

Analytical techniques A2

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Read first: [An introduction to AS Level organic chemistry](#), [An introduction to A Level organic chemistry](#)

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What you need to know

This topic has two halves: **chromatography**, which separates a mixture and tells you what is in it and how much, and **NMR spectroscopy**, which tells you how the atoms in one compound are joined. You should be able to:

1. **Thin-layer chromatography (TLC): the words.** Explain the **stationary phase** (a thin layer of a solid such as aluminium oxide on a glass, plastic or metal backing), the **mobile phase** (a solvent, which may be polar or non-polar), the **baseline** (where the spots start), the **solvent front** (how far the solvent got) and the R_f value.
2. **Use R_f values:** calculate them and use them to identify the substances in a mixture.
3. **Explain why substances have different R_f values,** in terms of how strongly each is attracted to the stationary phase and how soluble it is in the mobile phase.
4. **Gas/liquid chromatography (GLC): the words.** Explain the stationary phase (a non-polar liquid with a high boiling point, coated on a solid support), the mobile phase (an unreactive gas) and **retention time**.
5. **Read a gas/liquid chromatogram** to find the percentage composition of a mixture from its peak areas.
6. **Explain retention times** in terms of how strongly each substance interacts with the stationary phase.
7. **Carbon-13 NMR:** use a spectrum of a simple molecule to find how many different carbon environments it has and what kinds they are, and so suggest possible structures; predict or explain the number of peaks for a given molecule.
8. **Proton (^1H) NMR:** use a spectrum to find (a) the proton environments, from chemical shifts; (b) the relative numbers of each kind of proton, from relative peak areas; (c) how many hydrogens are on the neighbouring carbon, from the splitting pattern and the $n + 1$ rule (singlet, doublet, triplet, quartet and multiplet only); and (d) possible structures.
9. **Predict the chemical shifts and splitting patterns** of the protons in a given molecule.
10. **Describe why tetramethylsilane (TMS) is the standard** for chemical shifts.
11. **State why deuterated solvents such as CDCl_3 are needed** for proton NMR.
12. **Describe how D_2O identifies O–H and N–H protons** by proton exchange.

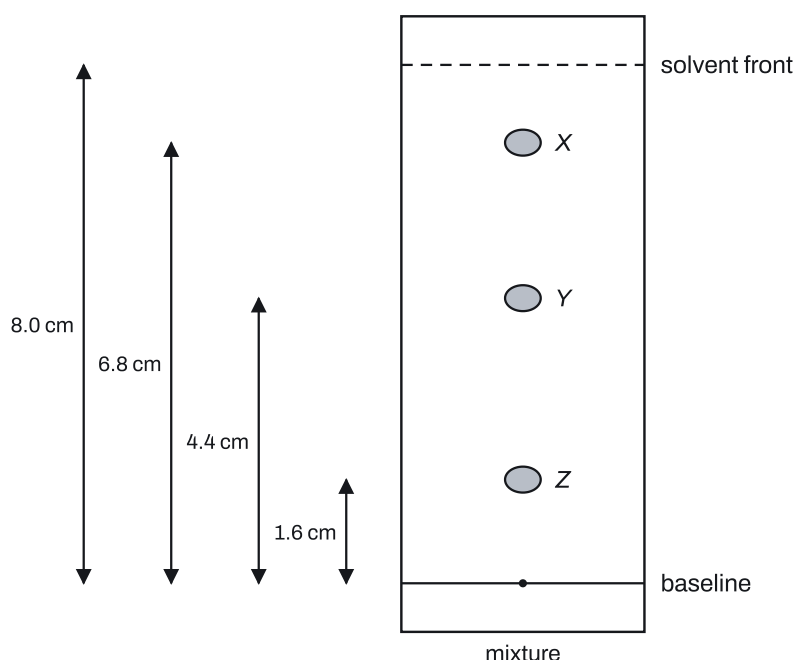
Infrared spectroscopy and mass spectrometry are AS topics. Electrophoresis belongs with amino acids (nitrogen compounds) and partition coefficients with equilibria, even when they appear in the same exam question as chromatography.

Understand it

How chromatography separates things

Every kind of chromatography has two phases. The **stationary phase** stays put; the **mobile phase** flows past it and carries the mixture along. Each substance in the mixture is constantly moving between the two: sticking to (or dissolving in) the stationary phase, then going back into the mobile phase and moving on. A substance that is **attracted more strongly to the stationary phase** spends more of its time there, so it moves more slowly. A substance that is **more soluble in the mobile phase** spends more time moving. Different substances travel at different speeds, so they separate.

Thin-layer chromatography



The stationary phase is a thin layer of a solid, such as **aluminium oxide** (or silica), on a flat backing. Its surface is **polar**: it is covered with oxygen atoms and O–H groups, so polar molecules are held to it by hydrogen bonds and dipole attractions. This holding on to a surface is called **adsorption**.

1. Draw a **baseline** in pencil about 1 cm from the bottom. Pencil (graphite) does not dissolve and move, but ink would.
2. Put a small spot of each sample on the baseline, including known substances for comparison.
3. Stand the plate in a covered beaker of solvent, the **mobile phase**, with the solvent level **below** the baseline, so the spots are not washed off into the solvent.
4. The solvent rises up the plate. Take the plate out before the solvent reaches the top and mark the **solvent front** straight away, before it evaporates.
5. Make colourless spots visible, for example under an ultraviolet lamp or with a locating agent.

