

Cambridge AS & A Level · Chemistry 9701 · Notes

Analytical techniques AS

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

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What you need to know

By the end of this topic you should be able to:

1. **Read an infrared spectrum of a simple molecule** and say which functional groups it has, using the table of infrared absorptions in the Data Booklet (it is also printed in the question).
2. **Read a mass spectrum** in terms of its m/e values and the abundances of the peaks, including peaks caused by isotopes. You don't need to know how a mass spectrometer works.
3. **Calculate the relative atomic mass, A_r , of an element** from the abundances of its isotopes or from its mass spectrum.
4. **Find the relative molecular mass of an organic molecule** from its molecular ion peak, M^+ .
5. **Suggest the formulae of fragment ions** made when a molecule breaks up in a given mass spectrum.
6. **Find the number of carbon atoms, n , in a compound** from the $[M + 1]^+$ peak, using $n = \frac{100 \times \text{abundance of } [M + 1]^+}{1.1 \times \text{abundance of } M^+}$.
7. **Show that a compound contains chlorine or bromine** from its $[M + 2]^+$ peak.

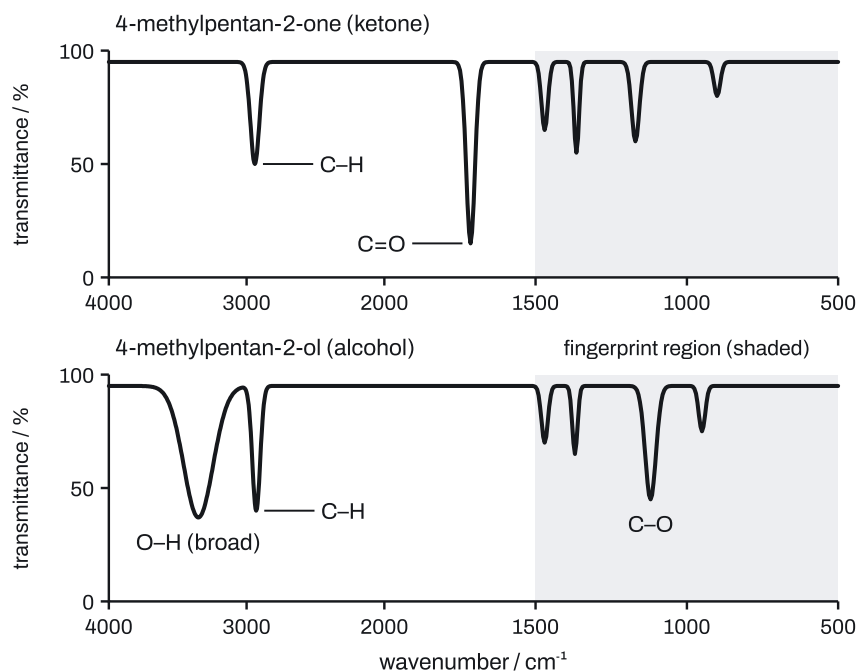
NMR spectroscopy (proton and carbon-13) is A Level only, and so is anything about how the machines work.

Understand it

Infrared spectroscopy: what the spectrum shows

The bonds in a molecule are always vibrating, stretching and bending like springs. Each kind of bond vibrates at its own frequency, which depends on the masses of the two atoms and the strength of the bond. When infrared radiation of exactly that frequency shines on the bond, the bond absorbs it.

An infrared spectrometer passes infrared through a sample and records how much gets through (the **transmittance**) at each frequency. Frequency is given as a **wavenumber** in cm^{-1} , running from 4000 on the left down to about 500 on the right. Wherever a bond absorbs, less radiation gets through, so the line **dips**. Those dips are the "peaks" or "absorptions".



The diagram shows two spectra. Reading them with the table below:

- **top, 4-methylpentan-2-one**, $(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_3$: the strong, sharp dip at 1715 cm^{-1} is **C=O** (carbonyl, 1670–1740); the dip near 2940 is C–H;
- **bottom, 4-methylpentan-2-ol**, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{OH})\text{CH}_3$: the broad, rounded dip centred near 3350 cm^{-1} is **O–H in an alcohol** (hydroxy, 3200–3600), and the strong dip near 1120 is **C–O** (1040–1300). There is no C=O dip.

The Data Booklet table

Bond	Functional groups containing the bond	Absorption range / cm^{-1}
C–O	hydroxy, ester	1040–1300
C=C	aromatic compound, alkene	1500–1680
C=O	amide	1640–1690
C=O	carbonyl, carboxyl	1670–1740
C=O	ester	1710–1750
$\text{C}\equiv\text{N}$	nitrile	2200–2250
C–H	alkane	2850–2950
N–H	amine, amide	3300–3500
O–H	carboxyl	2500–3000
O–H	hydroxy	3200–3600

(Some papers print the hydroxy range as 3200–3650, or C–H as 2850–3100. Always use the table printed in your question.)

