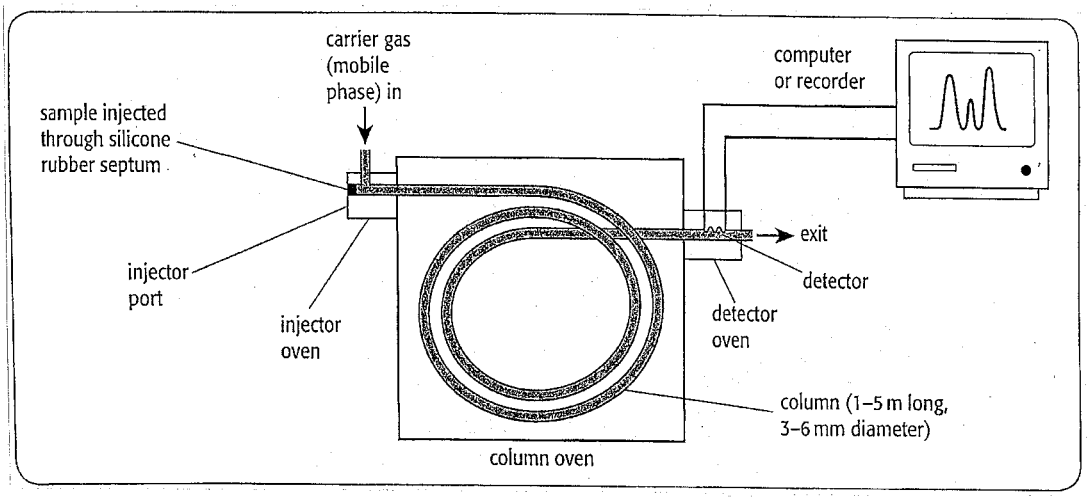
Gas-liquid chromatography (GLC)

GLC is used to seperate and identify very small samples of gases, liquids and volatile solids.

In this technique, a vaporised sample is carried by an inert gas (the mobile phase) over the surface of a liquid (the stationary phase).



GLC. The oven maintains a constant temperature, higher than the boiling point of the components in the mixture to be analysed.

The mobile phase, which is called the carrier gas, flows through the column of stationary phase at a constant rate.

The relatively unreactive gas nitrogen is frequently used as the carrier gas.

The stationary phase is a non-volatile liquid on a solid support, for example, a long-chain alkane of high boiling point coated on the surface of SiO_2.

GLC is partition chromatography.

The components of the mixture are partitioned between the mobile and stationary phases to different extents, so that they move through the column at different rates depending on:

i) their volatility

ii) their relative solubilities in the mobile and stationary phases.

When the stationary phase is non-polar, the rate of movement of each component through the column is determined principally by its valatility, which is related to boiling point.

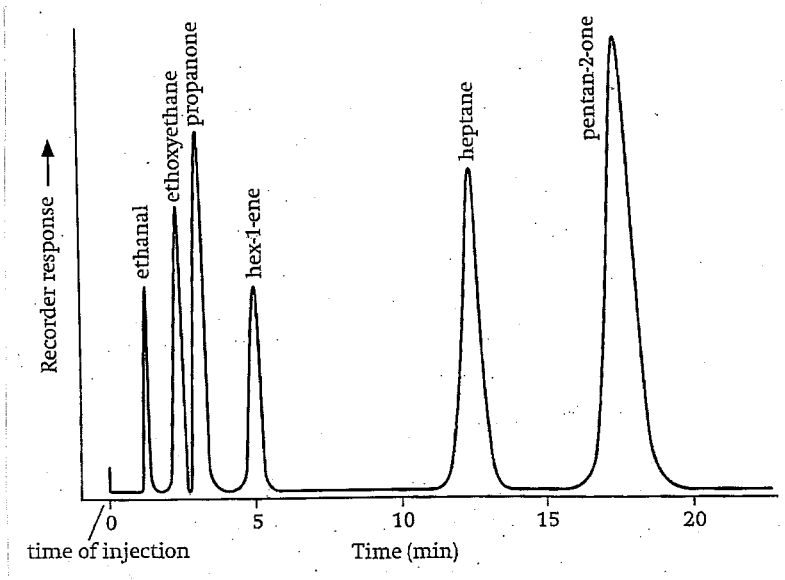
When the stationary phase is polar, it will tend to retain polar components.

For example, if a mixture of non-polar octane (C_8H_{18}) and polar pentanol ($C_5H_{11}OH$) is seperated using a polar stationary phase, the octane would leave the column before the pentanol.

Stationary phases, that is, the non-volatile liquids coated onto the solid support, are selected for their suitability for the seperation of different substances.

The components of a mixture leave the column after definite intervals of time, characteristic of each component, and are monitored by a detector designed to record changes in the composition of the carrier gas as the components are separated.

An example of a GLC chromatogram of a mix of organic compounds is as below:



The time taken for each of these components to pass through the column is found by measuring the distance on the chromatogram between the injection of the mixture (defined as 0 minutes) and the centre of the peak for that component. This value is <u>retention time</u>.

Since each solute has its own retention time, unknown compound can be identified by comparing its retention time with the retention times of known compounds. However, the conditions used in the experiments with unknown compounds and with known reference samples must be the same:

- the same carrier gas
- the same flow rate
- the same stationary phase
- the same temperature.

Limitations of GLC.

Analysis by GLC does have some limitations. For example, similar compounds will have similar retention times and if a newly discovered compound is detected it will not have a match in the computer's database of retention times.