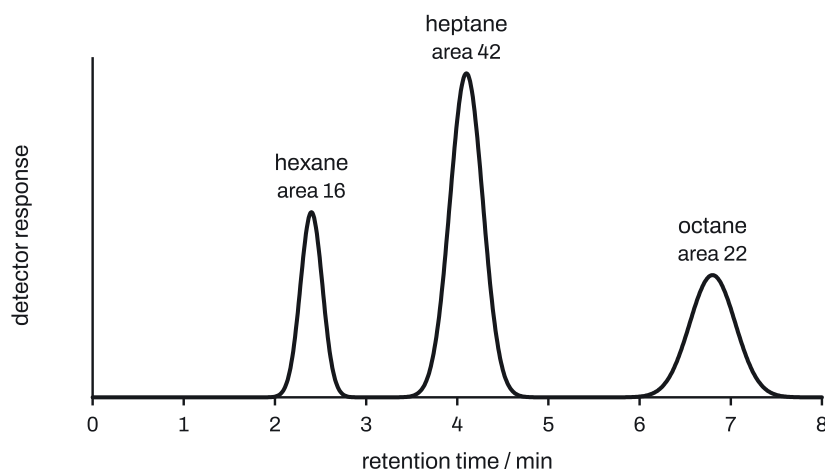
The R_f **value** compares how far a spot moved with how far the solvent moved, both measured from the baseline:

$$R_f = \frac{\text{distance moved by the spot}}{\text{distance moved by the solvent front}}$$

It has no units and is always between 0 and 1. On the plate above, spot Y has $R_f = \frac{4.4}{8.0} = 0.55$. For one compound, one stationary phase, one solvent and one temperature, R_f is always the same, so an unknown spot is identified by matching its R_f with a known substance's, ideally run on the same plate. Two different compounds can have the same R_f in one solvent by chance; matching in two different solvents is much stronger evidence.

Why R_f values differ. A **small R_f** means the substance is attracted strongly to the stationary phase (it is polar, or can hydrogen bond to the aluminium oxide) and/or is not very soluble in the mobile phase. A **large R_f** means weak attraction to the stationary phase and/or high solubility in the mobile phase. A spot that stays on the baseline is held very tightly or does not dissolve in the solvent at all. Changing the solvent changes the balance: a more polar solvent dissolves polar substances better and competes with them for the surface, so they move further; ions and very polar compounds hardly move in a non-polar solvent.

Gas/liquid chromatography



In GLC the **mobile phase is an unreactive gas** (the carrier gas), such as nitrogen or helium. The **stationary phase is a non-polar liquid with a high boiling point**, coated on to fine solid particles packed in (or lining) a long, thin column inside an oven. The liquid must have a high boiling point so it does not boil away and get carried off with the gas.

A tiny sample is injected, turns into vapour and is carried through the column. Each component keeps dissolving in the liquid and coming back out into the gas. At the end, a detector records each component as a peak.

- The **retention time** is the time from **injection** to **detection** of a component: how long it takes to pass through the column.

- A component with **stronger interactions (intermolecular forces) with the stationary phase** spends longer dissolved in the liquid and has a **longer retention time**. With a non-polar stationary phase, the forces are mainly instantaneous dipole–induced dipole forces, so larger molecules (more electrons, more contact) are held longer. These are also the less volatile ones with the higher boiling points.
- A component is identified by comparing its retention time with a known substance's under **the same conditions** (same column, temperature and gas flow rate).
- The **area** under each peak is proportional to the amount of that component (questions tell you when the area is proportional to the mass). So

$$\text{percentage of a component} = \frac{\text{area of its peak}}{\text{total area of all the peaks}} \times 100.$$

On the chromatogram above, the total area is $16 + 42 + 22 = 80$, so hexane is $\frac{16}{80} \times 100 = 20.0\%$ of the mixture.

What NMR measures

Some nuclei, including ^1H and ^{13}C , behave like tiny magnets. In a strong magnetic field they absorb radio waves of a particular frequency. The exact frequency depends on the electrons around each nucleus: an electronegative atom nearby (O, N, a halogen) or a C=O group or benzene ring pulls electron density away, and the peak moves to a **higher chemical shift**, δ , measured in ppm. Nuclei in the same surroundings, the same **environment**, absorb at the same δ and give one peak. Nuclei in different environments give different peaks. The Data Booklet gives typical shift ranges for each kind of environment.

TMS, tetramethylsilane $\text{Si}(\text{CH}_3)_4$, is added as the **reference**: its peak is defined as $\delta = 0$ and every other shift is measured from it. It is a good standard because all 12 of its hydrogens (and all 4 carbons) are in one environment, so it gives a **single, strong, sharp peak**; that peak is at a lower shift than almost every organic compound, so it is out of the way at the right-hand edge; and TMS is unreactive and volatile, so it is easy to remove afterwards. In a spectrum, the small peak at $\delta = 0$ is TMS.

Deuterated solvents. The sample is dissolved in a solvent with no ordinary hydrogen atoms, such as CDCl_3 (deuterium, D, is ^2H). There is far more solvent than sample, so a solvent containing ^1H , like CHCl_3 , would give a huge peak that could hide the sample's peaks. Deuterium does not absorb in the proton spectrum, so CDCl_3 gives no peak there. D_2O is used for compounds that dissolve in water.