Things worth knowing about the table:

- **Almost every organic molecule has C–H**, so a dip at 2850–2950 tells you nothing when you are choosing between organic compounds.
- **The two O–H bands look different.** In a carboxylic acid the O–H band is very broad and low (about 2500–3000) and often swallows the C–H band. In an alcohol it is a broad, rounded dip higher up, at 3200–3600. Both are broad because of hydrogen bonding between molecules.
- **C=O is the strongest, sharpest dip**, near 1700. The ranges for carbonyl, carboxyl and ester overlap, so the C=O dip alone rarely says which one it is. Look at the rest: C=O plus the broad 2500–3000 O–H means a carboxylic acid; C=O plus a strong C–O at 1040–1300 and **no** O–H means an ester; C=O with no O–H and no C–O means an aldehyde or ketone.
- **Below 1500 cm⁻¹ is the fingerprint region**: many overlapping dips that are unique to each compound. Apart from the C–O dip, questions usually ask you to use only absorptions **above** 1500 cm⁻¹.

Infrared spectroscopy in reactions

Because a reaction changes functional groups, it changes the spectrum. Absorptions from bonds that are destroyed **disappear**, and those from bonds that are made **appear**. For example, when ethyl pentanoate is hydrolysed by heating with dilute acid, the products are pentanoic acid and ethanol. Two new absorptions appear that the ester did not have: the very broad O–H of the acid at 2500–3000 and the broad O–H of the alcohol at 3200–3600. A C=O absorption is still there, now in the carboxyl range (1670–1740) rather than the ester range (1710–1750).

The same idea shows **purity**: if no absorption of a starting material's special bond is left, none of that starting material remains.

Mass spectrometry: what the spectrum shows

In a mass spectrometer, molecules (or atoms) lose one electron and become **positive ions**. The spectrum plots the **relative abundance** of each ion against its **mass-to-charge ratio**, m/e . The ions almost all have a charge of 1+, so m/e is simply the mass of the ion.

- **Elements**: each isotope gives its own peak, and the peak heights are the isotopes' abundances. So the spectrum of an element gives its A_r .
- **Molecules**: the whole molecule minus one electron is the **molecular ion**, M^+ . Its peak is the one with the highest m/e (apart from the small isotope peaks next to it), and its m/e is the **relative molecular mass**, M_r .
- Some molecular ions break apart. One bond breaks, giving a positive ion and a neutral **radical**. Only the **positive** fragment is detected, and it gives a **fragment peak**.

Relative atomic mass from a mass spectrum

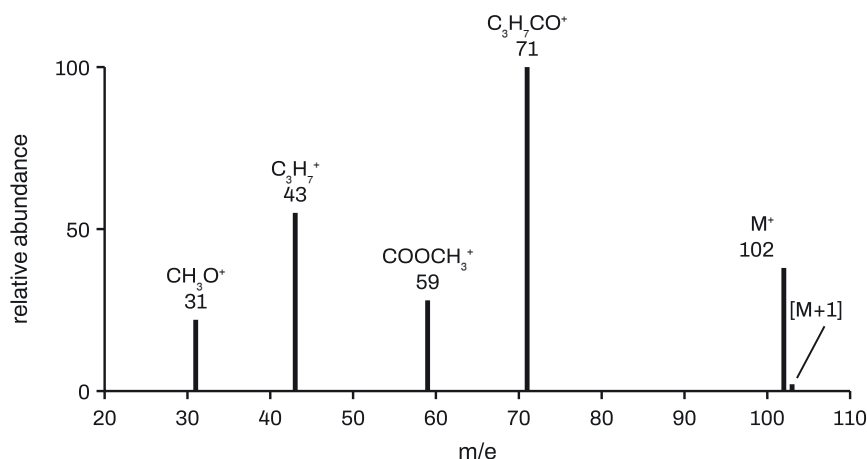
A_r is the weighted mean mass of the isotopes. Multiply each isotope's mass by its abundance, add them, and divide by the total abundance:

$$A_r = \frac{\sum(\text{isotope mass} \times \text{abundance})}{\sum \text{abundance}}$$

Copper has peaks at 63 (69.2%) and 65 (30.8%): $A_r = \frac{63 \times 69.2 + 65 \times 30.8}{100} = 63.6$ (1 d.p.). If the abundances are peak heights rather than percentages, divide by their total instead of 100.

Fragment peaks

The fragments come from breaking one single bond. Work out their mass from the formula, and always write a + **charge** on the ion.



In the spectrum of methyl butanoate, CH₃CH₂CH₂COOCH₃ ($M_r = 102$), each fragment peak matches one bond breaking: the bond between the C=O carbon and the OCH₃ oxygen gives C₃H₇CO⁺ at 71 (or CH₃O⁺ at 31), and the bond between the C₃H₇ and the C=O gives C₃H₇⁺ at 43 (or COOCH₃⁺ at 59).

