

Further synthesis and analysis Knowledge organiser

1. Keywords

Chemical shift (δ).	the resonant frequency (signal) of a nucleus relative to a standard in a magnetic field.
------------------------------	--

¹H NMR chemical shift data

Type of proton	δ /ppm
ROH	0.5–5.0
RCH ₃	0.7–1.2
RNH ₂	1.0–4.5
R ₂ CH ₂	1.2–1.4
R ₃ CH	1.4–1.6
	2.1–2.6
	3.1–3.9
RCH ₂ Cl or Br	3.1–4.2
	3.7–4.1
	4.5–6.0
	9.0–10.0
	10.0–12.0

¹³C NMR chemical shift data

Type of carbon	δ /ppm
	5–40
	10–70
	20–50
	25–60
	50–90
	90–150
	110–125
	110–160
	160–185
	190–220

2. Nuclear Magnetic Resonance - theory

- Neutrons and protons can be found in the nucleus spinning on their own axis. In many atoms, these spins cancel each other out, but in those with an odd number of protons the nucleus itself will have an overall spin.
- This generates a small magnetic field around the nucleus, much like that of a bar magnet.
- If we place a bar magnet in an external magnetic field, it aligns parallel to it, much like a compass aligns with Earth's magnetic field. If we place nuclei with spin in a magnetic field, they, too, will align with it.
- If we provide the required energy, we can 'flip' the nuclei. This energy required for this can be supplied in the form of radio waves it can be recorded as a spectrum which we can then use to find information on the compound's structure.
- This flipping of the atom from one magnetic alignment to the other by the radio waves is known as the resonance condition.
- Each atom of each compound will have its specific **chemical shift (δ)**.

There are two main types of NMR:

- ¹³C NMR C-13 - Only 1% of the carbons are ¹³C (sensitivity problems).
- ¹H (proton) NMR - ¹H NMR spectra are obtained using samples dissolved in deuterated solvents or CCl₄.

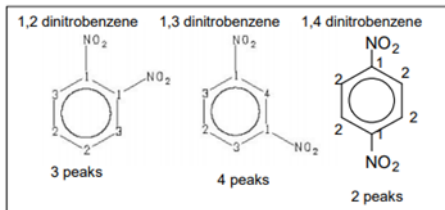
3. Interpretation

- Each ¹³C or ¹H atom of a specific functional group has its own δ .
- Tetramethylsilane, Si(CH₃)₄ (TMS) is used as a standard as all the hydrogen atoms are in identical environments. This means it produces a single peak, far away from most other absorption peaks. The single peak is given a chemical shift value of 0. It is also inert, non-toxic and volatile (easy to remove from the sample).
- The higher the electron density around the atom the higher the shielding hence the lower the δ on the NMR spectrum.
- In a NMR spectrum, there is one signal (peak) for each set of equivalent ¹³C or ¹H atoms.

¹H NMR

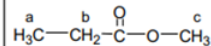
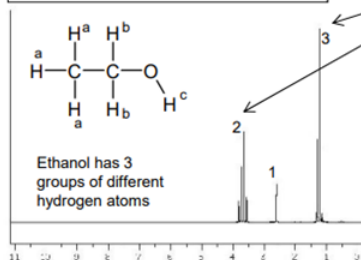
- The peaks can be split into multiple smaller peaks (spin-spin coupling). These split into the number of hydrogen atoms on the adjacent carbon plus one. Following the **n+1 rule**.
- The area of each peak is related to the number of H atoms producing it.
- The instrument produces a line called the integration trace. The relative heights of the steps show the relative number of each type of hydrogen.

¹³C NMR



Equivalent Hydrogen atoms.

In an ¹H NMR spectrum, there is one signal for each set of equivalent H atoms.



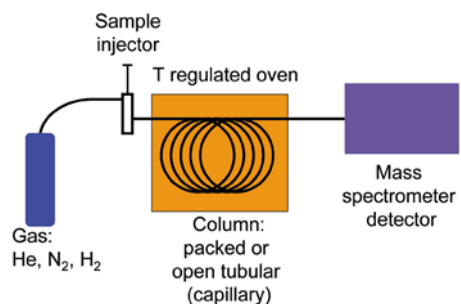
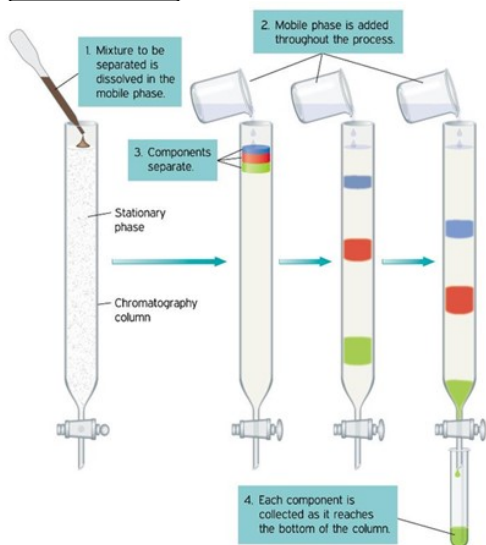
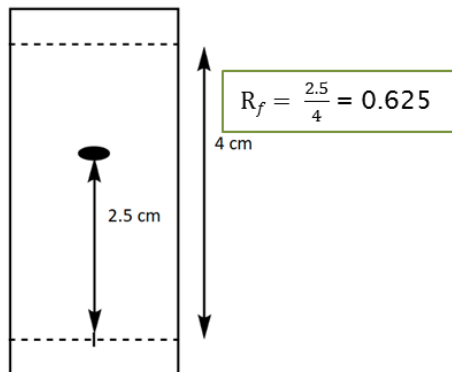
The peak due to group a will be a **triplet** as it is next to b (a carbon with 2 H's)

The peak due to group b will be a **quartet** as it is next to a (a carbon with 3H's)

The peak due to group c will be a **singlet** as it is next to a carbon with no H's)

signal	singlet	doublet	triplet	quartet
appearance				
Split number of peaks	1	2	3	4
number of neighbouring inequivalent H atoms	0	1	2	3
relative size		1:1	1:2:1	1:3:3:1

Further synthesis and analysis Knowledge organiser



1. General principles

Chromatography describes a range of separation techniques where a mixture can be separated if it is dissolved in a solvent and the resulting solution moves over a solid.

