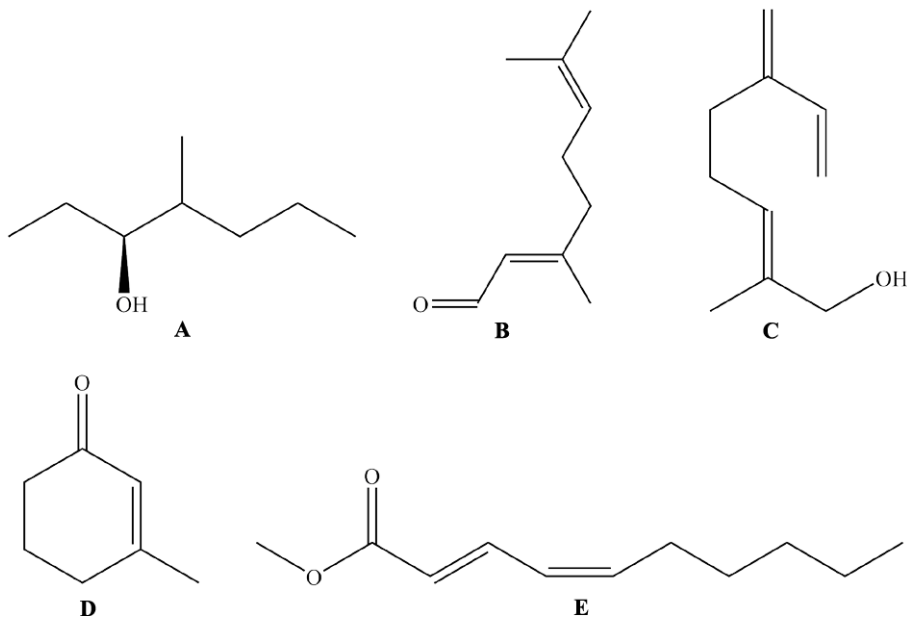




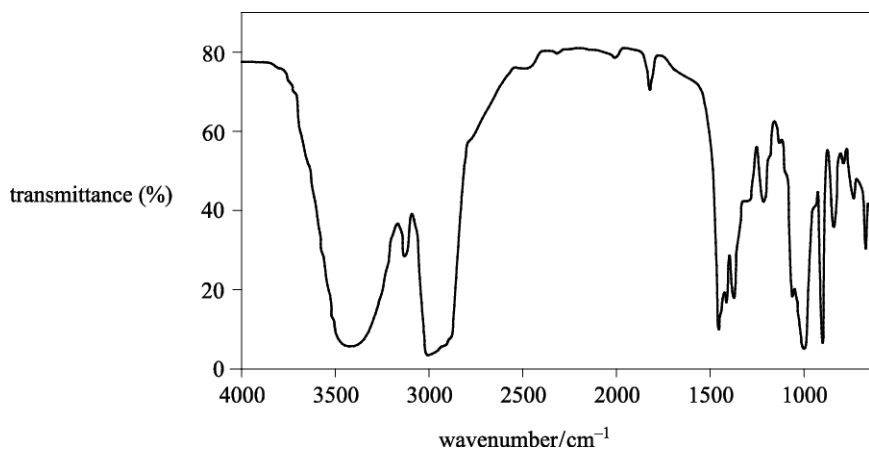
1. The organic compounds labelled **A** to **E** below are all produced by living organisms.



Analysis of one of the compounds **A** to **E** is shown below.

Percentage composition by mass: C, 78.94%; H, 10.53%; O 10.53%

Infrared spectrum:

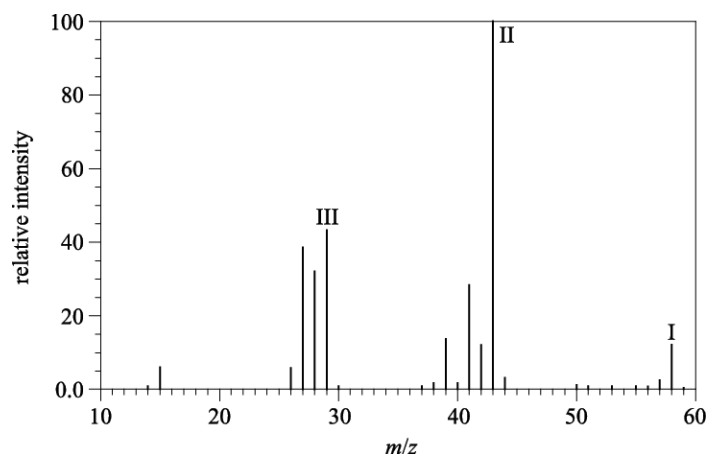




Use this information to identify the compound. Explain your reasoning, referring to **all** the evidence provided.

[3]

2. Two students were provided with the mass spectrum of an alkane, shown below.



One student analysed peaks **I** and **II** and concluded that the alkane was one of two structures.

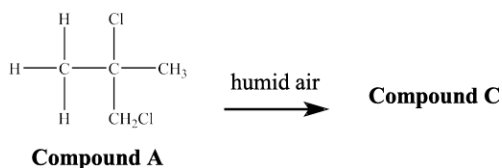
The other student analysed peaks **I**, **II** and **III** and was able to identify the alkane.

Analyse the peaks and explain why the two students obtained different conclusions.

[5]



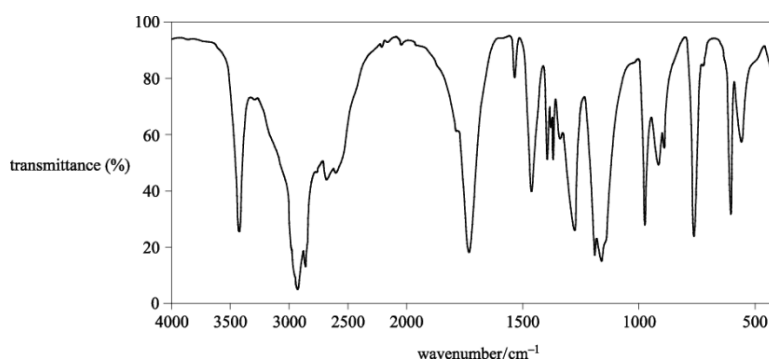
4. Compound **A** reacts slowly in humid conditions to form compound **C**.



Compound **C** contained the following percentage composition by mass:

C, 46.1%; H, 7.7%; O, 46.2%

The infrared spectrum of compound **C** is shown below.



Using the information on the previous page, deduce the structure of compound **C**.

Give your reasoning.

structure =

[5]



5. * A chemist isolates compound **L**, with empirical formula C_3H_6O , and sends a sample for analysis. The analytical laboratory sends back the following spectra.

Mass spectrum

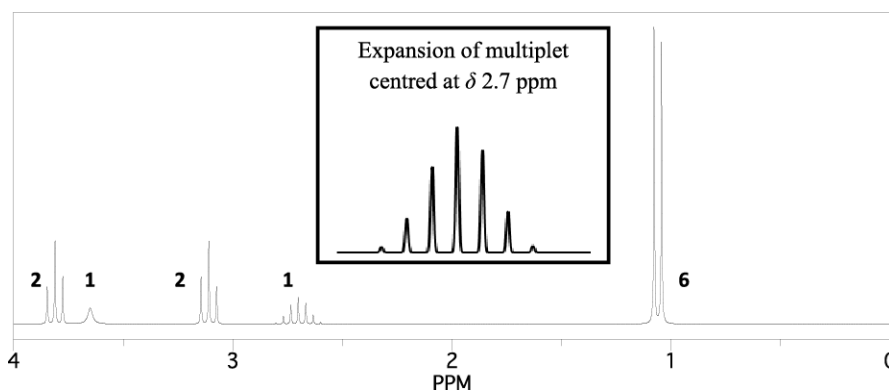
Molecular ion peak at $m/z = 116.0$.