Common fragments (using C = 12, H = 1, O = 16):

m/e	Fragment ions it could be
15	CH ₃ ⁺
17	OH ⁺ (from a compound with an O–H group)
29	C ₂ H ₅ ⁺ or CHO ⁺
31	CH ₃ O ⁺ or CH ₂ OH ⁺
43	C ₃ H ₇ ⁺ or CH ₃ CO ⁺
45	COOH ⁺ or C ₂ H ₅ O ⁺
57	C ₄ H ₉ ⁺ or C ₂ H ₅ CO ⁺

A fragment can also be named by what was lost: a peak at $M - 15$ means the molecule lost CH₃; $M - 17$ means it lost OH.

The [M+1] peak and the number of carbon atoms

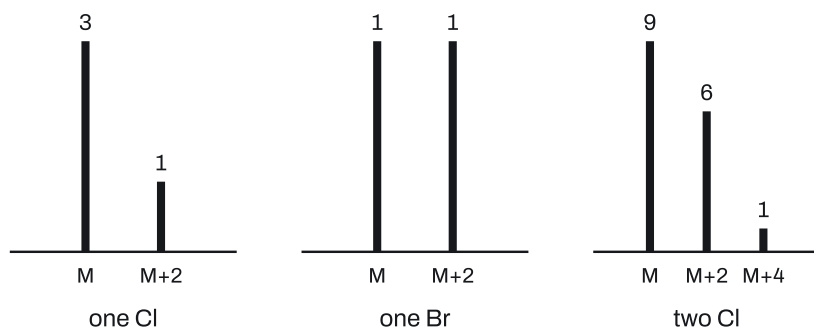
Carbon is mostly carbon-12, but 1.1% of carbon atoms are **carbon-13**. A molecule with one ^{13}C atom is one unit heavier, so there is a small peak at $M + 1$. The more carbon atoms a molecule has, the more likely one of them is ^{13}C : each carbon adds about 1.1% of the M^+ height to the $[M + 1]^+$ peak. So

$$\frac{\text{abundance of } [M + 1]^+}{\text{abundance of } M^+} = \frac{1.1 n}{100} \Rightarrow n = \frac{100 \times \text{abundance of } [M + 1]^+}{1.1 \times \text{abundance of } M^+}.$$

For methyl butanoate above: $n = \frac{100 \times 2.09}{1.1 \times 38.0} = 5.0$, so there are 5 carbon atoms. Round to the nearest whole number; real data give values like 5.96 or 6.04.

The [M+2] peak: chlorine and bromine

Chlorine has two isotopes, ^{35}Cl and ^{37}Cl , in the ratio about 3 : 1. Bromine has ^{79}Br and ^{81}Br in the ratio about 1 : 1. A molecule containing one of these atoms therefore has **two** molecular ion peaks, two units apart: M^+ (with the lighter isotope) and $[M + 2]^+$ (with the heavier one).



- $M : [M + 2] \approx 3 : 1$ **means one Cl atom**. A chlorine compound with M^+ abundance 12 has an $[M + 2]^+$ peak of about 4.
- $M : [M + 2] \approx 1 : 1$ **means one Br atom**. The two peaks are the same height.
- **Two Cl atoms** give three peaks, M , $M + 2$ and $M + 4$, in the ratio 9 : 6 : 1: the chances of $^{35}\text{Cl} + ^{35}\text{Cl}$, of one of each (two ways), and of $^{37}\text{Cl} + ^{37}\text{Cl}$ are $\frac{3}{4} \times \frac{3}{4}$, $2 \times \frac{3}{4} \times \frac{1}{4}$ and $\frac{1}{4} \times \frac{1}{4}$. Two Br atoms give 1 : 2 : 1.
- **One Cl and one Br** give M , $M + 2$ and $M + 4$ too. The middle peak is made two ways (^{37}Cl with ^{79}Br , and ^{35}Cl with ^{81}Br), so when asked for "the ions at each peak" list both.

The M_r of a halogen compound is taken from the M^+ peak, the one containing the lighter isotope, for example ^{35}Cl or ^{79}Br .

Which technique for which job

Job	Technique
Which functional groups are present	Infrared
Following a reaction, checking purity	Infrared

Job	Technique
A_r of an element, isotopes and their abundances	Mass spectrometry
M_r of a compound	Mass spectrometry (M^+ peak)
Number of carbon atoms	Mass spectrometry ($[M + 1]^+$ peak)
Whether Cl or Br is present	Mass spectrometry ($[M + 2]^+$ peak)
Which isomer (from how it breaks up)	Mass spectrometry (fragments)

Key facts and formulas

"Given" means it is in the Data Booklet (or printed in the question). "Learn it" means you must remember it.

