Gas Chromatography

In gas liquid chromatography (GLC) partition of solutes occurs between a mobile gas phase (the "carrier gas") and a stationary liquid phase present in the column. The gas-phase concentration of a solute depends on the vapor pressure of the solute, as does the boiling point of the solute. GLC, then, is basically a separation method dependent on differences in boiling point of solutes (components in a sample), and is sometimes regarded as high-efficiency distillation. The parallel is quite inexact, however, since GLC is much more rapid than distillation, much more efficient (separation via GLC is possible of solutes whose boiling points differ by no more than 2°) and, most important, GLC analysis requires only about 1-2 microliters (= 10⁻³ ml) of sample, at most. GLC can be an important tool for use in determining trace constituents in a sample mixture, and is especially useful where only tiny amounts of sample are available.

The five basic parts of a gas chromatograph are as shown:
1. **Carrier gas**: usually He, sometimes N₂.
2. **Injector**: a "T" in the carrier gas line, one branch of which is closed with a rubber septum, allowing sample injection.
3. **Column**: usually metal, sometimes glass or teflon; packed with stationary phase (silicone grease, or stopcock grease) distributed over a material with high surface area (sand, firebrick, diatomaceous earth).
4. **Detector**: most often is of a "thermal conductivity" type. Two states are possible in the detector: either it sees only carrier gas (State I) or a mixture of carrier gas and an eluted component (State II). The detector itself is a filament which is heated electrically; when pure carrier gas flows through the detector the heat produced in the filament is carried away by the carrier gas, and the filament temperature is stable. In state II, however, some component is eluted, altering the thermal conductivity of the gas in contact with the filament. If the carrier gas is a light gas (H₂ or He) with high thermal conductivity, any solute present in the carrier will decrease its conductivity, so the filament heats up and its resistance changes. This change in resistance is converted to a change in voltage, which is plotted as a function of time, resulting in the chromatogram.
5. **Recorder**: plots the detector output on chart paper.

A schematic diagram of a gas chromatograph
Temperature controllers, in various places:

a. Injector: to vaporize the sample so that it is present in the gas phase and hence can enter the column.
b. Column: so that the separation can be performed at temperatures above room temperature.
c. Detector: to maintain constancy of the detector's temperature to avoid signal drift, and so that components don't condense in the detector.

Note that operation at temperatures other than room temperature considerably extends the range of GLC, since we require only that samples may be volatized for introduction into the column. At the same time, however, we have a built-in limitation, since sample components must be stable with respect to temperature (i.e., should not decompose, explosively or otherwise, or char) when heated. This limitation as to temperature stability is the major problem encountered in analysis by GLC.

Chromatographic Analysis

GLC is "semiquantitative" since the information it yields is supporting rather than conclusive in the identification of a given component. This information is the retention time, measured from the point of injection to the maximum of a peak eluted from the column (see illustration below). The retention time is characteristic of a substance at a given temperature and flow rate of carrier gas. Retention times decrease as the temperature or flow rate is increased. Since these variables are not easy to reproduce precisely, the retention time may vary slightly from one injection to the next. For that reason, it is sometimes convenient to measure the retention time relative to a known standard that is deliberately added to the mixture. The ratio of retention times will be independent of experimental variables, and this ratio can be useful in identifying an unknown substance. Modern analytical laboratories use more expensive instruments that allow precise control over GLPC temperature and flow rate. The retention times from such instruments are more reliable, and can often be used to identify unknowns.
Two properties from a given chromatogram may be measured:

1) the distance (proportional to time) on the recorder chart that a given component requires to be eluted, and
2) the relative size (area) of the peak produced by a component.

The first property, (the retention time) yields supporting qualitative information, while the second property (the magnitude of the elution peak) is proportional to the amount of component present in the peak. Although different components have differing thermal conductivities, the differences are small enough that we will assume that peak area ratios correspond to molar ratios. This assumption does not work for more sophisticated GLC instruments that use other types of detectors. For these highly sensitive instruments, a correction for peak areas has to be made using the equation:

\[ \text{peak size (area)} = m \times \text{amount (moles) of component} \]

where \( m \) is the "response factor". In principle, \( m \) is different for each component. Hence a chromatographic process must be calibrated using standard mixtures of known concentration (i.e., \( m \) values must be determined for each component) before exact quantitative data are feasible.

The response factors normally run from 0.8 to 1.2, so a reasonable estimate can be made simple by measuring the peak area. Most peaks are approximately the shape of an isosceles or a right triangle, whose areas are simply:

\[ A = \frac{1}{2} \times \text{base} \times \text{height} \]

The measurement of the base of most GC peaks is difficult because more abnormalities in the shape occur in this region than in any other. A more accurate estimate of peak area is:
\[ A = \text{height} \times \text{width-at-half-height} \]

where instead of measuring the width of the base and multiplying it by 1/2, you simply measure the width of the peak at half of its height (see illustration below for isoamyl alcohol and isoamyl acetate).

Often the following relation finds use:

\[ \%B_{\text{AREA}} = \frac{\text{Area of peak B}}{\text{all peak areas}} \]

A calculation of \( \%B \) yields the fraction of the total area that is due to B; this value is often close (to within 5-10\%) of the weight \% of B in the original sample, if a thermal conductivity detector is used.

Therefore a chromatogram of a mixture allows:
(1) rough calculation of component amounts and
(2) exact calculation of the same amounts if the system has been calibrated
Note especially that only those components which are volatile at the operating conditions of the chromatograph will be eluted and hence determined. Nonvolatile components will remain at the head of the column and their existence may not be suspected without supplementary information.