1H NMR spectra

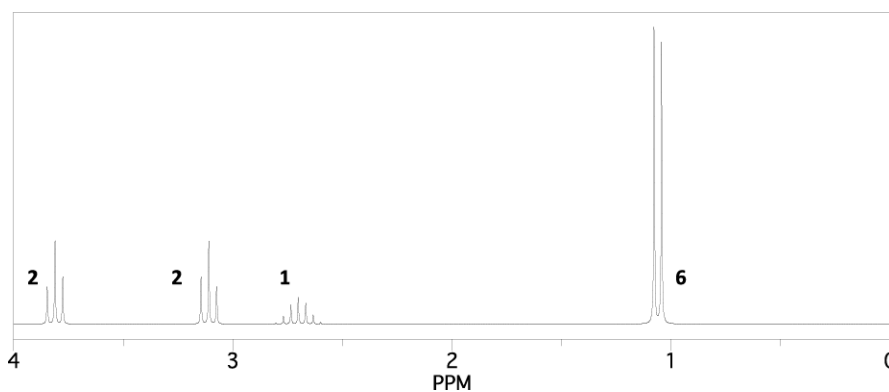
The numbers next to each signal represent the number of 1H responsible for that signal.

Two 1H NMR spectra were obtained: one without D_2O and one with D_2O added.

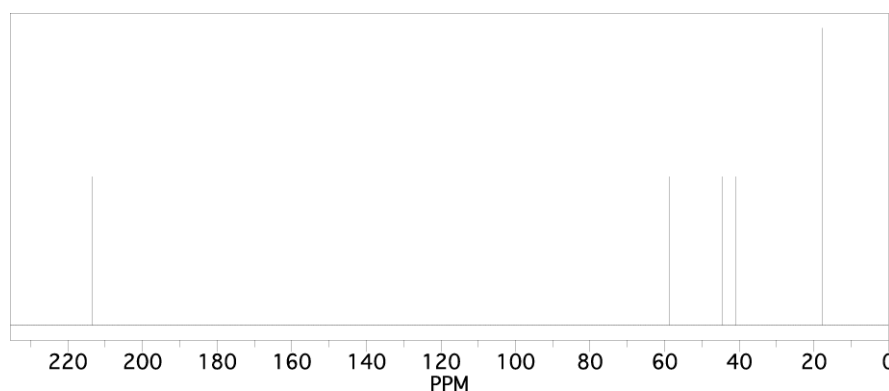
1H NMR spectrum with no D_2O :



1H NMR spectrum with D_2O added:



^{13}C NMR spectrum:



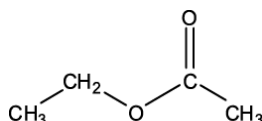


Use the information provided to suggest a structure for compound L.

Give your reasoning.

[6]

6. The structure of an ester is shown below.



Which statement is most likely to be true about the mass spectrum of the ester?

- A. The peak at $m/z = 45$ is due to the fragment $[\text{C}_2\text{H}_5\text{O}]^+$.
- B. The peak at $m/z = 44$ is due to the fragment $[\text{C}_3\text{H}_8]^+$.
- C. The peak at $m/z = 88$ is the $M+1$ peak.
- D. There is no peak at $m/z = 43$.

Your answer

[1]



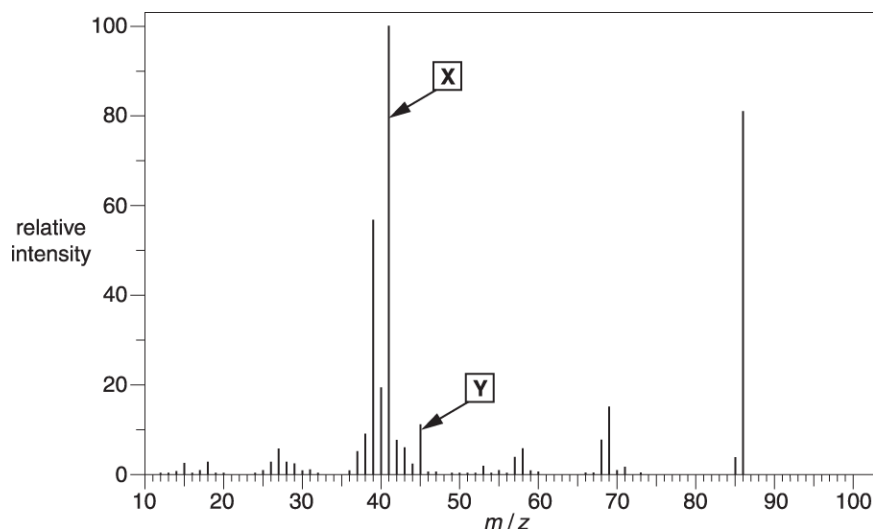
8. Compound **G** is a branched-chain organic compound that does **not** have *E* and *Z* isomers.

Elemental analysis of compound **G** gave the following percentage composition by mass:

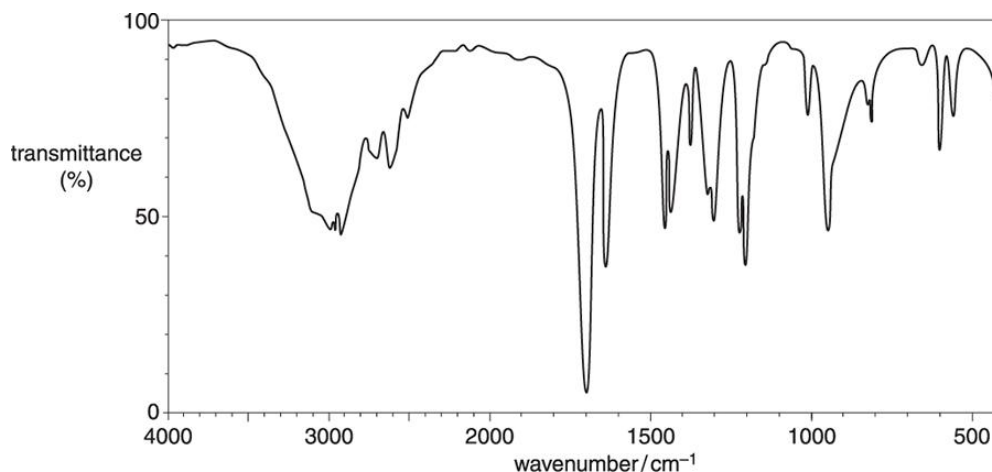
C, 55.8%; H, 7.0%; O, 37.2%.

The mass spectrum and infrared spectrum of compound **G** are shown below.

Mass spectrum



Infrared spectrum



- Calculate the empirical and molecular formulae for compound **G**.
- Write the formulae for the particles responsible for peak **X** and peak **Y** in the mass spectrum.
- Draw the structure of compound **G**.

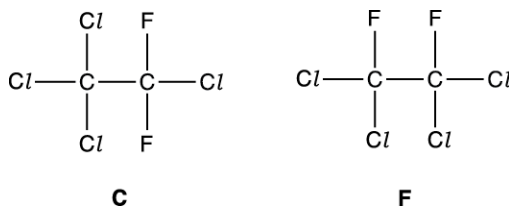


9. Give chemical explanations for the following statements.

IR spectroscopy distinguishes ketones from carboxylic acids.

[1]

10. Compounds **C** and **F** can be analysed to obtain infrared and mass spectra.



i. What happens to molecules when infrared radiation is absorbed?

[1]

ii. Suggest the molecular formulae of **two** ions responsible for peaks in the mass spectrum of **C** that are **not** in the mass spectrum of **F**.

[2]



(b). The alcohol **J** is soluble in water.

Explain why alcohol **J** is soluble in water.