Formula	Status
Table of characteristic infrared absorptions (bond, group, range in cm^{-1})	Given
Relative atomic masses (C = 12.0, H = 1.0, O = 16.0, Cl = 35.5, ...)	Given
$A_r = \frac{\sum(\text{isotope mass} \times \text{abundance})}{\sum \text{abundance}}$	Learn it
$n = \frac{100 \times \text{abundance of } [M + 1]^+}{1.1 \times \text{abundance of } M^+}$	Learn it
abundance of $[M + 1]^+ = \frac{1.1 n \times \text{abundance of } M^+}{100}$	Learn it
$^{35}\text{Cl} : ^{37}\text{Cl} \approx 3 : 1$, so one Cl gives $M : [M + 2] \approx 3 : 1$	Learn it
$^{79}\text{Br} : ^{81}\text{Br} \approx 1 : 1$, so one Br gives $M : [M + 2] \approx 1 : 1$	Learn it
Two Cl: $M : [M + 2] : [M + 4] \approx 9 : 6 : 1$; two Br: $1 : 2 : 1$	Learn it
m/e of $M^+ = M_r$ of the compound (with ^{12}C , ^{35}Cl , ^{79}Br)	Learn it
Carboxylic acid O–H: very broad, 2500–3000; alcohol O–H: broad, 3200–3600	Given (ranges); learn the shapes

How to do it

In the Paper 1 and Paper 2 questions we have tagged for this topic (70 questions, 2021–2025), the types came up this often. Some questions mix more than one type, so the counts add up to 92.

Question type	Questions
Identify a compound or functional group from its infrared spectrum	23
Number of carbon atoms from the $[M + 1]$ peak (or predict the $[M + 1]$ abundance)	22
Chlorine and bromine isotope peaks; count or assign molecular ion peaks	13

Question type	Questions
Use the molecular ion and fragment peaks to find M_r , a formula or a structure	12
Predict or compare infrared absorptions from structures	10
Label absorptions on an infrared spectrum and name the bond	8
A_r from the mass spectrum of an element	3
Choose infrared or mass spectrometry	1

1. Identify a compound or functional group from its infrared spectrum (23 questions)

- Look above 1500 cm^{-1}** and list the absorptions: roughly where each dip is and its shape (broad or sharp).
- Match each to a bond** with the table. Ignore C–H at 2850–2950: nearly every organic compound has it.
- Decide the functional group**, using what is **missing** too:
 - broad dip at 3200–3600, no C=O: **alcohol**;
 - C=O near 1700, no O–H: **aldehyde or ketone** (or ester, if there is a strong C–O at 1040–1300);
 - C=O and a very broad 2500–3000: **carboxylic acid**;
 - 2200–2250: **nitrile**; 1500–1680 with no C=O: **alkene**; 3300–3500 with no C=O: **amine**.
- Choose the compound** and give **one** absorption with its range and bond as the reason, for example "absorption at 2200–2250 cm^{-1} , so $\text{C}\equiv\text{N}$, so it is the nitrile".

Variations you will meet:

- Several spectra, several compounds** (multiple choice): match each spectrum by its one special band.
- After a reaction.** "X is oxidised to Y; here is Y's spectrum; what was X?" Identify Y first, then work back: a ketone came from a secondary alcohol, a carboxylic acid from a primary alcohol.
- With a mass spectrum as well.** The M^+ peak gives M_r ; only one of the compounds that fit the infrared spectrum will also have that M_r .
- "Why is the 2850–2950 absorption no use?"** Because all the compounds have C–H bonds.

2. Number of carbon atoms from the $[M+1]$ peak (22 questions)

- Find the two abundances:** the M^+ peak (the molecular ion) and the $[M+1]^+$ peak one unit higher. They may come from a table, a bar chart, peak heights in mm, or a ratio.
- Substitute** into $n = \frac{100 \times [M+1]}{1.1 \times [M]}$, with the formula written out.
- Round to a whole number** and state it.

For example, M^+ abundance 20.0 and $[M+1]^+$ abundance 1.10 give $n = \frac{110}{22} = 5$.

Variations you will meet:

- A ratio.** If $M : [M+1] = 10 : 1$, use $[M] = 10$ and $[M+1] = 1$: $n = \frac{100}{11} = 9.09$, so 9. Check which way round the ratio is written.

- **Working backwards.** You know n (from the formula) and the M^+ abundance; find $[M + 1] : [M + 1] = \frac{1.1 n \times [M]}{100}$. With $n = 5$ and $[M] = 40.0$, $[M + 1] = 2.2$.
- **"Show that the compound has n carbon atoms":** write the full expression with the numbers and the value it gives (for example 9.04), then the whole number ("so 9").
- **Then find M_r or the formula.** From n and a clue (a ring, an alkane, one O atom, a halogen), write the formula and its M_r . For example, an alkane with $n = 11$ is $C_{11}H_{24}$, $M_r = 156$. Atoms such as O and P have only one common isotope, so they don't add to the $[M + 1]$ peak.

3. Chlorine and bromine isotope peaks; count or assign molecular ion peaks (13 questions)

1. **Look at the peaks two units apart** at the high-mass end.
2. **Compare their heights:** about 3 : 1 means one Cl; about 1 : 1 means one Br; three peaks 9 : 6 : 1 means two Cl; 1 : 2 : 1 means two Br.
3. **Explain** by linking the ratio to the natural abundances of the two isotopes ($^{35}\text{Cl} : ^{37}\text{Cl} = 3 : 1$). Mentioning the $[M + 1]$ peak here is wrong: that is carbon-13.

