Gas Chromatography

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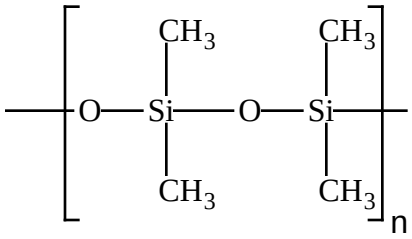
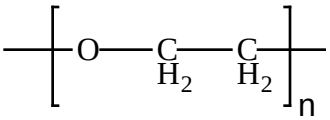
We will use gas chromatography (GC) to check the purity of the product in expt. 8. GC works on the same principles as discussed in the chromatography expt. 4, but here the mobile phase is a gas and the stationary phase is a liquid. The components of the sample are continually partitioned between the vapor phase and absorption in the liquid phase. Those compounds which spend a greater proportion of time in the gas phase elute more rapidly. Hence, the dominant factor determining the retention time in GC is the vapor pressure of the compound. Compounds with higher vapor pressure (lower boiling point) will elute faster than those with lower vapor pressure (higher boiling temperature). Any compound can be made to elute faster by simply raising the temperature of the chromatography column – this is housed in an oven so that the temperature may be controlled anywhere up to about 300 °C. Since all compounds have higher vapor pressure at higher temperatures, they will elute faster. As for TLC and column chromatography, the retention time (T_R) for a given set of chromatography conditions can be used to help identify a compound.

Two of the most common stationary phases used in GC are the non-volatile polymers dimethylsilicone and polyethylene glycol,. This relatively non-polar liquid phase is coated onto



Dimethylsilicone
Trade names: SE-30, OV-1



Polyethylene glycol
Trade name: Carbowax

the surface of an inert support material such as diatomaceous earth, and packed in a glass or metal tube as the column. A schematic diagram of a gas chromatography system is given in Figure 1. The column is coiled and kept in an oven where the temperature can be controlled. The mobile phase, called the carrier gas, flows through the column. Helium is typically used. At the upstream end of the column is the injection port, where the sample is introduced. Only small amounts of sample are used, usually between 0.5 – 5 μl, and the sample is injected into the column with a microsyringe. The compounds separate as they pass through the column, and elute in order of increasing boiling point. A detector at the end of the column generates a signal when a compound elutes – this is recorded using a strip-chart recorder. Several types of detectors are available. We will be using gas chromatographs equipped with thermal conductivity ("hot-wire") detectors. As the name implies, this detector consists of a wire placed across the end of the column. The electrical resistance of the wire depends on its temperature. An electrical current is maintained across the wire, and the voltage drop, which varies directly with the resistance, can be measured. Normally, only the helium carrier gas is passing over the wire - this carries away a certain amount of heat and leads to a particular voltage. When a

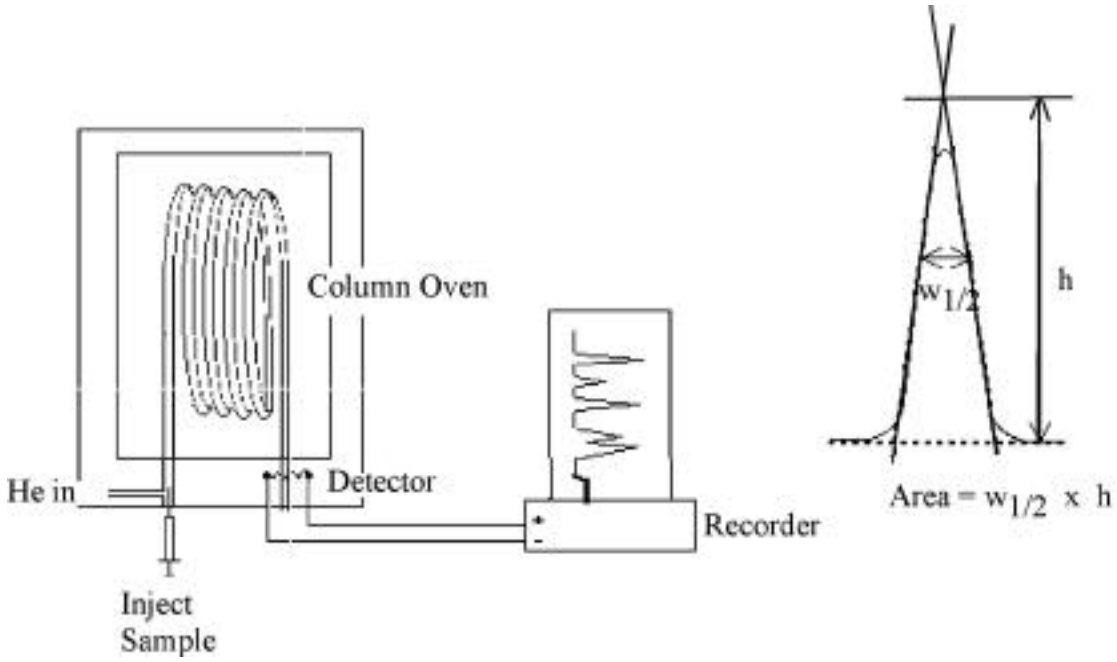


Figure 1. A simple diagram illustrating the components of a typical gas chromatograph. The recorder prints the chromatogram, a peak for each component, proportional in area to the amount of that compound present in the mixture. Right: peak areas by triangulation.

component from the mixture elutes from the column and passes over the wire, a different amount of heat is carried away (the compound has a different thermal conductivity than He), and the temperature of the wire changes. This leads to a change in voltage, which is amplified and sent to the recorder. Each component appears as a peak on the recorder trace, called the chromatogram. The area of each peak is proportional to the amount of that compound – if twice as much sample is injected, the areas of the peaks will double. Therefore, the peak areas can be used as a quantitative measure of the amount of each component in the mixture.

The areas of the peaks can be determined by the *triangulation method*. In this method, the individual peaks in the chromatogram are approximated by triangles. Straight lines are drawn along the up- and down-slopes of the peak, and the intersection of these lines is the top of the triangle. The base of the triangle is drawn to coincide with the baseline of the chromatogram. Now, the area of this triangle is very close to the true area of the peak, and can be obtained by multiplying one-half of the height of the triangle by its width at the base. Since, however, the width at the base is sometimes difficult to measure accurately, a better formula to use is to take the height of the triangle multiplied by the width of the triangle at one-half that height (sometimes referred as the width at half-height). When the areas of the individual peaks have all been determined this way, the fraction of each compound in a mixture can be determined by dividing each area by the total area of all the peaks.

Most of the unreacted starting material will be separated from the isopentyl acetate by distillation, but some may remain in the sample to be analyzed by GC. This, of course, will also give a peak in the chromatogram, which appears earlier than the (higher boiling) product. In addition, a small amount of air is always injected along with the sample, and this also gives a small peak. Since air spends all of its time in the mobile phase, the T_R for the air corresponds to the time interval for the mobile phase to pass through the column.