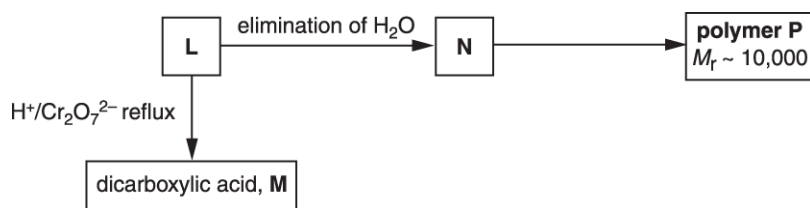
Use a labelled diagram to support your answer.

Include relevant dipoles and lone pairs.

[1]

12(a). **L**, **M**, **N** and **P** are straight-chain organic compounds containing C, H and O only.

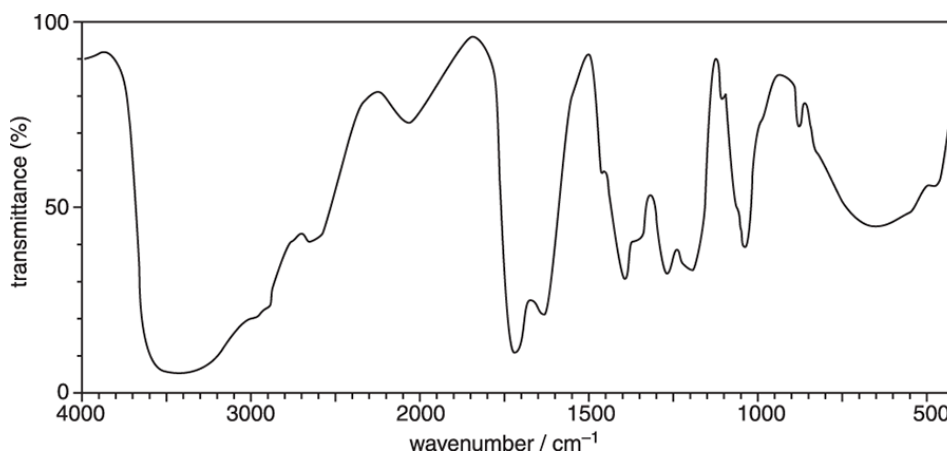
The flowchart shows reactions involving these compounds.



Analysis of compound **L** shows the following.

- Percentage composition by mass: C, 40.00%; H, 6.67%; O, 53.33%.
- Relative molecular mass of 90.0.
- The infrared spectrum below.

IR spectrum of **L**





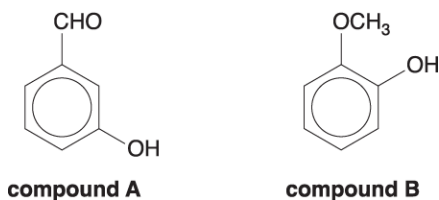
(c). Determine the structures of compounds **N** and **P**.

Estimate the number of repeat units in polymer **P** and write the equation for the formation of **P** from **N**.

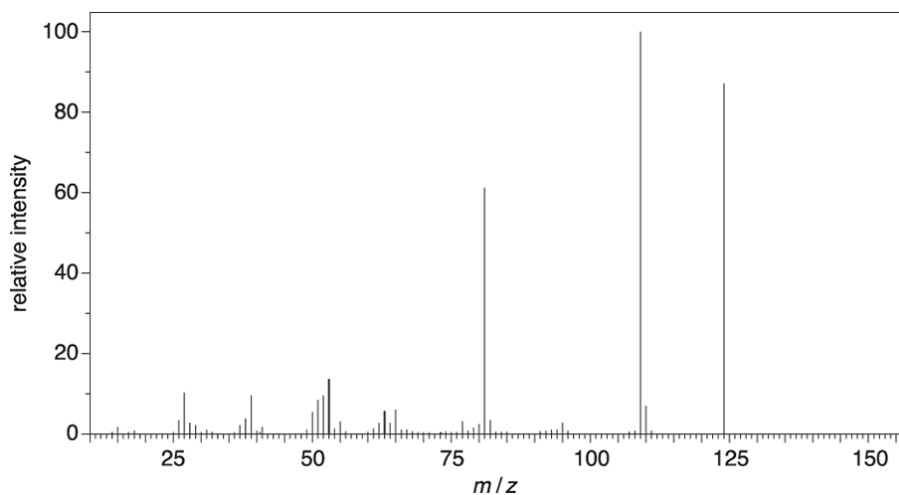
[4]

13. A student analysed a mixture of compounds found in red wine using gas chromatography followed by mass spectrometry (GC-MS).

Two of the compounds found to be present in the mixture are shown below.



The mass spectrum (MS) of the **first** compound to emerge from the column is shown below.





- i. Identify the compound responsible for this spectrum.

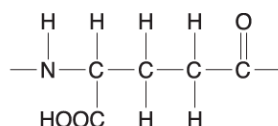
Give a reason for your answer.

[1]

- ii. What does your answer to **(b)(i)** suggest about the interaction of this compound with the phases present in the column?

[1]

14. Poly(glutamic acid) is a polymer of the amino acid, glutamic acid.



repeat unit of poly(glutamic acid)

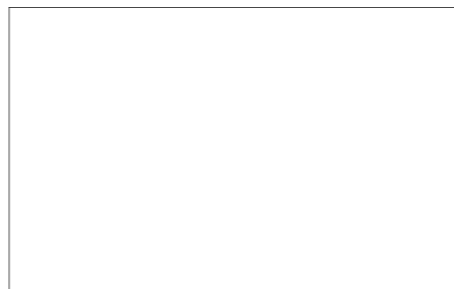
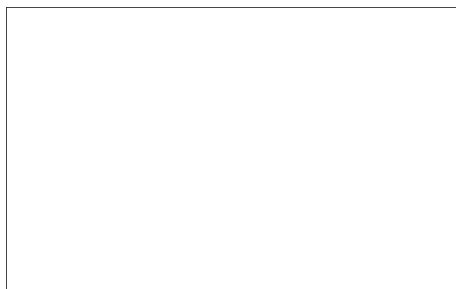
- i. Draw the structure of glutamic acid.

[1]

- ii. A student tried to prepare poly(glutamic acid) from glutamic acid. No polymer was found in the product mixture.

The student isolated the two major compounds in the mixture. The mass spectra of these two compounds showed molecular ion (M^+) peaks at $m/z = 129$ and $m/z = 258$.

Suggest structures for these two compounds.

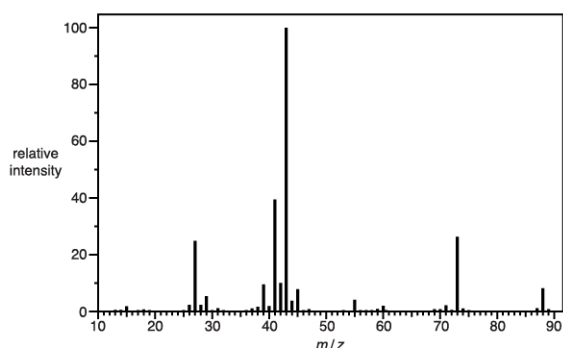
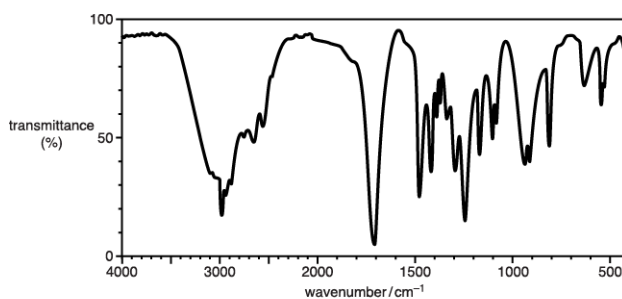


[2]



15. * Organic compound **C** has the following percentage composition by mass:
C, 54.5%; H, 9.1%; O, 36.4%.

The infrared spectrum and mass spectrum of compound **C** are shown below.



In the mass spectrum, a secondary carbocation is responsible for the peak with the greatest relative intensity.