Variations you will meet:

- **Predict the $[M + 2]$ abundance.** One Cl: divide the M abundance by 3. One Br: the same as M .
- **Write the ions** for each peak with their isotopes, for example $[\text{C}_2\text{H}_5^{79}\text{Br}]^+$ at 108 and $[\text{C}_2\text{H}_5^{81}\text{Br}]^+$ at 110.
- **Count the peaks.** List every combination of isotopes and its total mass, then count the **different** totals. Two Br atoms give three molecular ion masses ($79 + 79$, $79 + 81$, $81 + 81$). The same counting works for any element with several isotopes, even in a molecule of the element itself.
- **Name an element from its spectrum:** two peaks of equal height at 79 and 81 is bromine; peaks at 35 and 37 in the ratio 3 : 1 is chlorine.
- **M_r from equal peaks at m and $m + 2$:** the M_r (with ^{79}Br) is the lower value.

4. Use the molecular ion and fragment peaks to find M_r , a formula or a structure (12 questions)

1. M_r from the M^+ peak, the highest m/e apart from the small $[M + 1]$ and $[M + 2]$ peaks.
2. **Number of carbons** from the $[M + 1]$ peak, and **Cl or Br** from the $[M + 2]$ peak.
3. **Functional group** from the infrared spectrum (or a chemical test).
4. **Build the formula:** subtract the carbons and any O, N, Cl or Br from M_r ; what is left is hydrogen. If you know the empirical formula, M_r divided by the empirical formula mass gives how many times to multiply it.
5. **Fragments:** subtract each fragment's m/e from M_r to see what was lost (15 is CH_3 , 17 is OH , 29 is C_2H_5 or CHO , 31 is OCH_3 or CH_2OH). Write the fragment as a formula with a + **charge** that comes from breaking **one** bond, and check its mass with $\text{C} = 12$, $\text{H} = 1$, $\text{O} = 16$.
6. **Choose the structure** that fits every fragment, and state the evidence you used for each part.

For example, $M_r = 88$, $n = 5$, a broad absorption at 3200–3600 and no C=O point to an alcohol with one O atom: $88 - 5 \times 12 - 16 = 12$ hydrogen atoms, so $C_5H_{12}O$.

Variations you will meet:

- **Choose between isomers.** Say which isomer can give each fragment by breaking one bond, and which can't. A peak that is **missing** is evidence too: a compound with an OH group could give 17, so no peak at 17 rules out an alcohol or acid.
- **Halogens in fragments.** A fragment that still holds the Cl or Br atom comes as a pair of peaks two units apart (3 : 1 or 1 : 1); a fragment that has lost it is a single peak.

5. Predict or compare infrared absorptions from structures (10 questions)

1. **Draw or look at both structures** and list the bonds in each.
2. **Bonds in both** give absorptions in both; **bonds in only one** give absorptions that appear or disappear.
3. Answer with the **range**, the **bond** and the **group**: "the product has an absorption at 1670–1740 cm^{-1} for C=O in a carboxyl group; the alcohol does not".

Variations you will meet:

- **Tick a table** of ranges for the reactant and the product.
- **Monitor a reaction.** Pick a bond whose absorption changes, and say how: "the O–H absorption at 3200–3600 gets smaller" or "a C=O absorption appears". If the bond is in both the starting compound and the product, its absorption won't change, so choose a different one.
- **"Why is it hard to tell them apart?"** Because they contain the same bonds, so they absorb in the same ranges.
- **Purity:** show a starting material is gone because its special absorption is missing (for example no O–H band at 3200–3600 left after an alcohol has been turned into a chloroalkane with SOCl_2).

6. Label absorptions on an infrared spectrum and name the bond (8 questions)

1. For each dip you are asked about (or choose), read its wavenumber.
2. Find the range it falls in and write the **bond** (C=O, O–H, C–O, ...), not just the group. Add the functional group if the question asks.
3. If asked to **label the spectrum**, write the number or letter exactly on the dip you mean.

For an unsaturated alcohol, the three bands that prove it are O–H at 3200–3600 (broad), C=C at 1500–1680 and C–O at 1040–1300. For an ester, look for C=O at 1710–1750 together with C–O at 1040–1300.

Variations you will meet:

- **"Which bond causes the broad absorption at 2500–3000?"**: O–H in a carboxyl group, not C–H.
- **"Identify two absorptions in the product that the starting compound doesn't have"**: pick bonds made in the reaction and give each with its range.

7. A_r from the mass spectrum of an element (3 questions)

1. Read each isotope's m/e and abundance from the bars.
2. Multiply, add, and divide by the total abundance (by 100 for percentages, by the sum of the heights otherwise).
3. Give the answer to the number of decimal places asked, usually 1 d.p.

