC operation is provided on another handout.

Helium is used as the carrier gas for this GC. Aside from hydrogen, helium provides the most effective separations due to its low ratio of viscosity to diffusion. Hydrogen is not commonly used as a carrier gas due to its explosive characteristics, particularly with an FID.

The carrier gas is directed through a heated split/splitless injector. Due to the type of column being used (a megabore or 0.53 mm inner diameter column), the injector only can be run as a direct on-column injector with no split. This increases the sensitivity of the instrument, but also may cause tailing to occur for certain compounds. Sample is introduced manually to the injector using a 10μL syringe. Injection volumes should be approximately 1μL. Due to the imprecision associated with measuring such small volumes, it is recommended that an internal standard is used whenever quantitative measurements are required.

We will be using a Restek MTX-5, 15m x 0.53 mm I.D., 1μm film thickness, mega-bore capillary column. This is a very stable, non-polar stationary phase (5% diphenyl/95% dimethyl polysiloxane), packed in a fused silica-lined stainless steel column. The column has an upper temperature range of 360^{o}C; however, we will not need to go above 250^{o}C. For the most part, compounds are separated according their boiling points. The oven temperature can be ramped from near ambient (effectively 45^{o}C due to the injector and detector heater) up to 250^{o}C. The upper limit is set by an alarm circuit on the GC that may be changed if necessary, although in no case should 280^{o}C be exceeded as this is the maximum temperature of another column in the GCs that are used in another class.

After leaving the column, the sample is directed to the FID. The FID is a universal detector for any compound that will burn, is highly linear, and is relatively inexpensive. The FID requires the additional gases air and hydrogen. Inside the FID a small H_2 flame burns compounds as they pass through and produces ions. The ions increase the conductivity which is

measured between 2 plates that have a potential applied across them. The change in current across the plates produces the signal output. The flow of the air and H_2 is important for maintaining a flame that will produce a high output of ions. Adjusting the flows of these gases will have an effect on the sensitivity of the detector. The FID should be maintained at a temperature greater than the highest oven temperature of your GC run so that there is no chance of semivolatile compounds condensing in the detector.

Things to keep in mind when using the Buck GCs:

Check the pressure in the He, H_2, and air tanks before beginning. Unless there is a leak, these should not decrease much over a period of a few hours. Be sure to bring the oven temperature down to below 100°C before shutting off the He flow to the column. It is not good for the column to be at high temperature without carrier gas flow. The worst thing that can happen to the column is for oxygen (including air) to pass through the column at high temperature (>100°C). This will ruin the column.

Check all of the set points and actual temperatures for heated zones on the GC before beginning (inlet, oven and FID). The computer does not monitor these, and will not tell you if one is not at its proper temperature. Although the computer does control the GC's temperature, it does not monitor it; so make sure that the GC is at the proper starting temperature before beginning a new run. It can take several minutes to cool down after reaching a high temperature.

When finished using the Buck GC, close down the Peak Simple software first, then you may turn off the main power to the GC. After the oven is cool, the gases may be turned off at the cylinder (remember that the gas cylinders are shared with the other Buck GC).

Keep track of your control and other files. These should be stored in your own directory on the computer. Be sure not to save changes you have made to somebody else's existing method or sequence file. This is best done by renaming any file before making changes.

Experiment

You will be separating a mixture of $C_7 - C_{12}$ aliphatic hydrocarbons, dissolved in n-hexane. The pure liquids will be provided, but you must make all of your own solutions. You will then investigate the response of the FID towards various organic functional groups.

Separation

Make up a solution containing about 100 μg/mL of each of the 6 straight-chain hydrocarbons. Since you know the separation occurs according to boiling point, it will not be necessary to make an individual solution of each compound for peak identification. To make this solution, use gas-tight syringes (at least 100μL) to measure the volume of each pure compound. Be sure to rinse the syringe with dichloromethane between compounds. In addition, weigh the amount of compound delivered from the syringe on an analytical balance. It is important that you make this solution as accurately and precisely as possible. It is suggested that you start by making a concentrated solution then dilute to the appropriate concentration for the GC analysis. Be sure to keep a stopper or lid on your solution container to avoid volatilization of any compounds.

Before analyzing your solution by GC, measure if necessary, and record all of the GC parameters. These will include: column flow rate, detector gas flows (air and H_2), and injector and detector temperature. Make sure that the FID is lit before beginning your analysis. This is done by holding a mirror, or other shiny surface to the FID outlet and checking for condensation.