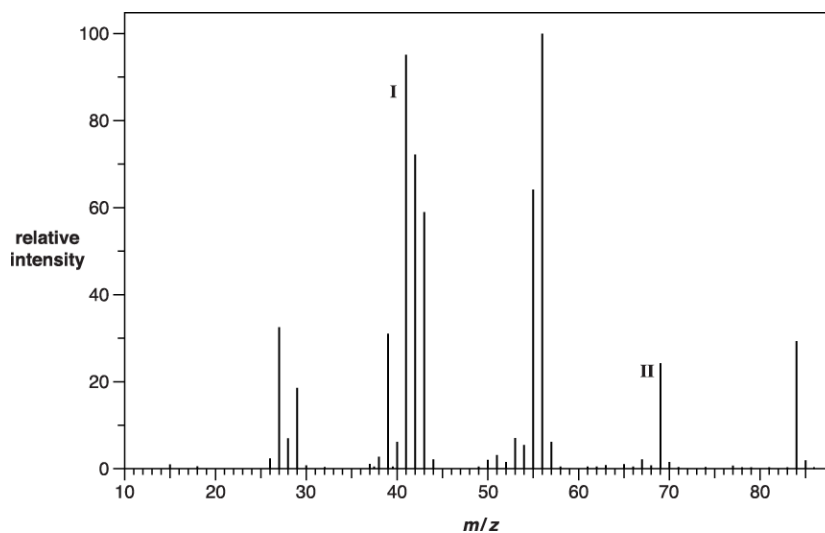
Identify compound **C**. In your answer you should make clear how your conclusion is linked to all the evidence.

[6]



16. This question is about several unsaturated hydrocarbons.

The mass spectrum of an alkene is shown below.



- i. The empirical formula of the alkene is CH_2 .

Use the empirical formula and the mass spectrum to confirm the molecular formula as C_6H_{12} .

[1]

- ii. Further analysis showed that the alkene was hex-2-ene.

Suggest possible structures for the species responsible for the labelled peaks I and II in the mass spectrum of hex-2-ene shown opposite.

peak I	peak II
---------------	----------------

[3]



17(a). A student was provided with a mixture of two structural isomers. Each isomer has the percentage composition by mass C, 29.29%; H, 5.70%; Br, 65.01%. The relative molecular mass of each isomer is less than 150.

Determine the structures of the two structural isomers.

Show your working.

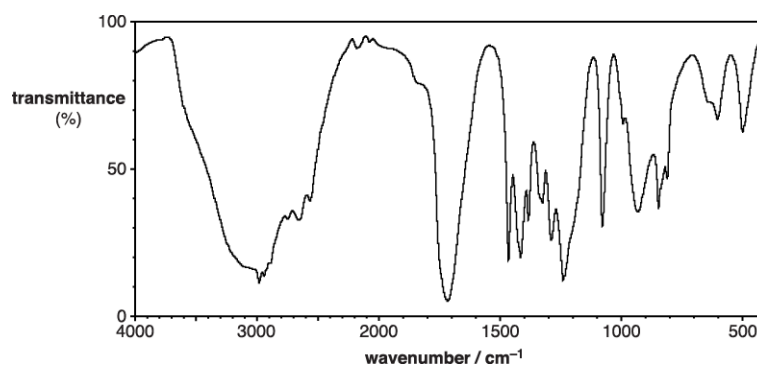


In your answer you should link the evidence with your explanation.

[5]

(b). The student heats the mixture of the two structural isomers from **(a)** under reflux with aqueous sodium hydroxide to form two compounds, **E** and **F**. The student separates the two compounds.

Compound **E** is heated under reflux with acidified potassium dichromate(VI) to form compound **G**, which gives the infrared spectrum below.





- ii. Compound **G** is heated with compound **F** in the presence of a small amount of concentrated sulfuric acid to form organic compound **H**.

Draw the structure of the organic compound **H**.

[2]

18(a). A chemistry teacher carries out an experiment to synthesise 2-aminopropan-1-ol, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$.

The teacher asks a university chemistry department to test the 2-aminopropan-1-ol using proton NMR spectroscopy and mass spectrometry.

- i. For the ^1H NMR analysis, the sample was dissolved in D_2O .

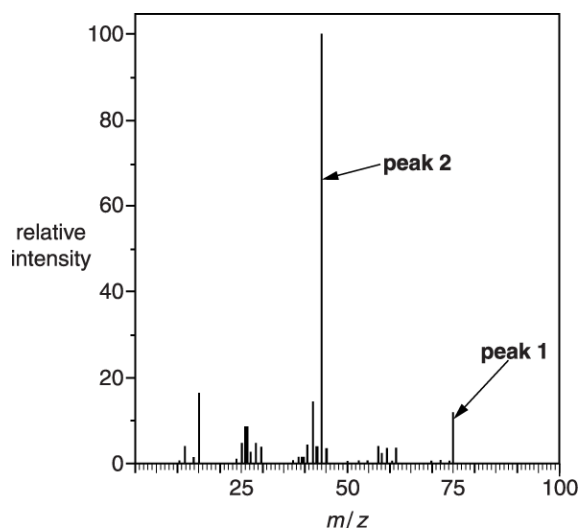
Complete the table to predict the ^1H NMR spectrum of $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$ after dissolving in D_2O .

^1H NMR spectrum for $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$, dissolved in D_2O		
Chemical shift, δ / ppm	Relative peak area	Splitting pattern

[3]



ii. The mass spectrum for $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$ is shown below.



Give the formulae for the species responsible for **peak 1** and **peak 2** in the mass spectrum.

peak 1

peak 2

[2]

(b). The teacher synthesises 2-aminopropan-1-ol, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$, from 2-chloropropan-1-ol, $\text{CH}_3\text{CHClCH}_2\text{OH}$.

i. State the reagents and conditions required for this synthesis.

[1]



- ii. The sample prepared by the teacher from 2-chloropropan-1-ol is not pure. It also contains compound **D**.

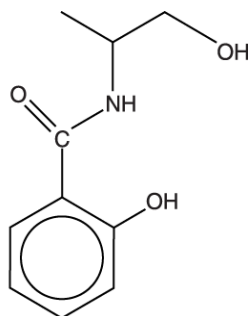
Compound **D** has a molecular formula of $C_6H_{15}NO_2$.

Suggest the structure of compound **D**.

Compound **D**

[1]

- (c). In a separate experiment, the chemistry teacher prepares compound **E** from 2-aminopropan-1-ol.



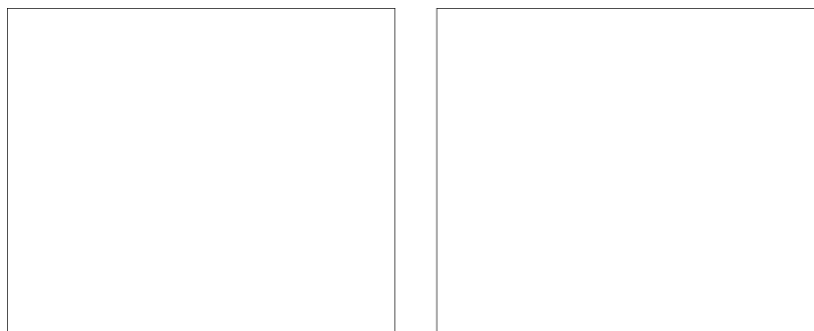
compound **E**

- i. One of the functional groups in compound **E** is a phenol.

Name the other functional groups in compound **E**.

