CIE Chemistry A Level

22 : Analytical Techniques

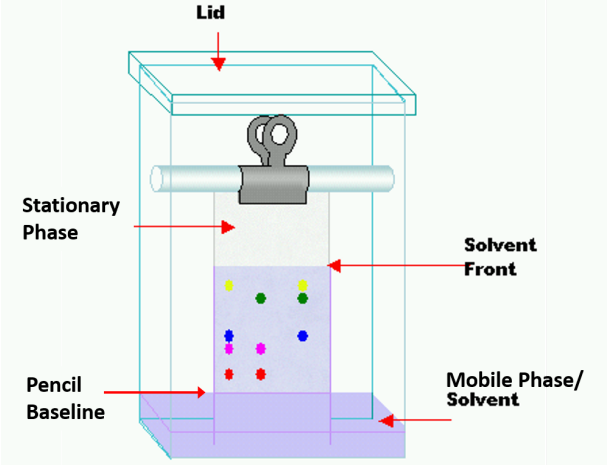
Notes

Chromatography (A level only)

Chromatography is a process used to separate a mixture of substances.

Thin-layer chromatography

In thin-layer chromatography, the **mobile phase** is a solvent and the **stationary phase** is typically a layer of silica gel or alumina on a piece of glass. A spot of the substance being analysed is put on the pencil **baseline** before the stationary phase is placed into the solvent.



'Paper chromatography', Wikipedia
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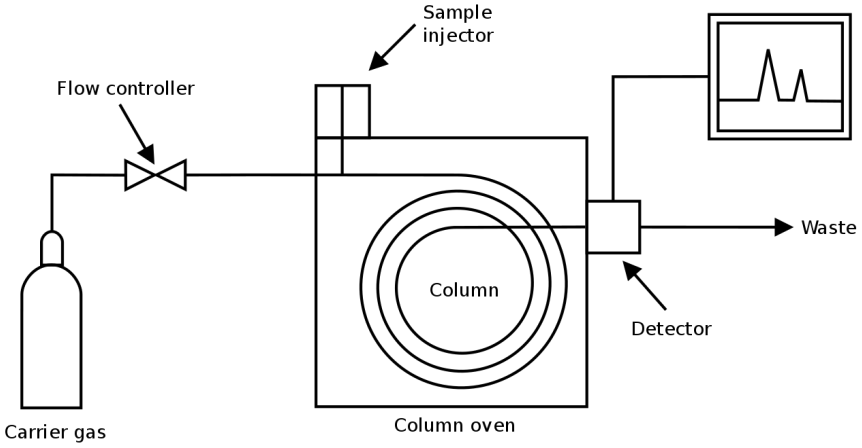
The **Rf value** (or retention factor) can be calculated after chromatography is completed:

$$Rf = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent front}}$$

Substances are separated because different compounds have **different solubilities** in the solvent and **different attraction** to the stationary phase.

Gas-liquid Chromatography

In gas-liquid chromatography, the **mobile phase** is a carrier gas (such as helium) and the **stationary phase** is a liquid with a high boiling point which is **adsorbed** onto a solid. The stationary phase is found inside the coiled column.



'File:Gas chromatography-vector.svg' CC0 1.0

Retention time is the time taken for a sample to travel from the injector to the detector.

The retention time of a compound is affected by:

- **Boiling point** - compounds with higher boiling points will condense sooner in the column so the retention time will be longer.
- **Solubility in the liquid stationary phase** - more soluble compounds will have a longer retention time as they will spend less time in the carrier gas.
- **Temperature** - the higher the temperature of the column, the shorter the retention times of all the compounds will be because the molecules have more kinetic energy.