Determination of the percentage composition of a mixture by GLC

For quantitative analysis the component peaks are first identified and then the area of each is measured. The peaks are roughly triangular in shape so their area is approximately:

The area $= \frac{1}{2} \times$ base $\times$ height

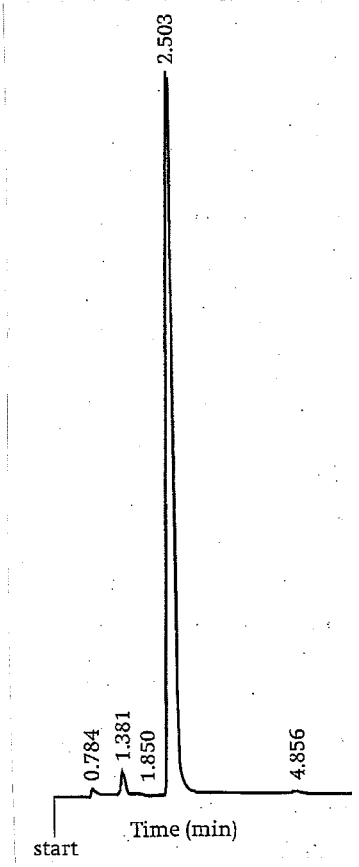
(ie. the area of a triangle)

The GLC machine usually measures the area of the peak automaticly and prints the results with the chromatogram. If the peaks are very narrow or have similar base widths, then peak height may be used instead of peak area to estimate the proportion of components in a mixture.

Example:

The chromatogram and printout giving the peak areas for a compound tested for impurity.

RT	% Area
0.784	0.27846
1.381	2.35848
1.850	0.09042
2.503	96.37168
4.856	0.90098



For determination of the percentage composition:

- the chromatogram must show peaks for all the components in the mixture.
- all the components of the mixture must be seperated.
- the detector must respond equally to the different components so that peak area is directly proportional to the component concentration.

The amount of each component in the mixture is found by expressing it as a percentage of the sum of the areas of all the peaks.

For example, for a mixture of three ketones A, B and C:

$$\%\text{ of ketone A} = \frac{\text{peak area (or height) of A}}{\text{sum of the areas (or heights) of A, B and C}} \times 100$$

Applications of GLC.

GLC is used for testing for steroids in competing athletes and for testing the fuels used in Formula One motor racing.

It is also used for medical purposes where it has been found possible to determine the percentages of dissolved oxygen, nitrogen, carbon dioxide and carbon monoxide in blood samples as small as $1 cm^3$.

An interesting example of the use of the combined technique of GLC and mass spectrometry in forensic science is the case of a husband who killed his wife while she was a patient in hospital.
He poisoned her with cyanide and then had her body cremated.
However, the police found strands of the victim's hair on a hospital pillow and detected cyanide in the hair follicles. This led to a criminal conviction.

Exercise 1

a. For GLC seperations explain:
   i) how retention time is measured.
   ii) how the areas under the component peaks are used.

b. What can you use as an approximate measure of the proportion of a component in a mixture from a GLC chromatogram which produces sharp peaks?

Workings

a. i) retention time – the time taken for a substance to travel through the stationary phase (column) and be detected by the detector.
   ii) the areas under the component peaks – give the relative proportion of each component of the mixture.

b. A GLC chromatogram which produces sharp peaks – use the height of the peaks as an approximate measure of the proportion of a component in a mixture.

Exercise 2

Select a suitable chromatographic technique for the seperation of each of the following mixtures:

a. a solution of sugars.

b. North Sea oil.

c. a solution of carbohydrates of high molecular mass.

Workings

a. sugars – polar molecules with different solubility in aqueous solution.

seperation technique – paper chromatography or thin-layer chromatography.

b. oil – consists of volatile components

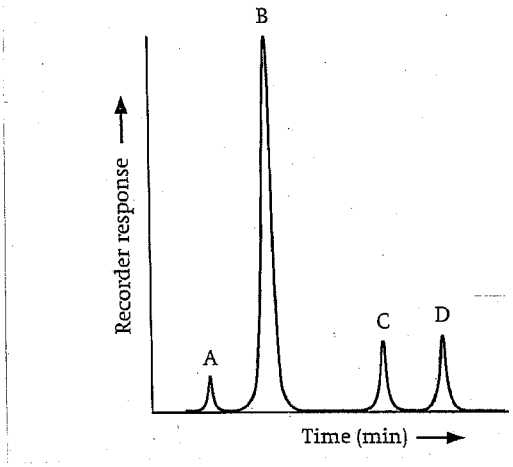
seperation technique – GLC

c. carbohydrates of high molecular mass – big molecule with low solubility in aqueous solution

seperation technique – HPLC or TLC

Exercise 3

A gas-liquid chromatogram of the alcohols found in the space above the beer in a beer can showed the presence of ethanol, butan-1-ol, methanol and 2-methylbutan-1-ol.



alcohol	peak areas [arbitrary unit]
A	50
B	500
C	100
D	100

a. Suggest which peak on the chromatogram was formed by each alcohol.

b. Determine the percentage composition of each alcohol in the mixture of alcohols.

Workings

ethanol	butan-1-ol	methanol	2-methylbutan-1-ol
CH_3CH_2OH	$CH_3CH_2CH_2CH_2OH$	CH_3OH	$CH_3CH_2CH(CH_3)CH_2OH$
$M_r = 46$	$M_r = 74$	$M_r = 32$	$M_r = 84$

a. volatility depends on boiling points (M_r higher → Tb higher)

A - methanol ; B - ethanol ; C - butan-1-ol ;

D - 2-methylbutan-1-ol .

b. A : % composition $= \frac{50}{50+500+100+100} \times 100 = 6.7\%$

B : % composition $= \frac{500}{750} \times 100 = 66.7\%$.

C : % composition $= \frac{100}{750} \times 100 = 13.3\%$; D : % compotition $= 13.3\%$