[1]

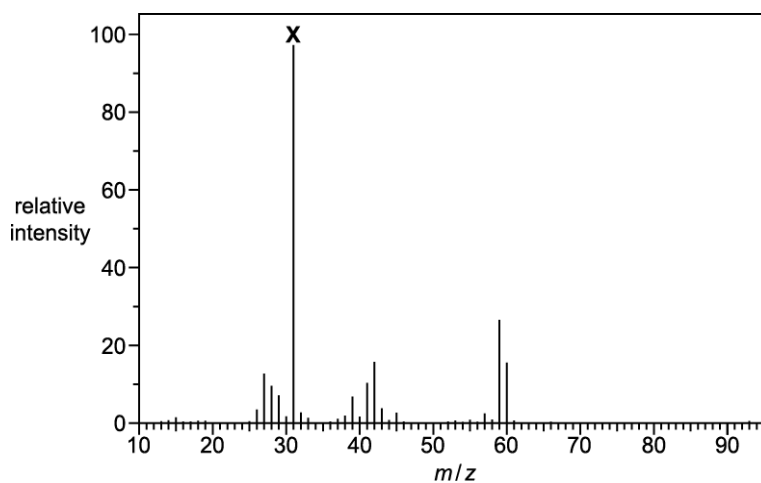
- ii. Draw the structures of the **two** organic products formed when compound **E** is heated under reflux with dilute hydrochloric acid.



[2]



19. The mass spectrum of alcohol **A** is shown below.



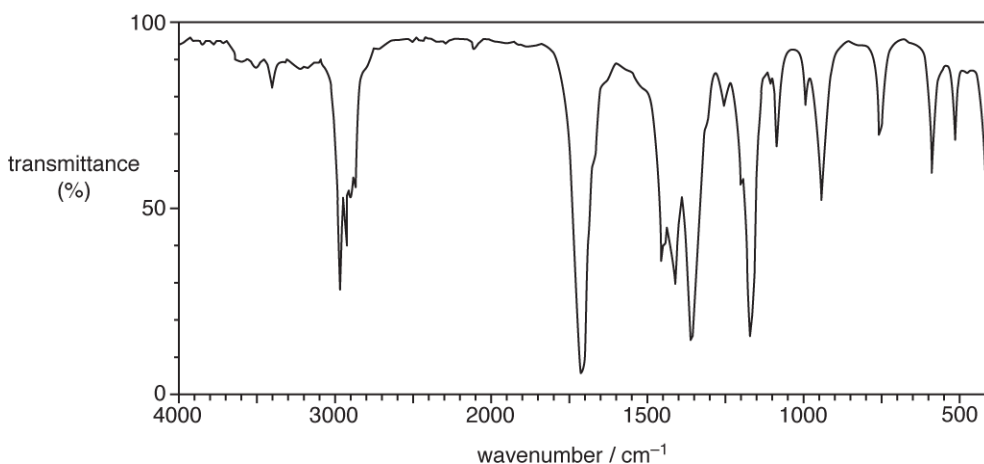
Determine the structure of alcohol **A** and fragment ion **X**.

Explain your reasoning.

[3]

20. An alcohol **A** is heated under reflux with sulfuric acid and potassium dichromate(VI).

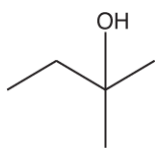
The organic compound formed produces the infrared spectrum below.



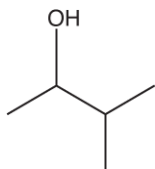
Which compound could be alcohol **A**?



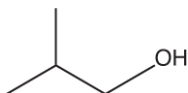
A



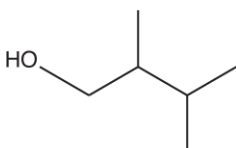
B



C



D



Your answer

[1]

21. Which alcohol is **not** likely to have a fragment ion at $m/z = 43$ in its mass spectrum?

- A $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
- B $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
- C $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_3$
- D $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$

Your answer

[1]

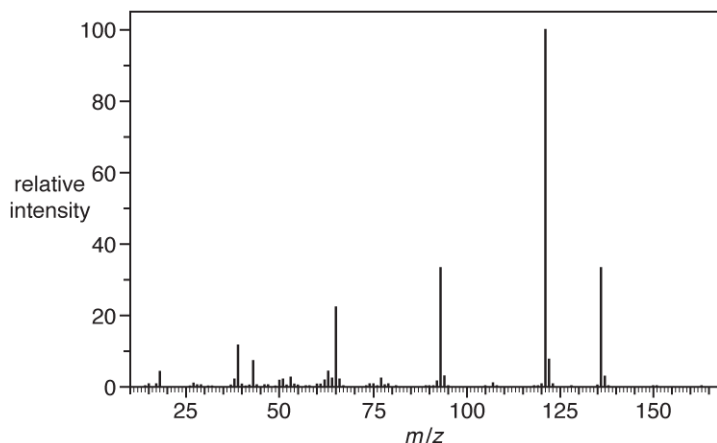


22(a). A chemist analyses a naturally occurring aromatic compound.

The percentage composition and mass spectrum of the compound are shown below.

Percentage composition by mass: C, 70.58%; H, 5.92%; O, 23.50%.

Mass spectrum



Determine the molecular formula of the compound.

Show your working.

molecular formula = [3]

(b). Qualitative tests are carried out on the aromatic compound. The results are shown below.

Test	Acidity	Na ₂ CO ₃ (aq)	2,4-DNP	Tollens' reagent
Observation	pH = 5	No observable change	Orange precipitate	No observable change

Determine the functional groups in the compound. Explain your reasoning.

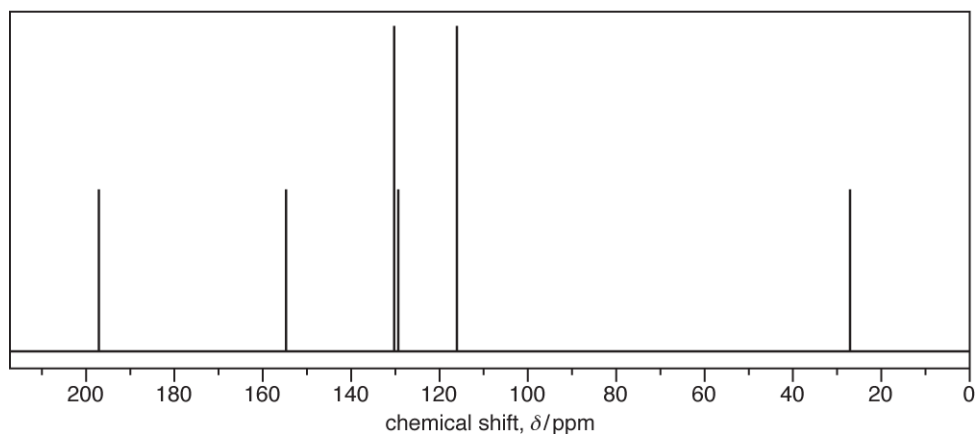
Functional groups

Explanation

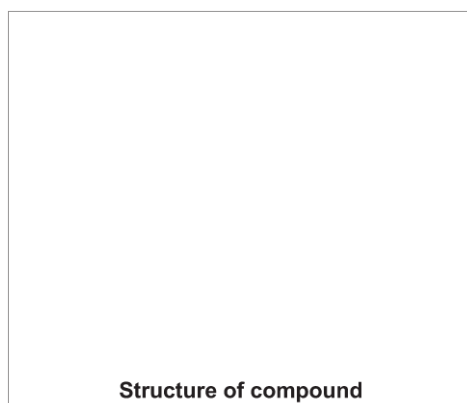
[3]



(c). The carbon-13 NMR spectrum of the compound is shown below.



Using the spectrum and the results from (a) and (b), determine the structure of the compound. Explain your reasoning.



[3]

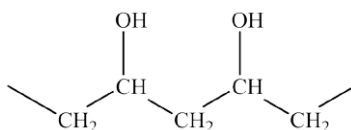
23. Why are scientists concerned about the release of methane into the atmosphere?

[1]



24. Poly(ethenol) is used to make soluble laundry bags.

A section of the structure of poly(ethenol) is shown below.



i. Draw a structure to represent one repeat unit of poly(ethenol).

