

Reminder: These notes are meant to supplement, not replace, the lab manual.

## Gas Chromatography notes

Application: Gas Chromatography (GC) provides a quick, accurate and relatively inexpensive way to analyze very small samples for composition. Simple GC machines may cost in the area of \$5,000<sup>i</sup>. This is fairly inexpensive as far as analytical instrumentation goes. They can be installed in a variety of laboratories designs including mobile testing units. GC's are easy to operate and provide reliable results.

1. Here is some terminology related to this experiment:

Chromatography is a technique in which compounds to be separated are distributed between a mobile phase and a stationary phase. Different distributions or partitioning between the two phases give rise to the separation.

Gas Chromatography (GC) is useful for separating and analyzing volatile liquid or gas mixtures. GC does not work on most solids.

The stationary phase in gas chromatography (GC) is almost always a relatively nonvolatile liquid, like a wax. This liquid is coated on either solid particles or the inside of a capillary tube.

The mobile phase in gas chromatography is an inert (nonreactive) gas, usually helium or nitrogen. This mobile phase is often called the *carrier gas*.

The retention time is the time (in seconds or minutes) between the injection of a sample and the top of a peak of a component of the sample. These times are used like  $R_f$  values in TLC, to establish the identity of the compound giving the peak by comparison.

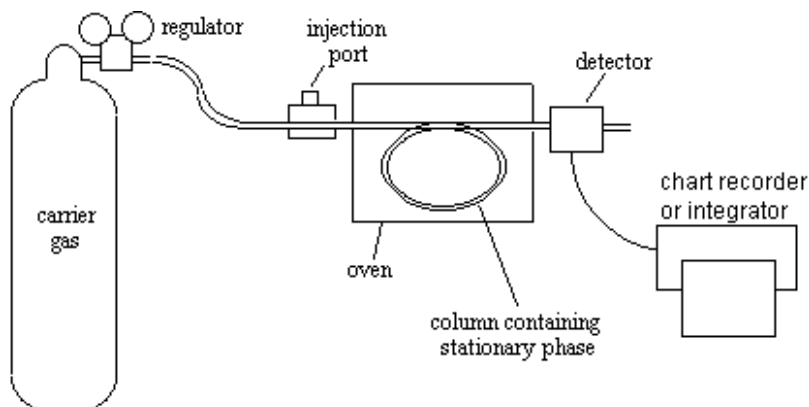
To elute a compound means to have it emerge from or come off of a column.

The fact that the mobile phase is a gas usually makes it necessary to use a more elaborate setup to confine the gas and direct its flow. Nevertheless, this is still chromatography; there is a sample, a mobile phase, and a stationary phase. In GC the stationary phase is a liquid and the mobile phase is a gas. The separation occurs by different partitioning or distribution of compounds between the stationary and the mobile phase. What physical characteristic describes the energy needed to move a compound from the liquid to the gas phase? A compound that spends more of its time in the gas phase (mobile phase) would have a shorter retention time than a compound that spends more of its time in the liquid phase (stationary phase). The boiling point of compounds is the primary means of predicting the order of elution from a GC. The lower the boiling point the shorter the retention time (RT). Secondly to boiling point is polarity.

Two different types of Gas Chromatographs (GCs) may be used in this lab. The first type is the more typical set up drawn below which has an external pressurized gas cylinder attached. In addition, new Vernier mini-GC's may be

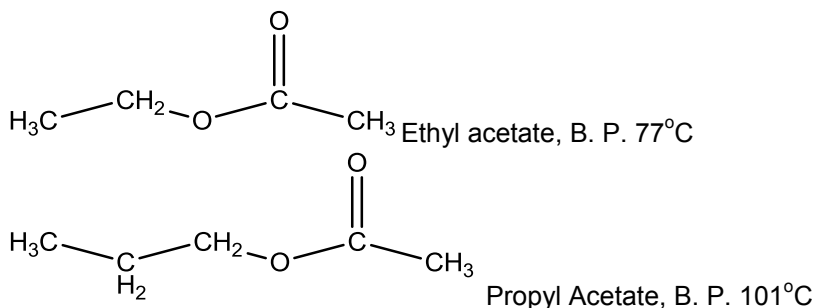
used. These mini-GC's use air from the room and do not need a separate pressurized gas tank.