Carbon-13 NMR: counting environments

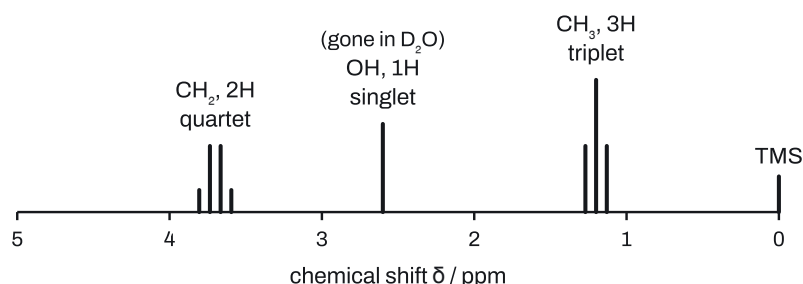
In the carbon-13 spectra you meet, **each carbon environment gives one peak** (a single line, no splitting). So the number of peaks is the number of **different** carbon environments. Carbons are in the same environment when the molecule's symmetry swaps them: they are joined to identical groups in identical ways.

- $\text{CH}_3\text{CH}_2\text{OH}$: 2 peaks. Propanone, CH_3COCH_3 : 2 peaks (the two CH_3 are identical). 2-methylpropan-2-ol, $(\text{CH}_3)_3\text{COH}$: 2 peaks. Butan-2-ol, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$: 4 peaks (the two CH_3 are **not** the same: one is next to CH_2 , the other next to CHOH).

- **Benzene rings.** Benzene itself has 1 peak. With **one** group on the ring there are **4** ring environments: the carbon holding the group, the two next to it, the two after that, and the one opposite. With **two identical** groups: 1,4 gives **2** ring environments, 1,2 gives **3**, 1,3 gives **4**. With **two different** groups: 1,4 gives **4**, while 1,2 and 1,3 give **6** (no symmetry left). Then add the carbons in the groups.

The **chemical shift** of each peak tells you what kind of carbon it is (Data Booklet): 0–50 for alkyl carbons, 50–70 for a carbon joined to oxygen, 110–160 for alkene and benzene-ring carbons, 160–185 for the C=O of acids and esters, 190–220 for the C=O of aldehydes and ketones. Peak **heights** in carbon-13 spectra do not tell you how many carbons there are, so use only the number and positions of the peaks.

Proton NMR: four pieces of information



Each peak in a proton spectrum gives four things.

1. **Number of peaks = number of proton environments.** All the hydrogens on one carbon are usually in the same environment, and so are hydrogens on carbons that symmetry swaps. Ethanol has 3: CH₃, CH₂ and OH.
2. **Chemical shift = kind of environment**, read from the Data Booklet table. In ethanol the CH₂ is next to oxygen, so it is at 3.2–4.0 (here 3.7); the CH₃ is a plain alkyl group, 0.9–1.7 (here 1.2). O–H and N–H peaks can be almost anywhere in their range, because they depend on the solvent and concentration.
3. **Relative peak area = relative number of hydrogens.** The areas of the ethanol peaks are in the ratio 2 : 1 : 3. The spectrum may show this as numbers, or as an **integration trace** whose step heights are in the same ratio. The ratio gives the simplest whole numbers; scale it to the total number of H in the molecular formula.
4. **Splitting pattern = number of hydrogens on the neighbouring carbon(s).** A peak is split by the hydrogens on the **adjacent** carbon atoms. If there are n of them, the peak splits into $n + 1$ lines (the $n + 1$ rule):

H on adjacent carbons, n	Lines, $n + 1$	Name	Line heights
0	1	singlet	1
1	2	doublet	1 : 1
2	3	triplet	1 : 2 : 1
3	4	quartet	1 : 3 : 3 : 1
4 or more	5 or more	multiplet	

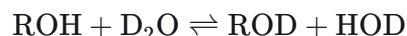
In ethanol, the CH_3 has a CH_2 next door ($n = 2$), so it is a **triplet**; the CH_2 has a CH_3 next door ($n = 3$), so it is a **quartet**. A **triplet and quartet with areas 3 : 2** is the fingerprint of an ethyl group, CH_3CH_2- . Similarly, a **doublet of area 6** with a **multiplet of area 1** shows $(\text{CH}_3)_2\text{CH}-$, as in 2-chloropropane.

Rules that go with it:

- Only hydrogens on **neighbouring carbons** count. Hydrogens on the same carbon, or equivalent hydrogens, do not split each other.
- Add up the hydrogens on **all** the neighbouring carbons. The CH_2 in the middle of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ has $3 + 2 = 5$ neighbours: a multiplet.
- **O–H and N–H protons** show as singlets and do not split their neighbours (they swap between molecules too fast). So the CH_2 of ethanol is a quartet, not split further by the OH.
- A carbon with **no hydrogens** next door gives a **singlet**: CH_3 joined to $\text{C}=\text{O}$, to O, to a benzene ring carbon, or to a carbon with no H, as in $(\text{CH}_3)_3\text{C}-$. An aldehyde H next to a carbon with no H is also a singlet.
- The hydrogens on a benzene ring appear at 6.0–9.0. Count the ring-hydrogen environments like the ring carbons; exam questions often tell you to treat them as one peak, and ring hydrogens do not split alkyl groups on the ring (the CH_2 of ethylbenzene, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$, is a quartet).

Finding O–H and N–H protons with D_2O

Because O–H and N–H peaks can be anywhere in a wide range, they are hard to pick out. Shake the sample with a little D_2O (or use D_2O as the solvent) and record the spectrum again. The O–H and N–H hydrogens swap with deuterium:



Deuterium gives no peak in a proton spectrum, so **the O–H and N–H peaks disappear**. The C–H peaks are unchanged, because C–H hydrogens do not exchange. In the ethanol spectrum above, the singlet at 2.6 would vanish. A compound with no O–H or N–H (a hydrocarbon, ketone, ester or ether) gives **exactly the same spectrum** with and without D_2O .