A gas-liquid chromatogram can also be used to work out the **percentage composition of a mixture**. The area under a peak shows the relative amount of that substance which can be calculated using the formula ½ x base x height. To convert this into a percentage:

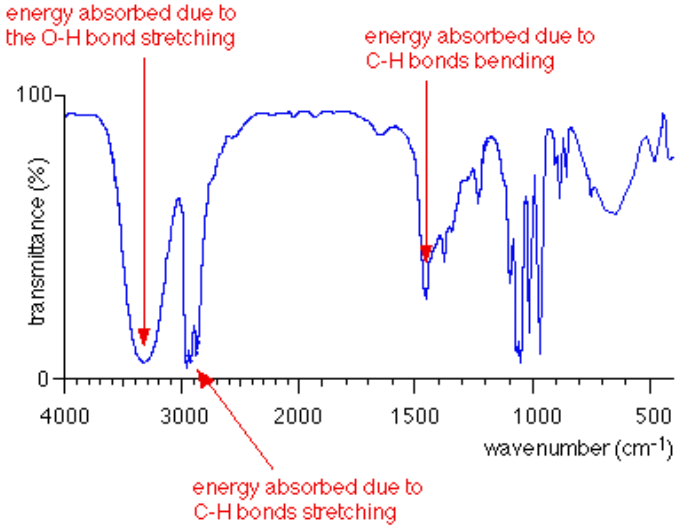
$$\text{Percentage composition} = \frac{\text{area under one peak}}{\text{total area under all peaks}} \times 100$$

Infra-red spectroscopy

When infra-red radiation is directed at a compound, **specific frequencies are absorbed** by bonds in the molecule. The percentage transmittance of infra-red at each frequency is recorded by a detector and then plotted on a graph.

Energy that is absorbed by the compound causes bonds to **vibrate**, meaning the bond **stretches or bends**. The amount of vibration depends on the **length of the bond** and the mass of the atoms.

The peaks on an infra-red spectrum can be used to identify the functional groups present in a molecule as **each bond absorbs a specific frequency of IR radiation**. A peak can be compared with known values in the data book to identify the bond.

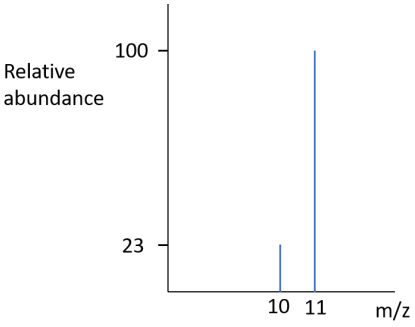


'What is an infra-red spectrum?', Jim Clark, Chemguide

The **fingerprint region** on an infra-red spectrum is the region (typically between 1500cm^{-1} and 500cm^{-1}) that contains a complicated series of absorptions. Every compound has a **unique** fingerprint region.

Mass Spectrometry (A level only)

During mass spectrometry, a **vaporised** sample (atoms or molecules) is turned into positive ions. The ions are then accelerated, deflected by a magnetic field and then detected. A graph is produced with the **mass to charge ratio (m/z)** on the x axis and **relative abundance** on the y axis:



Molecular mass

The molecular ion peak (M^+) is the peak with the **greatest mass to charge ratio**. The molecular mass of a compound is equal to the m/z value of this peak.

M^{+1} peak

The M^{+1} peak is a tiny peak which is 1 unit to the right of the molecular ion peak. This is **caused by the presence of the ^{13}C isotope** (the relative abundance of ^{13}C is 1.11%). ^{13}C has one more neutron than ^{12}C meaning that the relative formula mass is increased by 1.

The relative heights of the M^+ and M^{+1} peaks can be used to predict the number of carbon atoms (n) in a molecule:

$$n = \frac{100}{1.1} \times \frac{\text{abundance of } M^{+1} \text{ ion}}{\text{abundance of } M^{+} \text{ ion}}$$

M^{+2} peak

Compounds which contain **chlorine** or **bromine** also have a M^{+2} peak on their mass spectrum.

<u>Chlorine</u>

Chlorine in these compounds can be one of **two isotopes**: ^{35}Cl or ^{37}Cl. Compounds containing the ^{37}Cl isotope will have a relative formula mass that is 2 units larger than compounds containing the ^{35}Cl isotope which causes the M^{+2} peak. The peak heights of the M^+ and M^{+2} ions are in the **ratio 3:1** because the chlorine atom is 3 times more likely to be ^{35}Cl than ^{37}Cl.

Bromine

Bromine has **two isotopes**: ^{79}Br and ^{81}Br. The heights of the M^+ and M^{+2} peaks will be in the **ratio 1:1** because the ratio of the two isotopes is 1:1.

