

CAIE Chemistry A-level

37: Analytical Techniques (A-level only)

Notes

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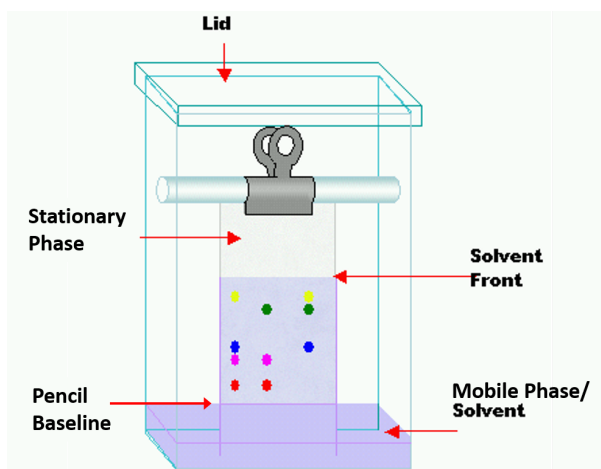


Chromatography

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, [CC BY-SA 3.0](https://creativecommons.org/licenses/by-sa/3.0/)

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

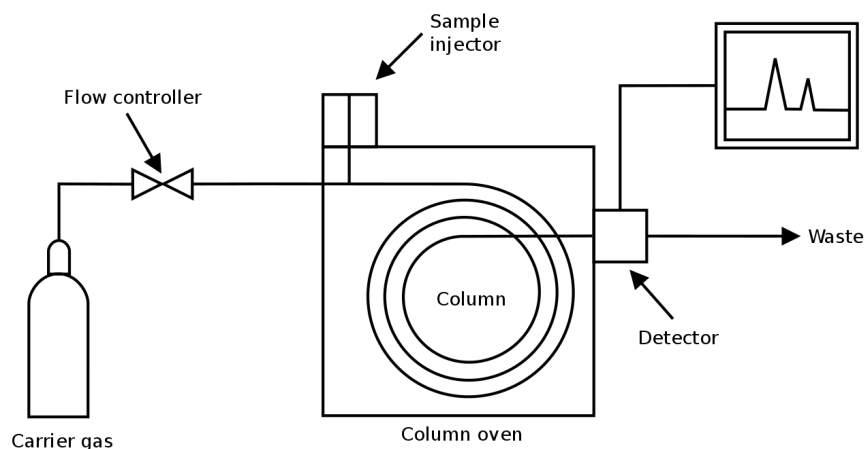
$$R_f = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent front}}$$

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 $\frac{1}{2} \times \text{base} \times \text{height}$. To convert this into a percentage:

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

Carbon-13 NMR Spectroscopy

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 or groups of atoms that the carbon is bound to 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 the environment the carbon atoms are in.

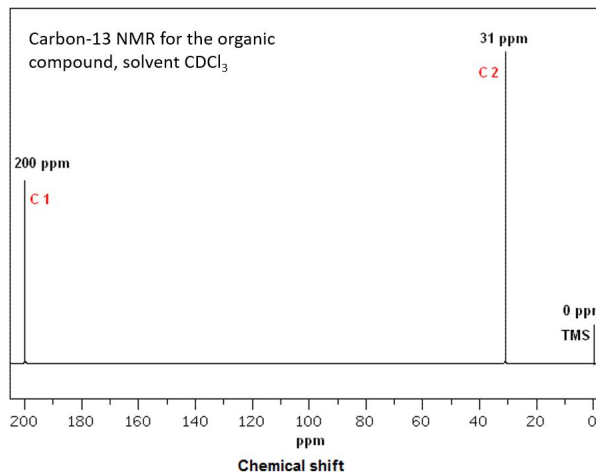
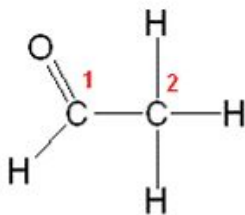


When using a ^{13}C NMR spectrum to predict structures of compounds, it is important to consider the number of **carbon environments** and the **functional groups** present (identified using the chemical shift values).

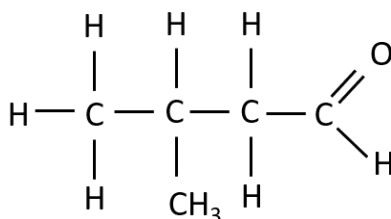
Example questions: These questions will require the chemical shift values from the formula book.

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

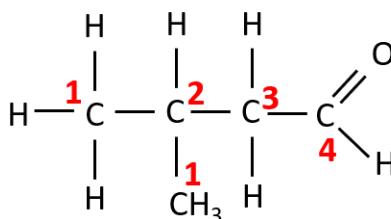
- The compound contains two carbons.
- There is a peak at 200 ppm meaning the compound must contain $\text{C}=\text{O}$.
- The ^{13}C NMR spectrum shows 2 peaks so there are 2 different carbon environments. This means the two carbons are in different environments.
- The chemical is ethanal.



- 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 (^1H) NMR Spectroscopy

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:

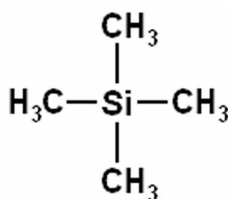
Number of peaks in splitting pattern	Name	Number of adjacent protons (n)
1	Singlet	$n + 1 = 1 \rightarrow n = 0$
2	Doublet	$n + 1 = 2 \rightarrow n = 1$
3	Triplet	$n + 1 = 3 \rightarrow n = 2$
4	Quartet	$n + 1 = 4 \rightarrow n = 3$

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**.