Variation: the spectrum of a diatomic element, such as Cl_2 , has atom peaks (35, 37) and molecule peaks (70, 72, 74). A_r comes from the two atom peaks; the M_r of the molecule from the three molecule peaks.

8. Choose infrared or mass spectrometry (1 question)

Infrared finds **functional groups**. Mass spectrometry finds **masses**: A_r , M_r , isotopes, the carbon count, halogens and fragments. Neither measures ionisation energies.

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) The mass spectrum of a sample of silicon has three peaks, at $m/e = 28, 29$ and 30 . The tallest peak is given a height of 100; the other two have heights 5.1 and 3.4. Calculate the relative atomic mass of silicon to one decimal place. **[2]**

(b) Boron has two isotopes, ^{10}B and ^{11}B . Its A_r is 10.8. Calculate the percentage of boron atoms that are ^{10}B . **[2]**

(c) Fluorine has one isotope, ^{19}F . Give the m/e values of the molecular ion peaks of boron trifluoride, BF_3 , and the ratio of their heights. **[2]**

(a)

$$A_r = \frac{28 \times 100 + 29 \times 5.1 + 30 \times 3.4}{100 + 5.1 + 3.4} = \frac{3049.9}{108.5}.$$

M1 for multiplying each m/e by its height and dividing by the **total** height (108.5, not 100).

$$A_r = 28.11 = 28.1 \text{ (1 d.p.)}. \textbf{A1}$$

(b) Let $x\%$ be ^{10}B , so $(100 - x)\%$ is ^{11}B :

$$\frac{10x + 11(100 - x)}{100} = 10.8 \Rightarrow 1100 - x = 1080.$$

M1 for the weighted-mean equation.

$x = 20$, so 20% of boron atoms are ^{10}B . **A1**

(c) $[^{10}\text{BF}_3]^+$ at $10 + 3 \times 19 = 67$ and $[^{11}\text{BF}_3]^+$ at 68. **B1**

The heights are in the same ratio as the boron isotopes, $20 : 80 = 1 : 4$. **B1**

Example 2

Compound **N** contains carbon, hydrogen and nitrogen only. Its mass spectrum has a molecular ion peak at $m/e = 125$ with relative abundance 30.0, and a peak at $m/e = 126$ with relative abundance 2.64.

(a) Show that a molecule of **N** contains 8 carbon atoms. **[1]**

(b) Above 1500 cm^{-1} , the infrared spectrum of **N** has a sharp absorption at 2245 cm^{-1} and C–H absorptions only. Identify the bond and functional group responsible, and deduce the molecular formula of **N**. It has one nitrogen atom. **[3]**

(c) **N** is either octanenitrile, $\text{CH}_3(\text{CH}_2)_6\text{CN}$, or 2,2-dimethylhexanenitrile, $\text{CH}_3(\text{CH}_2)_3\text{C}(\text{CH}_3)_2\text{CN}$. The mass spectrum of **N** has a peak at $m/e = 40$. Suggest the formula of this ion and identify **N**. **[2]**

(a) $n = \frac{100 \times 2.64}{1.1 \times 30.0} = 8.0$, so 8 carbon atoms. **B1** for the expression and the value.

(b) 2245 is in the range 2200–2250: $\text{C}\equiv\text{N}$, a **nitrile** group. **B1**

$125 - 8 \times 12 - 14 = 15$ hydrogen atoms. **M1**

Molecular formula $\text{C}_8\text{H}_{15}\text{N}$. **A1**

(c) 40: CH_2CN^+ ($12 + 2 + 12 + 14 = 40$). **B1**

Octanenitrile gives it by breaking the bond between the second and third carbon atoms (counting the CN carbon as the first), losing C_6H_{13} . In 2,2-dimethylhexanenitrile the carbon next to the CN carries no hydrogen, so no single bond break can give CH_2CN^+ . **N** is **octanenitrile**. **B1**

Example 3

Hept-1-ene, $\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{CH}_3$, reacts with bromine to form 1,2-dibromoheptane, $\text{C}_7\text{H}_{14}\text{Br}_2$.

(a) Describe how the infrared spectrum above 1500 cm^{-1} shows that the reaction is complete. **[2]**

(b) The mass spectrum of the product has three molecular ion peaks, at $m/e = 256$, 258 and 260, with heights in the ratio 1 : 2 : 1. Explain this pattern. **[2]**

(c) The peak at $m/e = 256$ has relative abundance 20.0. Calculate the relative abundance of the peak at $m/e = 257$. **[1]**

(d) There are also two peaks of equal height at $m/e = 177$ and 179. Suggest the formulae of these ions and explain why their heights are equal. **[2]**

(a) The C=C absorption at $1500\text{--}1680\text{ cm}^{-1}$ is no longer there, so no hept-1-ene is left. **B1**

No new absorption appears above 1500: the only one left is C–H at $2850\text{--}2950$, because the C–Br bond absorbs in the fingerprint region. **B1**