For a compound with 4 bromine atoms, there will be **5 molecular peaks** because there are 5 combinations ways that you can have 4 bromine atoms (as there are 2 isotopes):

79 + 79 + 79 + 79
79 + 79 +79 + 81
79 + 79 +81 + 81
79 + 81 +81 + 81
81 + 81 +81 + 81

Fragmentation

Fragment ions are formed when an **unstable molecular ion breaks** up into a positive ion and an uncharged **free radical** (a species which contains an unpaired electron):

$$M^+ \rightarrow X^+ + Y\bullet$$

Only charged particles are detected so the free radical (Y●) will not produce a line on the spectrum. Each line on the mass spectrum represents a different fragment ion.

The combination of fragment ions in a mass spectrum can be used to identify a molecule.Below is a table showing some common fragment ions:

m/z value	Fragment ion
15	CH_3^+
17	OH^+
29	$C_2H_5^+$
43	$C_3H_7^+$
57	$C_4H_9^+$

Carbon-13 NMR Spectroscopy (A level only)

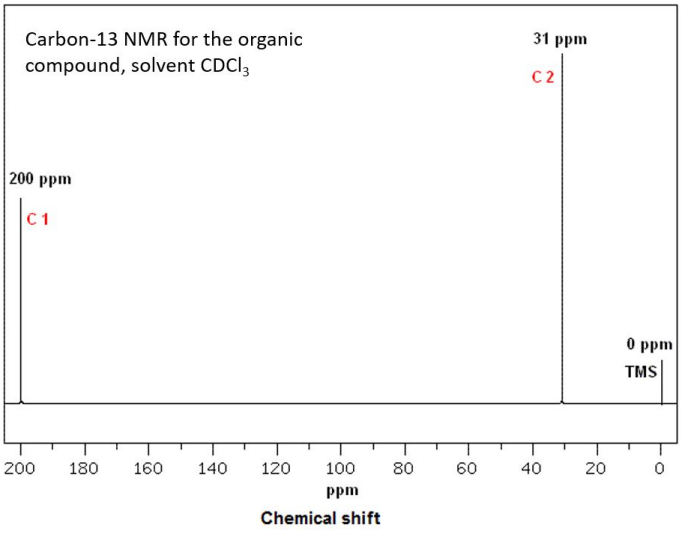
The **^{13}C nuclei** can align with or against a magnetic field. It is **less stable** for the nucleus to oppose the magnetic field than align with it as this is at a **higher energy**. Supplying energy (in the form of radio waves) to the nucleus can cause it to flip from the more stable alignment to the less stable alignment.

The atoms/ groups of atoms that the carbon is bound is called the **environment**. The environment that the carbon is in impacts the amount of energy that is required to cause the nucleus to oppose the magnetic field. On an **NMR** spectrum, the **number of peaks** shows the **number of carbon environments** there are. Comparing the **chemical shift** value of a peak (from the x axis) to the data book can identify what environment the carbon atoms are in.

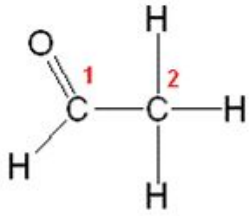
When using a ^{13}C NMR spectrum to predict structures of compounds, it is important to consider the number of **carbon environments** and the **functional groups** present (identified using the chemical shift values).

Example questions: These questions will require the chemical shift values from the formula book

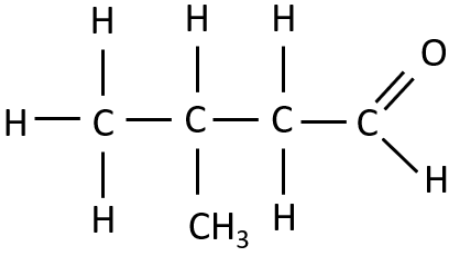
- An organic compound contains 2 carbons and has the ^{13}C NMR spectrum below. Determine the structure of the compound.



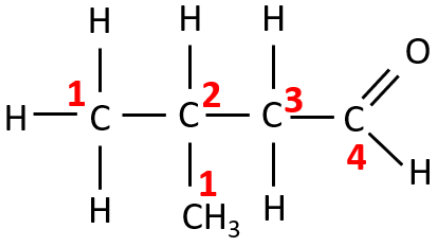
  - The compound contains two carbons.
  - There is a peak at 200 ppm meaning the compound must contain C=O.
  - The ^{13}C NMR spectrum shows 2 peaks so there are 2 different carbon environments. This means the two carbons are in different environments.
  - The chemical is ethanal.



