Gas Chromatography (GC) Technique

Gas chromatography (GC) is a powerful tool for the separation of organic molecules and has been used in several different areas of chemistry research and applications. With respect to environmental chemistry, GC is routinely used for the analysis of contaminants and is also used to study the components of complex systems such as gasoline, smoke, oil, and soil organic matter. The technique essentially involves heating a sample until its constituent compounds are vapourized into the gas phase, then separating the components using chromatography and detecting and quantifying the individual components with a detector and software system.

Chromatography is a general term that refers to the separation of mixtures based on their affinities for one or more phases.

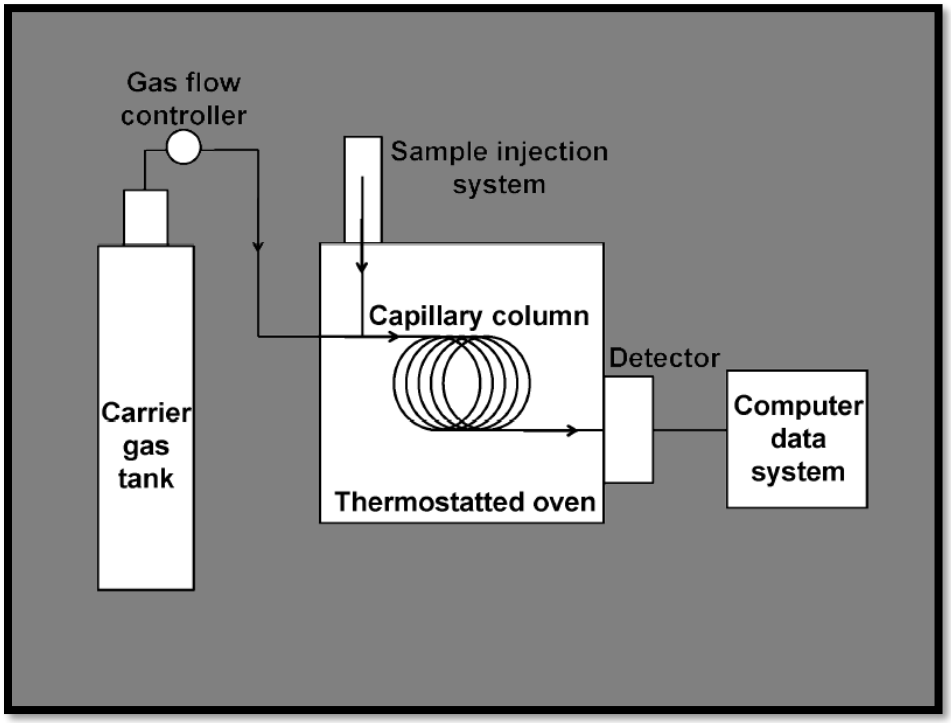

Figure 1: GC Schematics

The figure above shows a schematic of the basic components of a gas chromatograph. The sample injection system was traditionally operated manually but more modern instruments use automated injection systems that deliver more accurate volumes with better reproducibility. Newer instruments also have autosamplers that allow for multiple samples to be analyzed in sequence without the user having to be present. The injector needle delivers the liquid sample (typically 1-5 µL) to the sample inlet which is heated to high temperature (~300 °C) which causes the sample to vapourize. Depending on the sample concentration, the gaseous sample may be diluted with an inert carrier gas, usually helium but sometimes nitrogen or argon, so that the sample plug introduced onto the column is not too large. Split injection mode dilutes the sample with carrier gas by a precise ratio (typically ranging between 1:2 to 1:200) whereas in splitless mode no sample dilution occurs.

The gas-phase sample is then swept into the capillary column, which is a long, coiled, thin tube that is approximately 30 metres long but only a fraction of a millimetre in diameter. The inside of the capillary column is coated in a thin film of material known as the stationary phase which varies depending on the analyte of interest. A common stationary phase for nonpolar analytes is composed of silica bonded to long alkyl chains (C_{18}) that sometimes contains phenyl rings.

The column is housed inside a thermostatted oven whose temperature can be carefully controlled and increased at different rates as desired. Once the components pass through the column, they reach a detector which may be a flame ionization detector, mass spectrometer, or another type of detector which produces a signal that is proportional to the concentration of each component. The resulting chromatogram is a graph of signal intensity plotted versus retention time, the time required for the compound to pass through the column and reach the detector. For quantitative analysis, internal or external standards of known concentration may be analyzed along with unknown samples. Identification of molecules can be based on the retention time

of standards or using libraries of standard spectra when a mass spectrometer is used as the detector.

In order to be analyzed using GC, molecules must be thermally stable at the oven temperatures used which can sometimes exceed 300 °C. Molecules which thermally decompose at these temperatures cannot be analyzed by GC. Analyte molecules must also be volatile and not react with the stationary phase during the chromatographic separation. To alleviate this, molecules can be derivatized to add functional groups which improve their volatility and remove reactive functionalities such as hydroxyl groups.

Temperature is a critical experimental parameter in GC. Temperatures that exceed a compound's boiling point will increase its volatility and cause it to partition more into the gas phase. As a result, the compound moves through the column more quickly and interacts less with the stationary phase. Therefore, carefully controlling the oven temperature can assist with the separation of similar compounds with small differences in their boiling points.

As the gas-phase mixture components pass through the column, they are retained to varying degrees based on their affinity for the stationary phase, thus permitting the separation of similar compounds. As mentioned previously, a number of different stationary phase compositions can be used to target specific compounds. For example, a polar stationary phase consisting of polyethylene glycol units can be used to separate polar analytes such as free acids whereas a stationary phase with phenyl groups can be used to target aromatic compounds. All columns have advantages and disadvantages such as the ability to separate or interact with specific types of compounds as well as the maximum temperatures that they can withstand before they begin to degrade. Column bleed refers to the loss of stationary phase material from the column during a sample run which can contaminate the sample and result in peaks in the chromatogram which are unexpected and may obscure sample peaks.