(b) Bromine is about 1 : 1 $^{79}\text{Br} : ^{81}\text{Br}$. With two Br atoms a molecule can have $^{79}\text{Br} + ^{79}\text{Br}$ (256), one of each (258, made two ways) or $^{81}\text{Br} + ^{81}\text{Br}$ (260). **M1**

The chances are $\frac{1}{4}$, $\frac{1}{2}$ and $\frac{1}{4}$, giving 1 : 2 : 1. **A1**

(c) $[M + 1] = \frac{1.1 \times 7 \times 20.0}{100} = 1.54$. **B1**

(d) $177 = 256 - 79$: the molecular ion has lost one Br atom. The ions are $[\text{C}_7\text{H}_{14}^{79}\text{Br}]^+$ at 177 **B1** and $[\text{C}_7\text{H}_{14}^{81}\text{Br}]^+$ at 179; one Br atom is left, and its two isotopes are equally common, so the peaks are the same height. **B1**

Example 4

Compound **Q** contains carbon, hydrogen, oxygen and chlorine. The table shows the peaks with the highest m/e values in its mass spectrum.

m/e	108	109	110
relative abundance	24.0	1.06	8.0

(a) Explain how the peaks at 108 and 110 show that **Q** contains one chlorine atom. **[2]**

(b) Calculate the number of carbon atoms in a molecule of **Q**. **[1]**

(c) **Q** has one oxygen atom. Deduce its molecular formula. **[1]**

(d) Above 1500 cm^{-1} , the infrared spectrum of **Q** has a broad absorption centred at 3340 cm^{-1} and C–H absorptions only. It also has a strong absorption at 1050 cm^{-1} . Identify the functional group in **Q**. **[1]**

(e) The mass spectrum also has a single peak at $m/e = 73$, and a pair of peaks at 77 and 79 in the ratio 3 : 1. Suggest the formulae of the ions at 73 and 77, explain why only one of them has a partner two units higher, and suggest a structure for **Q**. **[3]**

(a) The peaks are in the ratio $24.0 : 8.0 = 3 : 1$. **M1**

That matches the 3 : 1 natural abundance of $^{35}\text{Cl} : ^{37}\text{Cl}$: 108 holds ^{35}Cl and 110 holds ^{37}Cl , so there is one Cl atom. **A1**

(b) $n = \frac{100 \times 1.06}{1.1 \times 24.0} = 4.02$, so 4 carbon atoms. **B1**

(c) $108 - 4 \times 12 - 35 - 16 = 9$ hydrogen atoms, so C_4H_9ClO . **B1**

(d) The broad absorption at 3200–3600 is O–H and 1050 is C–O; there is no C=O. **Q** is an **alcohol** (hydroxy group). **B1**

(e) $73 = 108 - 35$: $C_4H_8OH^+$ (that is, $C_4H_9O^+$), the ion left when the Cl atom is lost. **B1**

$77 = 108 - 31$: $C_3H_6^{35}Cl^+$, the ion left when CH_2OH is lost; 79 is the same ion with ^{37}Cl . The 73 ion has no Cl, so it has no partner; the 77 ion keeps the Cl, so it comes as a 3 : 1 pair. **B1**

Losing CH_2OH means **Q** has a CH_2OH group, for example 4-chlorobutan-1-ol, $ClCH_2CH_2CH_2CH_2OH$. **B1**
(any structure that fits the data scores)

Common mistakes

- **Leaving the charge off a fragment.** Only positive ions are detected, and examiners report every year that answers like " $C_2H_5^-$ " or " $C_2H_5^+$ " lose the mark. Write $C_2H_5^+$.
- **Breaking two bonds.** A fragment comes from breaking **one** bond. Answers that rearrange atoms or pull several groups off just to hit the m/e value don't score.
- **Using m/e values instead of abundances in the $[M + 1]$ formula.** n uses the **heights** of the M and $M + 1$ peaks, not their positions (not $\frac{201}{200}$, for example).
- **Forgetting the formula for n altogether**, and guessing from M_r . Examiners have noted it is rarely used in longer questions. When a question gives M and $M + 1$ abundances, it wants n .
- **Blaming the $[M + 1]$ peak for a 3 : 1 pattern.** $M + 2$ peaks come from ^{37}Cl or ^{81}Br ; $M + 1$ comes from carbon-13.
- **Missing the halogen.** Two tall peaks two units apart at the top of the spectrum always mean Cl or Br. Take M_r from the lower one.
- **Naming a group instead of a bond.** "Alkene" or "nitrile" is not a bond. Write $C=C$ or $C\equiv N$, and add the group if asked.
- **Calling the broad 2500–3000 band C–H.** In an acid it is O–H.
- **Giving C–H to tell compounds apart.** Nearly every organic compound has it.
- **Going vague:** "different O–H" or "a C=O peak" without a range earns nothing. Give the range in cm^{-1} , the bond, and whether it appears or disappears.
- **Forgetting what's missing.** To show a compound is an ester, say there is **no O–H** as well as that there is C=O and C–O.
- **Answering from memory instead of the data.** When a question says "use the spectrum", point to absorptions in the spectrum you were given; knowing the reaction is not enough on its own.