Key facts and formulas

"Given" means it is in the Data Booklet (and the shift tables are often printed in the question too). "Learn it" means you must remember it.

Formula	Status
Proton (^1H) NMR chemical shift ranges for each environment, relative to TMS	Given
Carbon-13 NMR chemical shift ranges for each environment, relative to TMS	Given
$R_f = \frac{\text{distance moved by the spot}}{\text{distance moved by the solvent front}}$, both from the baseline	Learn it

Formula	Status
Retention time = time from injection to detection	Learn it
Percentage of a component = $\frac{\text{its peak area}}{\text{total peak area}} \times 100$	Learn it
TLC: stationary phase aluminium oxide (or silica) on a support; mobile phase a polar or non-polar solvent	Learn it
GLC: stationary phase a high-boiling non-polar liquid on a solid support; mobile phase an unreactive gas (N ₂ , He)	Learn it
n hydrogens on adjacent carbons $\Rightarrow n + 1$ lines: singlet, doublet, triplet, quartet, then multiplet	Learn it
Relative peak areas = ratio of numbers of hydrogens	Learn it
TMS, Si(CH ₃) ₄ , defines $\delta = 0$	Learn it
ROH + D ₂ O $\rightleftharpoons$ ROD + HOD: O–H and N–H peaks disappear	Learn it

Shift ranges worth knowing by sight (they are given, but recognising them saves time): proton 0.9–1.7 alkyl, 2.2–3.0 next to C=O, 2.3–3.0 next to a ring, 3.2–4.0 next to O or Cl, 6.0–9.0 on a ring, 9.3–10.5 aldehyde, 9.0–13.0 carboxylic acid; carbon-13 50–70 C–O, 110–160 ring or alkene, 160–185 acid or ester C=O, 190–220 aldehyde or ketone C=O.

How to do it

In the Paper 4 questions we have tagged for this topic (53 questions, 2021–2025), the types came up this often. 40 of the 53 questions mix types, so the counts add up to more than 53.

Question type	Questions
Predict or count the peaks in a carbon-13 NMR spectrum	31
Complete a proton NMR table or assign peaks	23
Use D ₂ O exchange to spot O–H and N–H protons	17
Predict the number of proton peaks and their splitting for given structures	16
Define chromatography terms	12
Deduce a structure from NMR spectra and other data	10
State and explain the NMR solvent and standard	10
Explain a splitting pattern with the $n + 1$ rule	10

Question type	Questions
Calculate percentage composition from GLC peak areas	8
Explain differences in R_f values or retention times	6
Identify a substance from TLC R_f values or reference spots	3

1. Predict or count the peaks in a carbon-13 NMR spectrum (31 questions)

1. Draw or picture the full structure, with every carbon.
2. **Look for symmetry.** Is there a mirror line through the molecule? Identical groups on the same carbon, such as the two CH_3 in $(\text{CH}_3)_2\text{CH}-$ or the three in $(\text{CH}_3)_3\text{C}-$, are one environment.
3. **Rings:** use the counts in "Understand it" (one group: 4; two identical groups 1,2 / 1,3 / 1,4: 3 / 4 / 2; two different groups: 4 for 1,4, else 6). A ring that has three or more groups needs checking carbon by carbon.
4. Count the carbons in each different environment once, and add up.

For example, ethylbenzene has 4 ring environments plus CH_2 and CH_3 : **6 peaks**.

Variations you will meet:

- **A large molecule** (a drug or dye): work round it systematically, ticking off each carbon. If it has no symmetry, the answer is simply the number of carbons.
- **"Explain" the number:** say which carbons are equivalent and why ("all the carbon atoms are in the same environment because the molecule is symmetrical").
- **Peaks with shift ranges:** give the number of peaks in each range from the Data Booklet, for example "4 peaks in 110–160 (ring) and 1 in 0–50".
- **Telling isomers apart:** work out the count for each; the isomers can be distinguished if the counts differ.
- **Read the count off a printed spectrum:** count the lines, ignoring the TMS line at 0 and any solvent line if the question mentions one.
- **Draw an isomer with a given number of peaks:** try the most symmetrical arrangements first (1,4 on a ring, branched chains).

2. Complete a proton NMR table or assign peaks (23 questions)

1. Draw the structure (or deduce it first if the question asks). Label each proton environment.
2. For each environment, fill every column the table asks for:
 - **chemical shift:** the Data Booklet range for that environment (or the value read from the spectrum);
 - **number of H:** how many hydrogens are in that environment (from the structure or the relative peak area);
 - **number of H on adjacent carbons, n ;**
 - **splitting pattern:** $n + 1$ lines, named;
 - **group responsible:** CH_3 , CH_2 , CH , OH , ring H and so on.
3. **Check:** the numbers of H add up to the molecular formula's total, and each peak's shift matches its group.

Variations you will meet:

- **Only the shifts are given:** match each shift to an environment with the table, then fill in the rest.
- **Lettered protons on a structure** ("which protons are a triplet / have the lowest shift / are at 6.0–9.0?"): answer each part with the letters that fit.
- **Count the hydrogens in a range of δ** , for example "how many H could give peaks between 6.5 and 13.0?": go through the molecule group by group, decide which Data Booklet range each hydrogen belongs to (ring H 6.0–9.0, COOH 9.0–13.0, amide NH 5.0–12.0 and so on) and add up only those that fall in the range. An alcohol OH (0.5–6.0) does not count for 6.5–13.0.
- **Explain a shift:** a CH_3 at 1.1 is a plain alkyl group, not next to O or C=O.
- **A CH with many neighbours** (for example $(\text{CH}_3)_2\text{CH} - \text{O}$) is a **multiplet**.