- Predict the number of peaks in the ^{13}C NMR spectrum for 3-methylbutan-1-al.
  - The structure of 3-methylbutan-1-al is:



- Number the carbon environments:



- There are 4 carbon environments so there will be 4 peaks on the ^{13}C NMR for 3-methylbutan-1-al.

Proton (^{1}H) NMR Spectroscopy (A level only)

As with carbon-13 nuclei, hydrogen nuclei can align with or against a magnetic field. The direction of alignment can be flipped using a **specific frequency** of radio waves (known as resonance condition). This is because there is a **difference in the energy of the two alignments**. Hydrogen nuclei in different **environments** require different frequencies of radio waves to change their alignment.

The proton environment can be identified using **chemical shift** values and comparing them to known values in the data book. The **ratio of the areas** under the peaks indicates the number of protons in each environment.

The number of protons on the adjacent carbon atoms can be identified using the **splitting pattern** in the spectrum. The **n+1 rule** states that the number of peaks in the splitting pattern is equal to the number of adjacent protons + 1. Examples are shown in the table below:

Number of peaks in splitting pattern	Name	Number of adjacent protons (n)
1	Singlet	n + 1 = 1 n = 0
2	Doublet	n + 1 = 2 n = 1
3	Triplet	n + 1 = 3 n = 2
4	Quartet	n + 1 = 4 n = 3

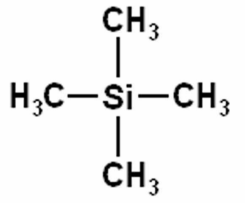
There are several cases where the n+1 rule doesn't work:

- **Alcohols** - the chemical shift for the hydrogen atom in -OH is variable and this peak is always a **singlet**. Also, the hydrogens in the -OH don't cause any splitting in adjacent hydrogens.

- **Equivalent hydrogens** - hydrogens which are bound to the same carbon/ are in the same environment have no effect on each other. This means that one hydrogen atom in a CH_2 group doesn't cause splitting of the other one on the spectrum.
- **Benzene** - the splitting pattern is generally very complicated so it is called a multiplet instead. The peaks for benzene rings will be found in the range 6.0 - 9.0.

TMS (Tetramethylsilane)

The peak at 0 ppm on a proton NMR spectrum is due to the hydrogens in TMS. TMS is used as a **standard for chemical shift measurements** during NMR spectroscopy.



TMS is used because:

- It has 12 hydrogen atoms in the same environment so a **single, strong peak** is produced in proton NMR.
- It **contains both carbon and hydrogen atoms** meaning it can be used in carbon and proton NMR.
- It contains 1 carbon environment so it produces a **single peak** in carbon-13 NMR.
- It's non-toxic.
- It's inert so it will not react with the compounds under analysis.

Deuterated solvents

NMR typically uses a solution containing the substance being analysed. The solvent can't contain any hydrogen atoms as these would produce peaks on the spectrum. **Deuterated solvents** (such as **$CDCl_3$**) contain deuterium (an isotope of hydrogen) and are often used in NMR. **Deuterium doesn't produce a peak on the proton NMR spectrum** so the solvent doesn't affect analysis.

Identifying O-H and N-H protons

The chemical shift values for O-H and N-H protons are variable, making it difficult to identify the peaks caused by these protons. To identify which peaks are caused by O-H or N-H:

1. Run a proton NMR to obtain a spectrum for the compound being analysed.
2. Shake the sample with D_2O (or heavy water, this contains 2 deuterium atoms instead of hydrogen).
3. Run a second proton NMR and compare the spectra. Any peaks caused by O-H or N-H protons will disappear.

Alcohols are slightly acidic meaning the hydrogen in the OH group transfers to one of the lone pairs on the oxygen in D_2O. The negative ion formed from the alcohol is likely to collide with D_2O which will regenerate the alcohol. Instead of reforming the OH group, an **OD group is formed**. The deuterium atom won't produce a peak on the NMR spectrum meaning the peak caused by the O-H proton will **disappear**.