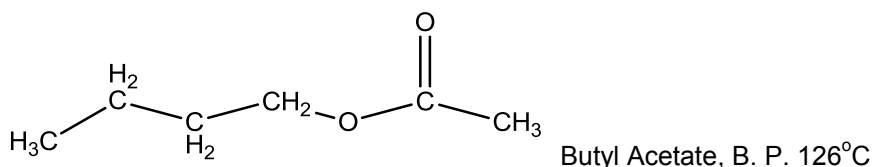
- Here is a schematic diagram of a typical gas chromatography apparatus. The components are not drawn to scale. There are gas chromatographs in the lab that you will be able to examine.



The carrier gas is typically kept in a large metal cylinder under high pressure. The gas flows through a valve into a regulator, which reduces the pressure to something the rest of the system can use. (Scuba divers use regulators for the same purpose). The gas flows past the injection port, where samples are injected using syringes. The injection port is heated, and the samples evaporate there. The sample and carrier gas mixture are carried into an oven that contains the chromatography column. (The heat prevents components of the sample from condensing). The separated components of the mixture pass through the detector, which sends a signal to the printer.

- The technique of gas chromatography is widespread in academic, industrial, and governmental labs. It is used to separate the components of volatile mixtures, identify the compounds (by comparison of retention times), and determine the amounts of the compounds present.
- Here are the structures of possible unknowns used in this experiment





All three of these compounds are esters of acetic acid (acetate). Each compound differs by one CH<sub>2</sub> group. As you can see the addition of a single CH<sub>2</sub> group raises the boiling point by over 20°C. Most esters have a pleasant scent and a moderately low toxicity. These three are no exceptions to this rule.

5. Safety considerations for this experiment include:

Syringes are sharp and can easily prick skin. If a syringe is left too long in the injection port without depressing plunger, the liquid will volatilize and expand, shooting the plunger out at an unsuspecting student. The injection port is hot and can easily burn skin. Be sure to wear goggles while operating GC.

Cylinders of gases under high pressure must be securely fastened to solid, permanent furniture or walls. If such cylinders fall and break, the escaping gas transforms them into potentially deadly missiles.

The organic materials analyzed in this experiment are highly flammable.

Notes for topics that may be included in quizzes given after the experiment:

6. Changes in the procedure can, as always, have a profound effect on the outcome of the experiment. Here are some possible changes in procedure and their effects.

Faster carrier gas flow rates and higher column temperatures give shorter retention times, but peaks may not be resolved as well. Slower flow rates and lower temperatures give longer retention times and better resolution.

The primary characteristic which determines which compound will have shorter retention times (elute quicker) is the boiling point. The more volatile compounds have lower boiling points and will elute the column faster.

The mobile phase is very nonpolar. The stationary phase is much more polar than the mobile phase. The higher the polarity of a compound the more affinity it will have to the stationary phase and the longer the retention time.

Less polar compounds generally have shorter retention times (there are exceptions to this).

Carrier gases should not react with the compounds in your sample, and shouldn't react with oxygen in the air either.

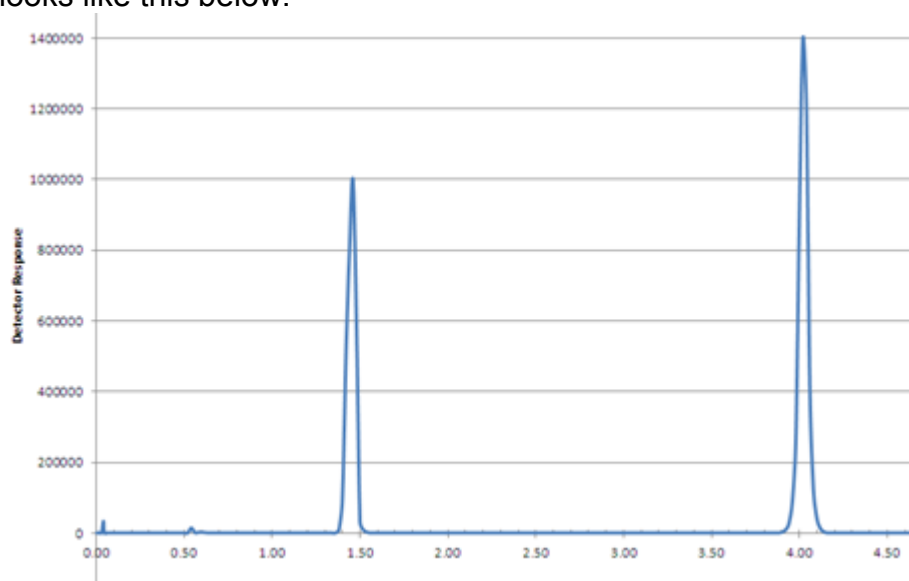
Stationary phases should not evaporate at the temperatures of the experiment, and should not react with the compounds under study.