3. Use D_2O exchange to spot O–H and N–H protons (17 questions)

1. Find every O–H and N–H in the molecule: alcohol, phenol, carboxylic acid, amine, amide.
2. Say **which peak(s) disappear** (give the shift or the group), or **how many hydrogens give no peak**.
3. Give the reason: **the O–H/N–H hydrogen exchanges with deuterium**, and D does not give a peak.

Variations you will meet:

- **No O–H or N–H** (a hydrocarbon, ketone, ester, ether): "no difference, because there are no hydrogens that can exchange with deuterium". This is a favourite trap.
- **Tick the peaks still present in D_2O :** all the C–H peaks.
- **Count the peaks in D_2O :** count the C–H environments only.
- **Why is the sample dissolved in D_2O ?** To remove the O–H/N–H peaks, identifying them (and because D_2O itself gives no peak).

4. Predict the number of proton peaks and their splitting for given structures (16 questions)

1. Count the proton environments (each different CH_3 , CH_2 , CH, OH, NH, ring-H set).
2. For each C–H environment, count n on the adjacent carbons and name the pattern. O–H and N–H are singlets.
3. List the patterns asked for.

For example, 2-chloropropane, $(\text{CH}_3)_2\text{CHCl}$, has 2 peaks: a doublet (6H) and a multiplet (1H).

Variations you will meet:

- **"Which of these isomers shows a doublet / a singlet / a triplet?":** a doublet needs a CH next door (often an isopropyl group); a singlet needs a group with no H next door ($\text{CH}_3\text{CO}-$, $\text{CH}_3\text{O}-$, $(\text{CH}_3)_3\text{C}-$, OH); a triplet needs a CH_2 next door.
- **Unusual ring or cage structures:** use symmetry exactly as for carbon-13; hydrogens on carbons that symmetry swaps are one environment.

- **Both spectra in one table:** count carbon-13 peaks and proton peaks separately; they are often different numbers.

5. Define chromatography terms (12 questions)

- **R_f value:** the distance moved by the spot (component) divided by the distance moved by the solvent front, both from the baseline.
- **Retention time:** the time between injection of the sample and detection of the component.
- **TLC phases:** stationary, aluminium oxide or silica (on a solid support); mobile, a named solvent or "a polar (or non-polar) solvent".
- **GLC phases:** stationary, a non-polar liquid with a high boiling point (on a solid support); mobile, an unreactive gas such as nitrogen or helium.

These are usually one mark each, often as a two-row table.

6. Deduce a structure from NMR spectra and other data (10 questions)

1. **Molecular formula:** note the number of C and H.
2. **Carbon-13:** number of peaks = carbon environments; shifts show C=O (and which kind), ring carbons, C–O.
3. **Proton:** for each peak, write down the group from the shift, the number of H from the area (scaled to the formula's H), and the neighbours from the splitting.
4. **D₂O or chemical tests:** loss of a peak means O–H/N–H; no loss means none. A test such as a yellow precipitate with alkaline iodine (CH₃CO– or CH₃CH(OH)–) or fizzing with Na₂CO₃ (COOH) adds another group.
5. **Join the pieces** into a structure, then **check every piece of data** against it, including symmetry for the number of carbon peaks.

Variations you will meet:

- **Choose from a list of isomers:** work out each isomer's pattern (peaks, splitting, areas) and pick the one that matches. Two singlets and nothing else, for instance, means no two neighbouring carbons both carry H.
- **"Explain your reasoning":** write linked statements, each **evidence** → **feature**, for example "the peak at δ 205 in the carbon-13 spectrum shows a ketone C=O"; "two peaks lost in D₂O show two O–H groups".

7. State and explain the NMR solvent and standard (10 questions)

- **Standard:** TMS, tetramethylsilane, Si(CH₃)₄; the reference at $\delta = 0$. The small peak at 0 in a spectrum is TMS.
- **Solvent:** CDCl₃ (or D₂O). Reason: it has no ¹H atoms, so it gives **no peak** and does not interfere with (hide) the sample's peaks, whereas CHCl₃ would give a peak.

8. Explain a splitting pattern with the $n + 1$ rule (10 questions)

1. **Name** the pattern.
2. Give the **number of hydrogens on the adjacent carbon(s)** and which group they are on: "triplet, because there are 2 H on the neighbouring carbon (the CH_2 group)".

Saying "because of the $n + 1$ rule" without the number of neighbouring H does not score. You may be asked to mark the protons responsible for a peak on a structure: label the hydrogens of that group, not its neighbours.

9. Calculate percentage composition from GLC peak areas (8 questions)

1. Add up **all** the peak areas.
2. Divide the one you want by the total and multiply by 100: peaks of area 12, 30 and 18 give $\frac{12}{60} \times 100 = 20.0\%$ for the first.
3. Give 3 significant figures.

Variations you will meet:

- **Describe the method** in words: "area of that peak divided by the total area of all the peaks, times 100".
- **Scale from one component to another:** if the areas are proportional to mass, the mass (or concentration) of each component is proportional to its area, so mass of B = mass of A $\times \frac{\text{area of B}}{\text{area of A}}$; divide by M_r to get moles if asked.
- **Mass of a component in a sample:** its fraction of the total area times the sample's mass.