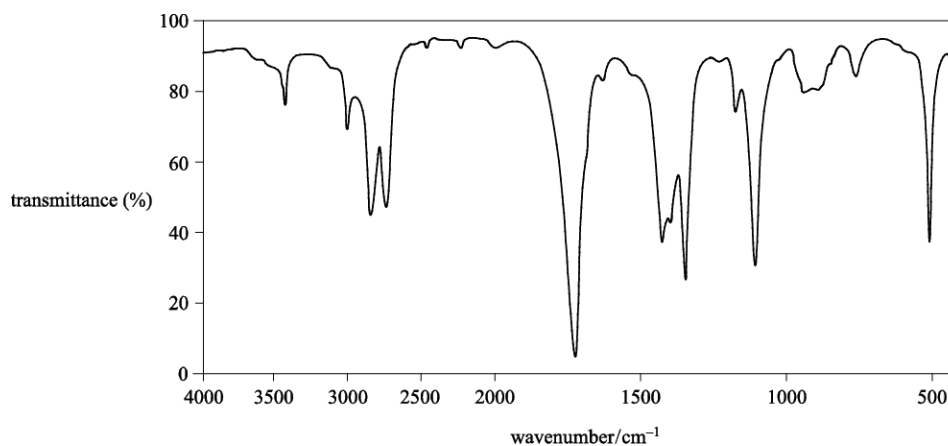
[1]

ii. Poly(ethenol) is not manufactured from ethenol.

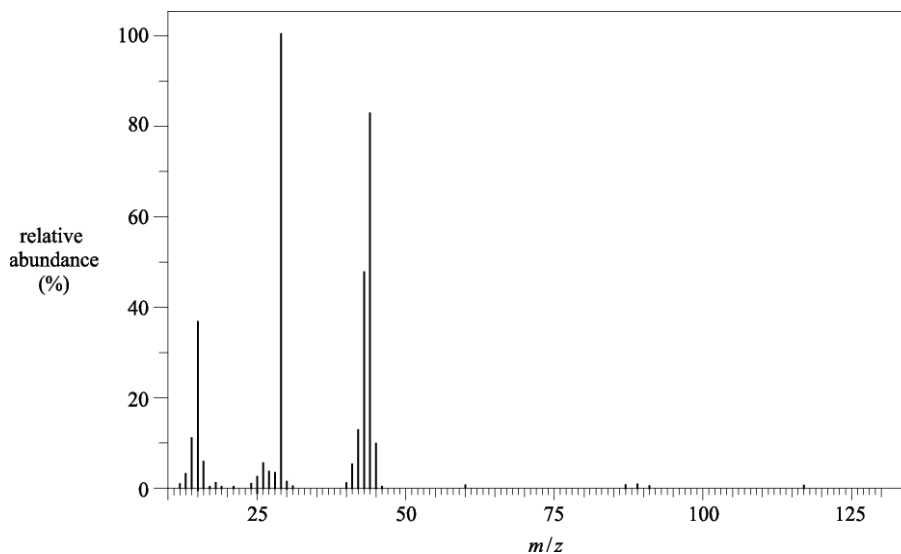
Ethenol is unstable and it forms a more stable structural isomer.

Analysis of the structural isomer gave the following data.

Infrared spectrum



Mass spectrum



Use **all** the data to show that the isomer is **not** ethenol.

Identify the structural isomer of ethenol.

In your answer you should make clear how your explanation is linked to the evidence.

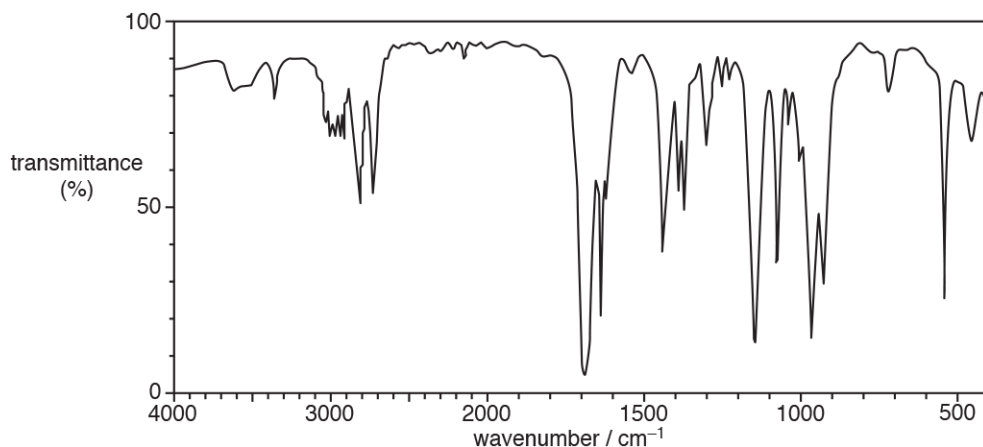
[4]

25. * Compound **F** is a *trans* stereoisomer which is a useful intermediate in organic synthesis.

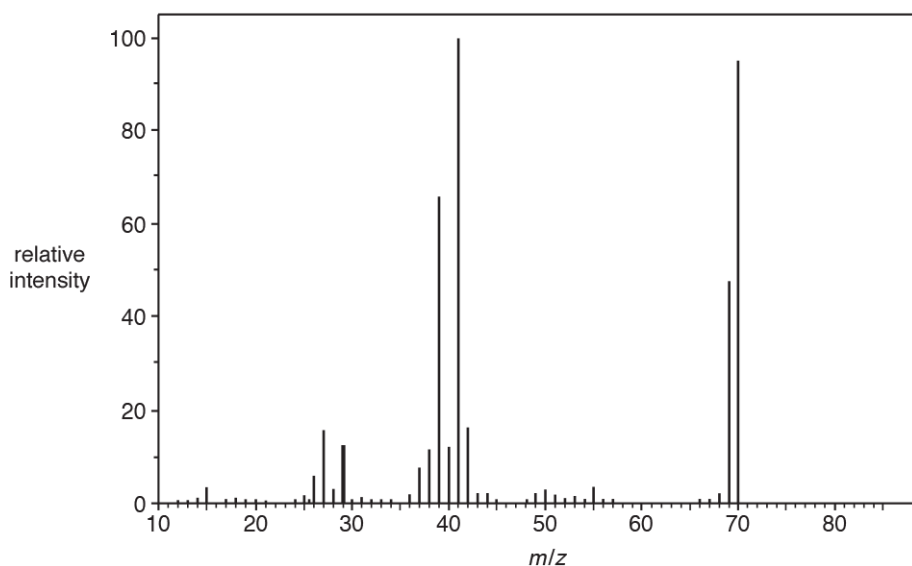
The results of elemental and spectral analysis of compound **F** are shown below.

Percentage composition by mass: C, 68.6 %; H, 8.6 %; O, 22.8 %.

Infrared spectrum



Mass spectrum



In the mass spectrum, the peak with the greatest relative intensity is caused by the loss of a functional group from the molecular ion of compound **F**.

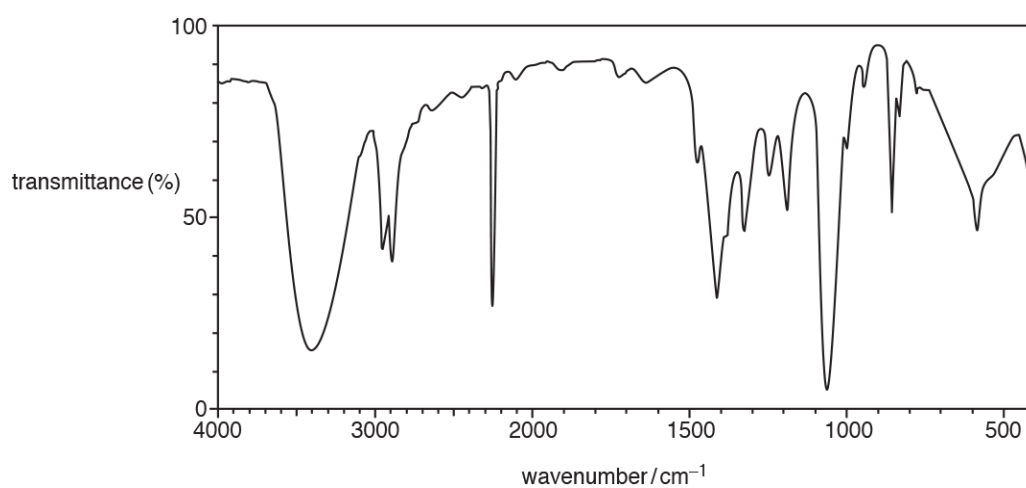
Determine the structure of compound **F**.