How to get the marks

- **Infrared answers need three parts:** the wavenumber (or range) in cm^{-1} , the bond, and the functional group. One absorption with all three usually earns the mark; a bond with no range often doesn't.
- **"Use absorptions above 1500 cm^{-1} "** means ignore the fingerprint region (C–O is the usual exception, when the question allows it).
- **Labelling a printed spectrum:** put each number or letter on the right dip. Each mark needs a dip in the right place linked to the right bond.
- **"Show that" with $[M + 1]$:** write the whole expression with the numbers, the value, and the whole number it rounds to.
- **Calculate:** give the value to the accuracy asked; A_r is normally to 1 d.p. Show the method (each abundance times its mass), since M1 is for the method.
- **Fragments:** formula plus + charge. A structural formula is fine if it's clear.
- **"Explain the relative abundance of the peaks":** give the ratio, and link it to the natural abundances of the two isotopes.
- **"Deduce the structure"** questions give marks for the structure **and** for the evidence: the M_r , the key absorptions (range + bond), and any fragments. Use every piece of data the question gives.
- **"Identify ... Explain your answer":** name the compound, then give one absorption with its range and bond that only that compound has.
- **"Suggest"** means use what you know on something new; any answer that fits the data scores.

Quick check

1. Rubidium has two isotopes, ^{85}Rb (72.2%) and ^{87}Rb (27.8%). Calculate the A_r of rubidium to one decimal place.
2. Compound **X** contains carbon, hydrogen and nitrogen only. Above 1500 cm^{-1} its infrared spectrum has two absorptions at 3380 and 3310 cm^{-1} and C–H absorptions at 2930 and 2870 cm^{-1} , and nothing else. Is **X** an amine, an amide or a nitrile? Give the evidence for your answer.
3. Explain why the $[M + 1]^+$ peak of hexadecane, $\text{C}_{16}\text{H}_{34}$, is about twice as tall, compared with its M^+ peak, as the $[M + 1]^+$ peak of octane, C_8H_{18} . Give each $[M + 1] : M$ ratio as a percentage.
4. Give the m/e values of the molecular ion peaks of 1,4-dichlorobutane, $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$, and the ratio of their heights. Explain the ratio.
5. Propyl pentanoate, $\text{CH}_3(\text{CH}_2)_3\text{COOCH}_2\text{CH}_2\text{CH}_3$, and pentyl propanoate, $\text{CH}_3\text{CH}_2\text{COO}(\text{CH}_2)_4\text{CH}_3$, are isomers. Explain why their infrared spectra above 1500 cm^{-1} can't tell them apart, and give a fragment peak in the mass spectrum of one of them that the other can't have.

Answers

1. $A_r = \frac{85 \times 72.2 + 87 \times 27.8}{100} = 85.556 = 85.6$ (1 d.p.).
2. An **amine**. 3380 and 3310 are in the range 3300–3500: N–H. There is no C=O absorption at 1640–1690, so it is not an amide, and no C≡N absorption at 2200–2250, so it is not a nitrile.
3. The $[M + 1]^+$ peak comes from molecules with one ^{13}C atom, and each carbon atom has a 1.1% chance of being ^{13}C . Hexadecane has twice as many carbon atoms, so twice the chance. Hexadecane: $1.1 \times 16 = 17.6\%$ of M ; octane: $1.1 \times 8 = 8.8\%$ of M .
4. 126 ($^{35}\text{Cl} + ^{35}\text{Cl}$), 128 (one of each) and 130 ($^{37}\text{Cl} + ^{37}\text{Cl}$), in the ratio 9 : 6 : 1. Chlorine is 3 : 1 ^{35}Cl : ^{37}Cl , so the chances are $\frac{3}{4} \times \frac{3}{4}$, $2 \times \frac{3}{4} \times \frac{1}{4}$ and $\frac{1}{4} \times \frac{1}{4}$.
5. Both are esters with the same bonds (C=O, C–O, C–H), so both absorb in the same ranges: C=O at 1710–1750, C–O at 1040–1300 and C–H at 2850–2950. Propyl pentanoate can break next to its C=O to give $\text{C}_4\text{H}_9\text{CO}^+$ at $m/e = 85$; pentyl propanoate has no $\text{C}_4\text{H}_9\text{CO}$ group, so no single bond break gives 85.

Past questions to try

- **9701/13/O/N/23 Q40**: the carbon count from an $M + 1 : M$ ratio, then an oxidation clue.
- **9701/21/M/J/23 Q3**: part (f), the molecular ions of a compound with both Cl and Br.
- **9701/22/M/J/24 Q5**: $[M + 1]$, fragments and two infrared spectra for an alcohol and its oxidation product.
- **9701/22/M/J/23 Q5**: part (d)(iv), infrared differences between two compounds above 1500 cm^{-1} .