10. Explain differences in R_f values or retention times (6 questions)

- **Larger R_f :** the substance is **more soluble in the mobile phase** and/or **less strongly adsorbed to (attracted to) the stationary phase**. Say why from the structure, for example "it has no O–H group, so it forms no hydrogen bonds with the aluminium oxide".
- **Longer retention time:** the substance is **attracted more strongly to the stationary phase** (stronger intermolecular forces with the liquid), so it spends longer dissolved in it.
- **Change of solvent:** a less polar solvent carries polar substances and ions less far, because they are less soluble in it.

11. Identify a substance from TLC R_f values or reference spots (3 questions)

1. Measure the unknown spot's distance and the solvent front's distance from the baseline, and calculate R_f .
2. Match it to the value in the table, or to the reference spot at the same height on the same plate.
3. With two solvents, the answer is the reference that matches the unknown **in both**: say that the others match in one solvent at most.

Worked examples

The bold codes show where marks are earned, as in Cambridge mark schemes. The number is how many marks.

- **M1** method mark: for a correct method, even if the numbers slip.
 - **A1** accuracy mark: for a correct answer; it needs the M mark before it.
 - **B1** mark for a correct result on its own, with no method needed.
-

Example 1

A mixture of naphthalene (a hydrocarbon, $C_{10}H_8$), methyl benzoate (an ester, $C_6H_5COOCH_3$) and phenylmethanol (an alcohol, $C_6H_5CH_2OH$) is spotted on an aluminium oxide TLC plate and developed with a fairly non-polar solvent. Three spots, **X**, **Y** and **Z**, are seen. The plate is the first diagram in "Understand it".

- (a) Calculate the R_f values of **X**, **Y** and **Z**. **[2]**
- (b) Identify **X**, **Y** and **Z**. Explain the order of the spots in terms of the stationary and mobile phases. **[3]**
- (c) Explain why the baseline is drawn in pencil and must be above the level of the solvent. **[2]**

(a) **X**: $\frac{6.8}{8.0} = 0.85$; **Y**: $\frac{4.4}{8.0} = 0.55$; **Z**: $\frac{1.6}{8.0} = 0.20$. **B1** for any two, **B1** for all three.

(b) **X** is naphthalene, **Y** is methyl benzoate and **Z** is phenylmethanol. **B1** The aluminium oxide surface is polar. Phenylmethanol's O–H group forms **hydrogen bonds** with it, so it is adsorbed most strongly and moves least. **B1** Methyl benzoate is polar (C=O and C–O bonds) but has no O–H, so it is held by weaker dipole attractions and moves further; naphthalene is non-polar, is hardly adsorbed and is the most soluble in the non-polar mobile phase, so it moves furthest. **B1**

(c) Pencil (graphite) does not dissolve in the solvent, so it does not move and add spots of its own; ink would. **B1** If the solvent covered the baseline, the samples would dissolve into the solvent in the beaker instead of travelling up the plate. **B1**

Example 2

A bottle of solvent sold as heptane is checked by gas/liquid chromatography, using a non-polar stationary phase. The chromatogram is the second diagram in "Understand it": peaks at 2.4, 4.1 and 6.8 minutes with areas 16, 42 and 22. Pure heptane, run separately, has a retention time of 4.1 minutes. The area of each peak is proportional to the mass of that substance.

- (a) Explain why the pure heptane must be run on the same column under the same conditions, and identify the heptane peak. **[2]**
- (b) The other two peaks are from hexane and octane. Identify which is which, and explain your answer in terms of the stationary phase. **[2]**

(c) Calculate the percentage by mass of heptane in the solvent. **[1]**

(d) Calculate the mass of octane in a 3.20 g sample of the solvent. **[1]**

(a) A retention time depends on the column, the temperature and the gas flow rate, so it can only be compared with a known substance's under identical conditions. **B1** The heptane peak is the one at 4.1 minutes, the same retention time as pure heptane. **B1**

(b) Hexane is at 2.4 minutes and octane at 6.8 minutes. **B1** Octane has the longest chain, so the most electrons and the largest surface: it has the strongest instantaneous dipole–induced dipole forces with the non-polar stationary liquid, is attracted most strongly to the stationary phase and spends longest dissolved in it. Hexane has the weakest forces. **B1**

(c) Total area = $16 + 42 + 22 = 80$. Heptane = $\frac{42}{80} \times 100 = 52.5\%$. **B1**

(d) Octane is $\frac{22}{80}$ of the mass: $\frac{22}{80} \times 3.20 = 0.880$ g. **B1**

Example 3

Butanone, $\text{CH}_3\text{CH}_2\text{COCH}_3$, is reduced with NaBH_4 to butan-2-ol, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$. A chemist uses NMR to check that the reduction has worked.