Explain your reasoning and show your working.



[6]

26. Which compound could have produced the IR spectrum below?



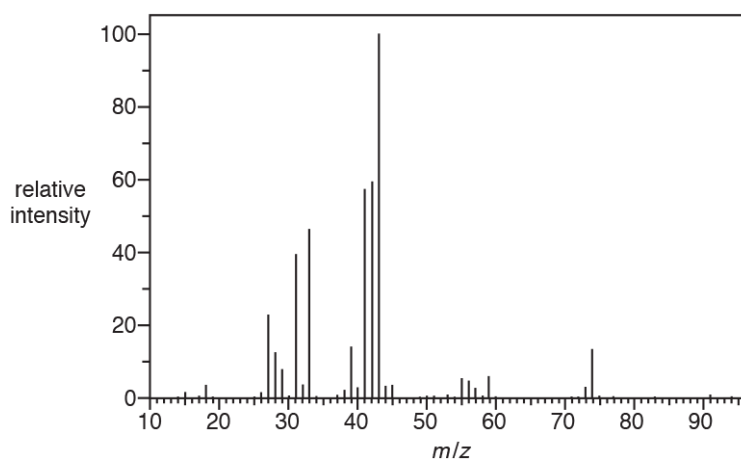
- A $\text{CH}_3\text{CH}_2\text{OH}$
- B CH_3CHOHCN
- C CH_3COOH
- D CH_3CONH_2

Your answer

[1]



27. The mass spectrum of $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ is shown below.



Which ion is responsible for the peak with the greatest relative intensity?

- A CHCH_2OH^+
- B $\text{CH}_3\text{CH}_2\text{CH}^+$
- C $(\text{CH}_3)_2\text{CH}^+$
- D CH_3CO^+

Your answer

[1]

28. A scientist is researching compounds that might be suitable as fuel additives. One of the compounds gives the analytical results below.

Elemental analysis by mass:

C: 54.54%; H: 9.10%; O: 36.36%

Mass spectrum:

Molecular ion peak at $m/z = 132.0$



29. Which alcohol is likely to have a fragment ion at $m/z = 31$ in its mass spectrum?

- A $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
B $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{OH})(\text{CH}_3)_2$
C $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_3$
D $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$

Your answer

[1]

30. An alcohol can be prepared by hydrolysing the haloalkane $\text{C}_2\text{H}_5\text{CHBrCH}_3$ with aqueous sodium hydroxide.

- i. Outline the mechanism for this reaction.

Show curly arrows and relevant dipoles.

[3]



- ii. The infrared (IR) spectrum for $\text{C}_2\text{H}_5\text{CHBrCH}_3$ is shown in **Fig. 25.2**. The C–Br bond absorption is labelled.

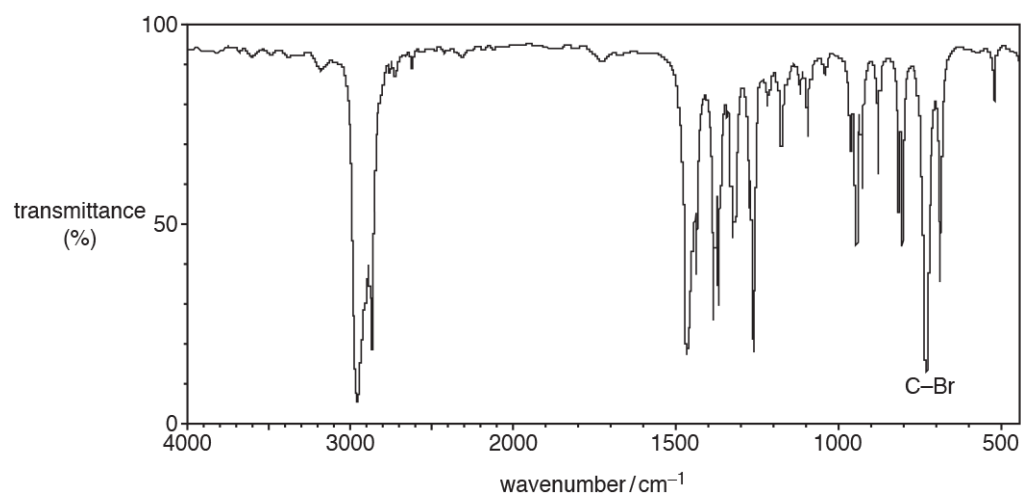


Fig. 25.2

Outline how IR spectroscopy could be used to show that the bromoalkane functional group has reacted and that the alcohol functional group has formed.

[2]



31. Which compound is **not** likely to have a fragment ion at $m/z = 43$ in its mass spectrum?

A	 <chem>CCC(=O)O</chem>
B	 <chem>CC(=O)O</chem>
C	 <chem>CC(C)CO</chem>
D	 <chem>CCC(O)</chem>

Your answer

[1]

32. Which statement about infrared radiation is **not** correct?

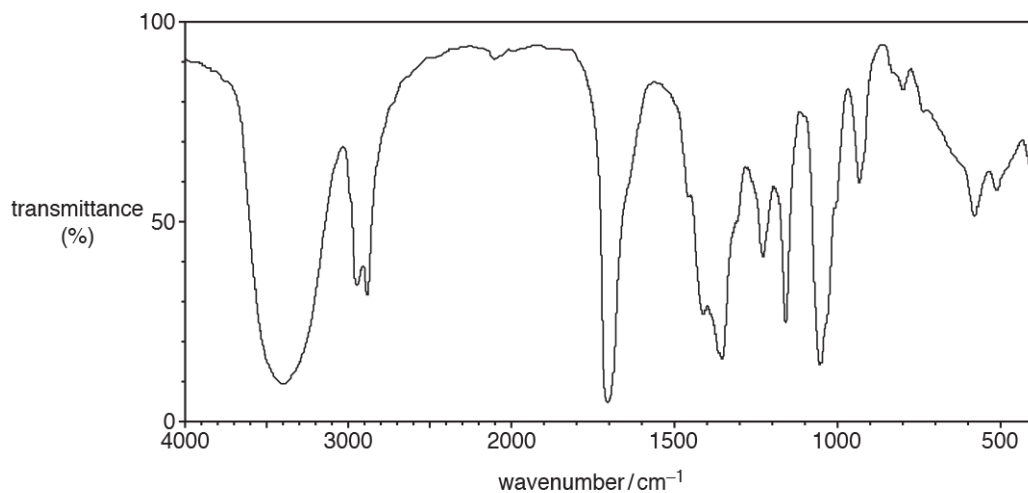
- A** The energy from IR radiation causes some covalent bonds to vibrate more.
- B** Absorption of IR radiation by some atmospheric gases is linked by some scientists to global warming.
- C** IR radiation is used to monitor gases causing air pollution.
- D** The action of IR radiation on CFCs in the upper atmosphere leads to the formation of chlorine radicals.

Your answer

[1]



33. An unknown compound produces the infrared spectrum below.



Which compound could have produced the infrared spectrum?