- The mobile phase flows through the stationary phase and carries the components of the mixture with it. It is a liquid or a gas.
- The stationary phase is a solid, or a liquid supported on a solid. It will hold back the components in the mixture that are attracted to it.

The more affinity a component in the mixture being separated has for the stationary phase, the slower it moves with the solvent.

2. Thin layer chromatography

Advantages compared to paper chromatography:

- Faster
- Plates are harder wearing than paper
- Smaller amounts of mixtures can be separated

Detection

- Once a sample has run UV or other developing agents are used to locate the spots.
- The distance travelled relative to the solvent is called the R_f value.

$$R_f = \frac{\text{distance travelled by the compound}}{\text{distance travelled by the solvent}}$$

3. High Pressure liquid chromatography

- HPLC is a column chromatography performed at high pressure.
- Pressure drives the elution rather than gravity.

4. Gas-liquid chromatography

- In Gas-liquid chromatography a column is packed with a solid or with a solid coated by a liquid, and a gas is passed through the column under pressure at high temperature.
- The sample is carried by the gas and the mixture separates as some of the components move along with the gas and some are retained by the oil.
- Different types of detectors are used to identify the emerging gas.
- In GCMS (Gas Chromatography-Mass Spectrometry) a mass spectrometer is used as the detector.

Chromatography	Mobile phase	Stationary phase	Support
Paper	Solvents	Paper	Paper
Thin layer	Solvents	Silica gel (SiO ₂) or Alumina (Al ₂ O ₃)	Glass or plastic
Column	Solvents	Silica gel (SiO ₂) or Alumina (Al ₂ O ₃)	Column
Gas-liquid	N ₂ or He	Powder coated with oil	Capillary

Further synthesis and analysis Knowledge organiser

1. Reactions

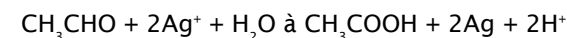
Functional group	Reagent	Result
Acyl chloride	Silver nitrate	Vigorous reaction steamy fumes of HCl rapid white precipitate of AgCl
Alkene	Bromine water	Orange colour decolourises
Aminoacids	Ninhydrin.	Blue-purple spot appears
Aromatic	Combustion	Smoky flames
1 ^{ary} or 2 ^{ary} alcohol	Sodium dichromate and sulfuric acid	Orange to green colour change
Aldehyde	Fehling's solution	Blue solution to red precipitate
	Tollens' reagent	Silver mirror formed
	Sodium dichromate and sulfuric acid	Orange to green colour change
Carboxylic acid	Sodium carbonate	Effervescence of CO ₂ evolved
	pH paper/indicator	Mildly acidic solution
Esters		Fruity smell
Haloalkane	Warm with aqueous NaOH then cool then add nitric acid then add silver nitrate	White precipitate (chloroalkane) Cream precipitate (bromoalkane) Yellow precipitate (iodoalkane)

2. Further observations

- Is the compound solid? (possible long unbranched carbon chain or ionic bonding)
- Is the compound liquid? (hydrogen bonds, branched carbon chain)
- Is the compound soluble? (can form hydrogen bond)

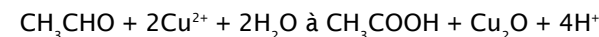
3. Tollens' Reagent

- Reagent: aqueous ammonia + silver nitrate.
- The active substance is the complex ion of $[\text{Ag}(\text{NH}_3)_2]^+$
- Conditions: heat gently
- Reaction: The silver(I) ions are reduced to silver atom and aldehydes/ alcohols oxidised.
- Observation: a silver mirror forms coating the inside of the test tube. Ketones result in no change.



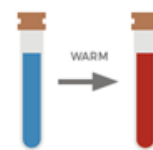
4. Fehling's Solution

- Reagent: Fehling's Solution containing blue Cu^{2+} ions. Conditions: heat gently
- Reaction: aldehydes only are oxidised and the copper (II) ions are reduced to copper(I) oxide.
- Observation: Blue Cu^{2+} ions in solution change to a red precipitate of Cu_2O . Ketones do not react Fehling's solution.



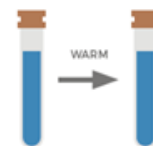
FEHLING'S SOLUTION

Contains complexed Cu^{2+} ions. Aldehydes reduce these ions to red copper (I) oxide. Ketones don't react with Fehling's solution.



ALDEHYDE

Blue → Red



KETONE

Solution remains blue: no reaction

TOLLEN'S REAGENT

Contains the diamine silver ion, $[\text{Ag}(\text{NH}_3)_2]^+$. Aldehydes reduce this to metallic silver, forming a silver mirror on the glass surface.



ALDEHYDE

Colourless → Silver mirror (or grey silver precipitate)



KETONE

Solution remains colourless: no reaction