(a) State the number of peaks in the carbon-13 spectrum of each compound, and describe one difference between the two spectra that shows the reaction has happened. **[3]**

(b) Complete a table for the proton NMR spectrum of butan-2-ol in CDCl_3 , giving the chemical shift range, the number of H and the splitting pattern for each peak. **[4]**

(c) In butanone, the peak for the CH_3 group on the $\text{C}=\text{O}$ carbon is a singlet. Explain why the peak for the same CH_3 group in butan-2-ol is a doublet. **[2]**

(d) Describe and explain how the proton spectrum of butan-2-ol changes when it is shaken with D_2O . **[2]**

(a) Both have **4** peaks: all four carbons are in different environments in each. **B1 B1** Butanone has a peak at 190–220 (ketone $\text{C}=\text{O}$); butan-2-ol has no peak there but has a peak at 50–70 instead (carbon joined to O). **B1**

(b) **B1** for every 3 correct cells, up to **[4]**:

Group	δ / ppm	Number of H	Splitting
CH_3 at the end ($\text{CH}_3\text{--CH}_2$)	0.9–1.7	3	triplet
CH_2	0.9–1.7	2	multiplet
CH (joined to O)	3.2–4.0	1	multiplet
CH_3 on the CHOH	0.9–1.7	3	doublet
OH	0.5–6.0	1	singlet

The CH_2 has $3 + 1 = 4$ neighbouring H and the CH has $2 + 3 = 5$, so both are multiplets. The numbers of H add up to 10, as in $\text{C}_4\text{H}_{10}\text{O}$.

(c) In butanone the neighbouring carbon is the $\text{C}=\text{O}$ carbon, which has no H, so $n = 0$: a singlet. **B1** In butan-2-ol the neighbouring carbon is the CH, with **1 H**, so the peak splits into $1 + 1 = 2$ lines: a doublet. **B1**

(d) The OH singlet **disappears**. **B1** The OH hydrogen **exchanges with deuterium** ($\text{ROH} + \text{D}_2\text{O} \rightleftharpoons \text{ROD} + \text{HOD}$), and D gives no peak in a proton spectrum; the C–H peaks do not change. **B1**

Example 4

Compound **W**, $\text{C}_8\text{H}_{10}\text{O}$, contains a benzene ring.

- Its carbon-13 spectrum has **6** peaks: four in the range 110–160, one in the range 50–70 and one in the range 0–50.
- Its proton spectrum in CDCl_3 has peaks at δ 6.8–7.3 (ring hydrogens), a quartet at δ 4.0 and a triplet at δ 1.4. The steps on the integration trace for these three are 25 mm, 10 mm and 15 mm high respectively.
- Its proton spectrum is unchanged when it is shaken with D_2O .

(a) Use the integration trace to find the number of hydrogens responsible for each signal. **[2]**

(b) State what the result with D_2O tells you about **W**. **[1]**

(c) Deduce the structure of **W**. Explain how each piece of evidence fits your structure. **[4]**

(d) A student suggests that **W** is 4-ethylphenol, $\text{HOC}_6\text{H}_4\text{CH}_2\text{CH}_3$. Give two pieces of evidence that rule this out. **[2]**

(a) $25 : 10 : 15 = 5 : 2 : 3$. **M1** This adds up to 10, the number of H in $\text{C}_8\text{H}_{10}\text{O}$, so 5 H are on the ring, 2 H give the quartet and 3 H the triplet. **A1**

(b) No peak disappears, so **W** has no O–H: it is not a phenol or an alcohol, so the oxygen must be in an ether, C–O–C. **B1**

(c) **W** is **ethoxybenzene**, $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$. **B1** Any three of these linked statements, **B1** each:

- **5 ring hydrogens** means only one group is attached to the ring: C_6H_5- .
- The **triplet (3H)** and **quartet (2H)** are an ethyl group, CH_3CH_2- : the CH_3 has 2 H next door, the CH_2 has 3.
- The quartet is at δ **4.0**, in the range 3.2–4.0, so the CH_2 is joined to O, not to the ring (2.3–3.0): $-\text{OCH}_2\text{CH}_3$.
- Carbon-13: a ring with one group has **4** ring environments (110–160), the CH_2 joined to O is at 50–70 and the CH_3 at 0–50: 6 peaks in all.

(d) Any two, **B1** each: 4-ethylphenol has an O–H, whose peak would disappear with D₂O; its CH₂ is joined to the ring, so its quartet would be at 2.3–3.0, not 4.0, and its carbon would be at 25–50, not 50–70; it has only 4 ring hydrogens (in two environments), not 5.

Common mistakes

- **A half-explained R_f or retention time.** "It is less soluble in the mobile phase" on its own is weak; examiners want the link to the phases and a reason from the structure: "it forms hydrogen bonds with the aluminium oxide, so it is adsorbed more strongly". For GLC, the reason is always the attraction to the **stationary** phase.
- **Not knowing the stationary phases.** Many candidates can name the TLC solvent but not the stationary phase. TLC: aluminium oxide or silica. GLC: a non-polar liquid with a high boiling point, not a solid and not a gas.
- **Miscounting carbon-13 peaks** in molecules with rings, by counting symmetrical carbons twice or missing that a ring with two different groups has lost its symmetry. Use the ring counts and check which side of the ring each group is on.
- **Leaving out the ring hydrogens**, or forgetting that they can be in more than one environment, when counting proton peaks.
- **Numbers of hydrogens that don't add up.** In a table, the total must equal the H in the molecular formula. Check before you move on.
- **Counting the wrong neighbours.** The $n + 1$ rule counts the H on the **adjacent** carbons, not on the carbon itself, and not O–H hydrogens. A CH between two CH₃ groups has 6 neighbours: a multiplet.
- **Swapping two environments with close shifts**, such as a CH₃ on a benzene ring (2.3–3.0) and a CH₂ next to C=O (2.2–3.0) or next to O (3.2–4.0). Look up each group in the table and use the peak areas and splitting to decide, rather than guessing from the order of peaks.
- **Missing the point of D₂O.** Some answers still include the O–H and N–H protons in a spectrum run in D₂O. Others say "the H exchanges with D" but never say that the **peak disappears**; both are needed.
- **"Duplet"** is not a word the mark scheme accepts: it is **doublet**. "Quadruplet" is accepted for quartet.
- **Using the wrong total for a percentage**, such as the tallest peak or only some of the peaks. Divide by the sum of all the areas.