Be careful not to touch the mirror on the outlet. For the first run use an oven program starting at 50°C and proceed to 250°C at 10°C/min. Use an injection volume of approximately 1μL. Adjust the temperature program accordingly until you are able to separate all of the compounds well; this includes separating the first peak from the solvent peak. Once you have a separation that you are satisfied with, analyze your solution at least three times. Remember, due to inaccuracies in the injection volume, the peak areas for each run shouldn't necessarily be the same; however, the areas should be constant relative to each other (in other words, the ratios of peak areas should be constant).

Determine the linear velocity of the carrier gas through the column. This parameter is often used rather than the flow rate to determine if the carrier gas flow is set correctly. The linear velocity at which the carrier gas produces the best separation is independent of column parameters, whereas the flow rate through the column at which the most effective separation occurs depends on the column volume, and may change from one column to the next. The data needed for determining the linear velocity may be obtained by taking the retention time for the first baseline disruption after the injection, or you can inject your sample at a high starting temperature, so that early eluting peaks are unretained. Knowing the length of the column, you should be able to calculate the linear velocity in cm/s.

FID Response

The FID is commonly referred to as a 'carbon counter'. This is because, in general, the response of the FID is the same for any carbon atom. For example, one mole of octane will have a response that is 8/7 as large as the response towards one mole of heptane. A major advantage of this feature is that as long as each peak in a chromatogram can be identified, only one calibration standard is necessary. Look at the integrated peak areas for your $C_7 - C_{12}$ solution. In order to be able to average your duplicate runs, normalize all of your peak areas by the dodecane peak area (in essence, use dodecane as the internal standard). Convert the μg/mL of compound in your solution to μg C/mL for each compound then divide the average normalized peak areas by the concentration (μg C/mL). If you have made your solution accurately, you should find that the values for each compound agree to within 15% or so. If your calculated values (normalized area/μg C/mL) diverge wildly, make a new solution and try one more time. Once you are convinced that the FID responds consistently per carbon atom, go to the 5th floor stockroom and look through the notebook that lists all of the chemicals in their inventory. Find an aliphatic hydrocarbon that has one or more alcohol, ketone, or aldehyde functional group. Before committing to the compound make sure that the boiling point is greater than that for heptane and less than that for dodecane. Accurately make a solution that contains your new compound and the two straight-chain hydrocarbons that bracket its boiling point temperature, all in the 100 μg/mL compound range; however, don't use heptane, as it seems to volatilize quite easily out of solution. Analyze this solution and adjust the temperature ramp so that all peaks are well resolved. Does your new compound elute where you expected based on boiling point? Make three replicate analyses. As you did for your original solution, determine the normalized area/μg C/mL using one of the two straight-chain hydrocarbons as the normalizing compound. How does the response of the functional group compound compare with that of the straight chain hydrocarbon? Assuming that each carbon in the straight chain hydrocarbon has an effective carbon number (ECN) of 1.0 (therefore, the compound octane would have an ECN of 8.0), determine the ECN for the functional group compound that you chose for this experiment.

Based on your results from the first part of the experiment, is the ECN statistically different than for a straight chain hydrocarbon with the same number of carbon atoms?

Report

If you choose this experiment for your written report, your report should be double spaced, with 12 pt Times New Roman font and 1 inch margins. Include your name, a title, a 2-3-sentence abstract, a short introduction, experiment description, results and discussion, and a short conclusion. In the experiment description be detailed regarding the GC description and operating parameters, and include how solutions were made. The results and discussion should include examples of chromatograms that you used to determine FID response to carbon in different compounds. Chromatograms should have the key peaks labeled with identity and retention time. Remember that every chromatogram (figure) included in the report must be referred to and discussed in the text of your report. Include and discuss the results of the data analysis that you performed (you may want to include a table for this). Make some conclusions regarding the utility of the FID as a 'carbon counter'.

If you choose the HPLC experiment for your written report, you should write a 1 to 2 paragraph summary of how the experiment went. You need to turn in all of the raw data that you collected with the data labeled. This needs to include a chromatogram of the 6 component standard (with all peaks readily integrated and peak areas within the 15% variation expected). Also indicate if the chosen compound eluted where expected and calculate its ECN.