Stationary phases have a significant impact on the retention time. To change a stationary phase means to physically remove the column (with wrenches) from the GC machine. This is not done frequently.

7. Gas chromatography can also be used in quantitative experiments, to determine the amount of a substance present in a sample. In general, the method works this way.

The area of a peak in GC is proportional to the amount of compound present and various instrument factors. Most integrators on gas chromatographs will give you information about areas of the peaks. If this feature is not available you can measure areas directly. Standards, samples that contain measured amounts of the compounds under study, are used to cancel out the instrument factors. For instance, if a certain compound gives relatively large peaks with a certain type of detector, it will do so with a standard sample as well as with a sample containing an unknown amount of the same compound. The method for manually determining peak area is described below.

8. The output of a GC detector is often recorded using a plotter. A typical plotter output looks like this below.



If the plotter is not also an integrator, the percentages of each compound can be calculated manually.

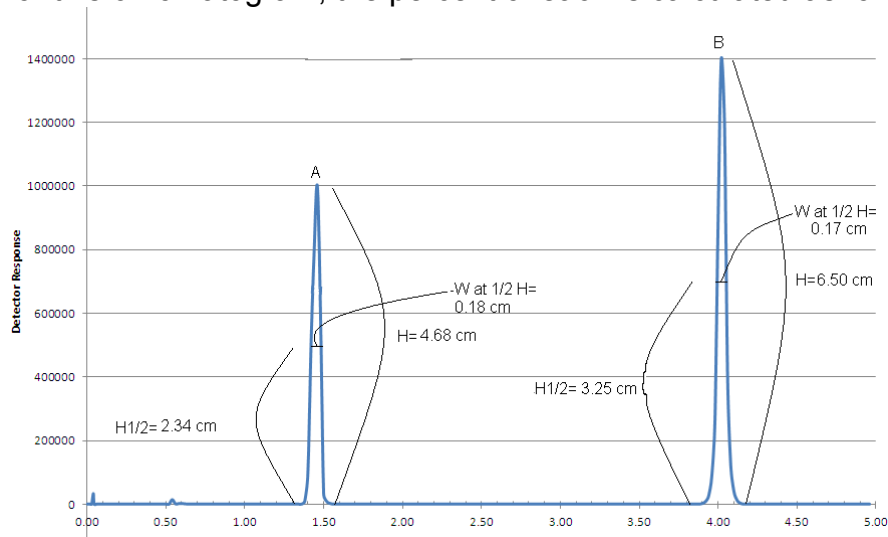
The area of each peak is defined by the height of the peak x width at half height.

$$\text{Area} = \text{Height (cm)} \times \text{Width at Half height (cm)} = \text{cm}^2$$

The percent of each compound in the mixture is the area of that peak, divided by the sum of all of the areas times 100%.

$$\text{Percent PEak 1} = \frac{\text{Area 1}}{\text{Area 1} + \text{Area 2} + \text{Area 3} \dots} \times 100\%$$

For this chromatogram, the percent of each is calculated as follows.



$$\text{Area A} = \text{Height times Width at Half Height} = 4.68 \text{ cm} \times 0.18 \text{ cm} = 0.84 \text{ cm}^2$$

$$\text{Area B} = \text{Height times Width at Half Height} = 6.50 \text{ cm} \times 0.17 \text{ cm} = 1.1 \text{ cm}^2$$

$$\text{Percent A} = \frac{\text{Area A}}{\text{Area A} + \text{Area B}} \times 100\% = \frac{0.84 \text{ cm}^2}{0.84 \text{ cm}^2 + 1.1 \text{ cm}^2} \times 100\% = 43\%$$

$$\text{Percent B} = \frac{\text{Area B}}{\text{Area A} + \text{Area B}} \times 100\% = \frac{1.1 \text{ cm}^2}{0.84 \text{ cm}^2 + 1.1 \text{ cm}^2} \times 100\% = 57\%$$

The retention time, if not given by the integrator is calculated by knowing the chart speed of the printer in cm per minute (cm/min) and multiplying by the distance it took from the injection to the tip of the peak. For peak A, the distance from the injection point at 0.0 to the point of peak A is 3.20cm. IF the chart speed was 0.75 cm/min then the retention time for peak A is calculated as following:

$$\text{Retention time of A} = \text{distance to A (cm)} \times \frac{\text{min}}{\text{cm}} = 3.25 \text{ cm} \times \frac{1 \text{ min}}{0.75 \text{ cm}} = 4.3 \text{ min}$$

<sup>i</sup> Shimadzu Instrumentation Price <http://www.shimadzu.com/an/gc/index.html> (January 22, 2012)