How to get the marks

- **Definitions carry one mark each** and need both halves: R_f needs both distances (spot and solvent front); retention time needs both ends (injection and detection).
- **Name things fully.** "An unreactive gas" or "nitrogen" for the GLC mobile phase; "a non-polar liquid with a high boiling point" for its stationary phase; TMS or tetramethylsilane (or Si(CH₃)₄); CDCl₃ as the solvent.
- **"Explain" a difference** needs a comparison linked to the phases: "A has the larger R_f because it is more soluble in the mobile phase / less strongly adsorbed to the stationary phase".

- **NMR tables are marked by cells**, for example "any three [1], any six [2]... all eleven [4]". Fill in every cell; a blank cell is a lost cell. Use the names singlet, doublet, triplet, quartet, multiplet.
- **Chemical shifts**: give the Data Booklet range or a value inside it. When reading a printed spectrum, give the value at the peak.
- **Splitting explanations** need the name **and** the number of H on the adjacent carbon: "triplet AND 2 H on the neighbouring carbon".
- **D₂O answers** need what you see (the O–H/N–H peak disappears, or no change) **and** why (the H exchanges with D; or there is no H that can exchange).
- **Solvent answers**: "CDCl₃ gives no peak / does not interfere", compared with CHCl₃, which would give a peak.
- **Calculations**: show the total area; give percentages to 3 significant figures (at least 2 are needed).
- **Counting peaks** usually earns one mark per number with no working needed, but tables of several compounds are often "any two [1], all [2]", so check each one.
- **"Suggest a structure... explain your reasoning"**: each mark is for a piece of evidence linked to the feature it shows. Give the evidence (the shift, the splitting, the test result) and the conclusion in the same sentence.
- **Identify a compound from a list**: give its letter or name clearly; if asked to draw it, draw the full structure.

Quick check

1. In a TLC experiment, the solvent front is 6.5 cm above the baseline and a spot has an R_f value of 0.42. (a) How far did the spot travel? (b) What would it mean if a spot did not move off the baseline at all?
2. In gas/liquid chromatography, explain why (a) the stationary liquid must have a high boiling point and (b) the carrier gas must be unreactive.
3. State the number of peaks in the carbon-13 NMR spectrum of (a) cyclohexene; (b) cyclohexanone; (c) propane-1,3-diol, HOCH₂CH₂CH₂OH. Which of the three has a peak at 190–220?
4. Predict the proton NMR spectrum of 1,2-dichloroethane, ClCH₂CH₂Cl: the number of peaks, and the chemical shift range, splitting pattern and number of H. Explain why the peak is not split, even though each carbon has a neighbouring carbon carrying hydrogens. How many peaks are in its carbon-13 spectrum?
5. (a) Give two reasons why TMS is a suitable standard for NMR. (b) Each CDCl₃ molecule has a deuterium atom bonded to its carbon. Explain why CDCl₃ does not give a peak in a proton NMR spectrum, and why this matters.

Answers

1. (a) Distance = $R_f \times \text{solvent front} = 0.42 \times 6.5 = 2.73$ cm, about 2.7 cm. (b) The substance is held very strongly by the stationary phase and/or is insoluble in the mobile phase (or it may be an ionic compound in a non-polar solvent).
2. (a) The column is heated in an oven; a liquid with a low boiling point would evaporate and be carried out of the column with the gas, so the stationary phase would be lost (and would give peaks of its own). (b) The gas only carries the vapour through the column; it must not react with the components (or the stationary phase), or they would be changed before they reach the detector.
3. (a) **3**: by symmetry, the two C=C carbons are equivalent, so are the two CH₂ next to them, and so are the other two CH₂. (b) **4**: by symmetry, the C=O carbon, the two carbons next to it, the next two, and the one opposite. (c) **2**: the two CH₂OH carbons are equivalent, plus the middle CH₂. Only cyclohexanone, a ketone, has a peak at 190–220.
4. **1 peak**: all four hydrogens are in the same environment (the molecule is symmetrical), at 3.2–4.0 (next to Cl), a **singlet**, 4 H. The hydrogens on the neighbouring carbon are **equivalent** to the ones being looked at, and equivalent hydrogens do not split each other, so there is no splitting. Carbon-13: **1 peak**, as the two carbons are equivalent.
5. (a) Any two: all its hydrogens are in one environment, so it gives one strong, sharp peak; its peak is at a lower shift than almost all organic compounds, so it does not overlap theirs (it is defined as $\delta = 0$); it is unreactive; it is volatile, so it is easily removed. (b) The hydrogen in CDCl₃ is deuterium, ²H, which does not absorb in the proton NMR spectrum, and there is no ¹H in the molecule; so the solvent gives no peak that could hide the sample's.

Past questions to try

- **9701/43/O/N/22 Q9**: GLC phases and a percentage, carbon-13 counts for isomers, and two structures from proton spectra.
- **9701/42/M/J/22 Q7**: parts (a) and (b), the uses of TMS and D₂O, then proton and carbon-13 peak counts and splitting for isomers.
- **9701/42/F/M/24 Q6**: part (d), a proton NMR table for an amino acid and which peaks survive in D₂O.
- **9701/42/F/M/23 Q6**: parts (a) and (b), identifying ions on a TLC plate from R_f values and the effect of changing the solvent.