A	
B	
C	
D	

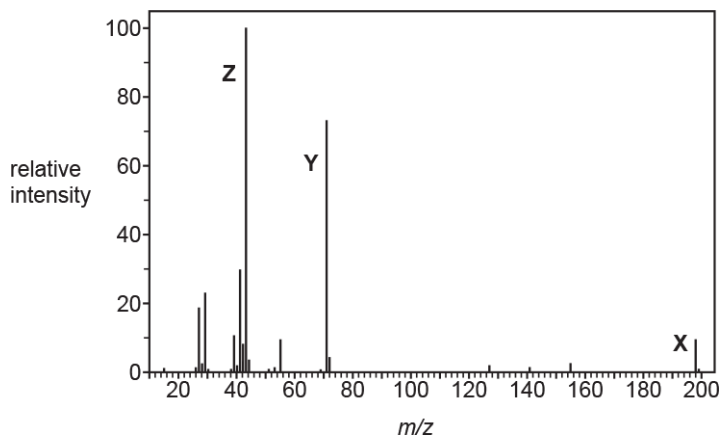
Your answer

[1]



34(a). This question is about 1-iodopentane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$.

The mass spectrum of 1-iodopentane is shown below.



- i. What information is given by the peak labelled **X** ($m/z = 198$)?

[1]

- ii. Write the structural formulae of the ions responsible for the peaks labelled **Y** and **Z**.

Y ($m/z = 71$)

Z ($m/z = 43$)

[2]

(b). 2-Iodo-2-methylbutane is an isomer of 1-iodopentane.

- i. Draw the structure of 2-iodo-2-methylbutane.

[1]

- ii. Suggest **one** similarity and **one** difference between the mass spectra of 1-iodopentane and 2-iodo-2-methylbutane.

Similarity

Difference

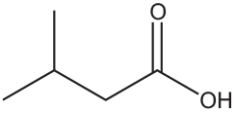
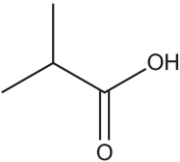
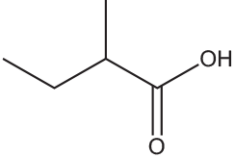
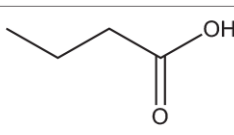
[2]



35.

The mass spectrum of a carboxylic acid contains peaks at $m/z = 29$ and $m/z = 102$.

Which compound could have produced the spectrum?

A	
B	
C	
D	

Your answer

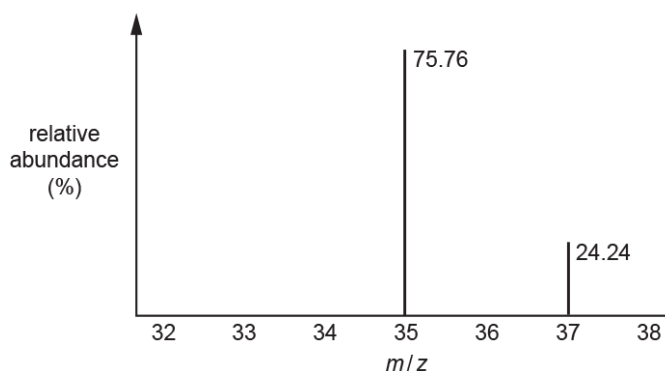
[1]



36. This question is about atoms, isotopes and mass spectrometry.

Mass spectrometry can be used to identify the isotopes of chlorine.

Part of the mass spectrum of chlorine is shown below.



i. Calculate the relative atomic mass of chlorine.

Give your answer to **2** decimal places.

relative atomic mass = [2]

ii. The mass spectrum of chlorine, Cl_2 , also contains three molecular ion, M^+ , peaks. One of the M^+ peaks has an m/z value of 72.

Suggest why an M^+ peak at $m/z = 72$ is observed and predict the m/z values of the other two M^+ peaks.

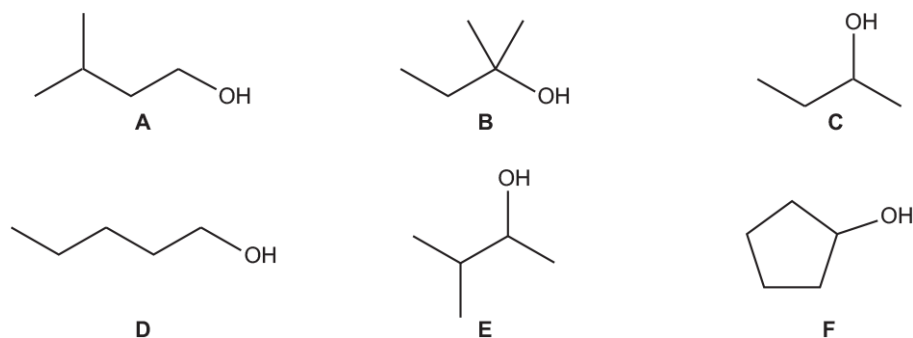
Peak at $m/z = 72$

m/z values of the other two M^+ peaks

[2]



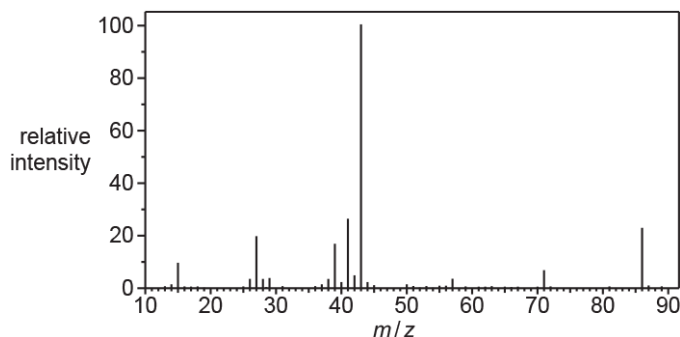
37. * The structures of alcohols A–F are shown below.



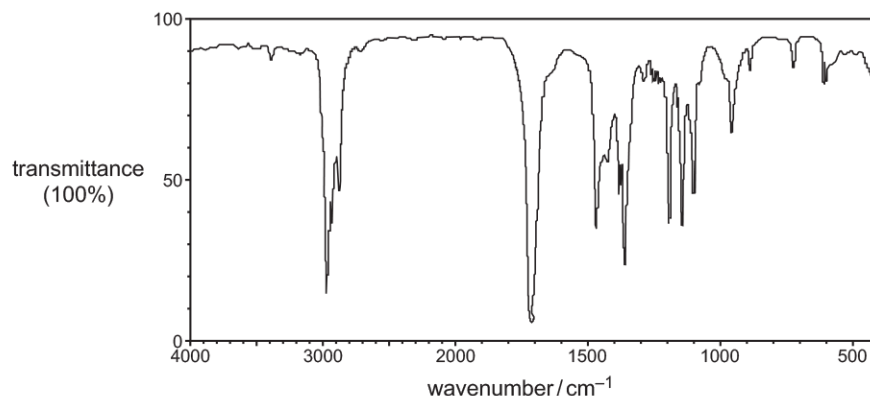
Compound **X** is one of the alcohols **A–F**.

A student refluxes compound **X** with acidified potassium dichromate(VI) as an oxidising agent. A pure sample of the organic product **Y** is obtained from the resulting mixture. The mass spectrum and IR spectrum of **Y** are shown below.

Mass spectrum of Y



IR spectrum of Y



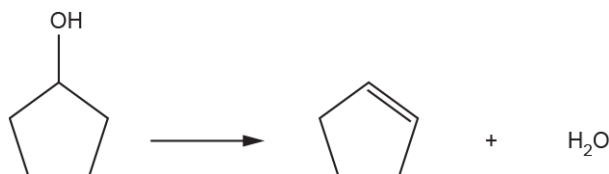


38. Cyclopentanol can be reacted to form cyclopentene.

Cyclopentene is a liquid with a boiling point of 44 °C and a density of 0.74 g cm⁻³.

A student plans to prepare 4.00 g of cyclopentene by reacting cyclopentanol (boiling point 140 °C) with an acid catalyst.

Equation

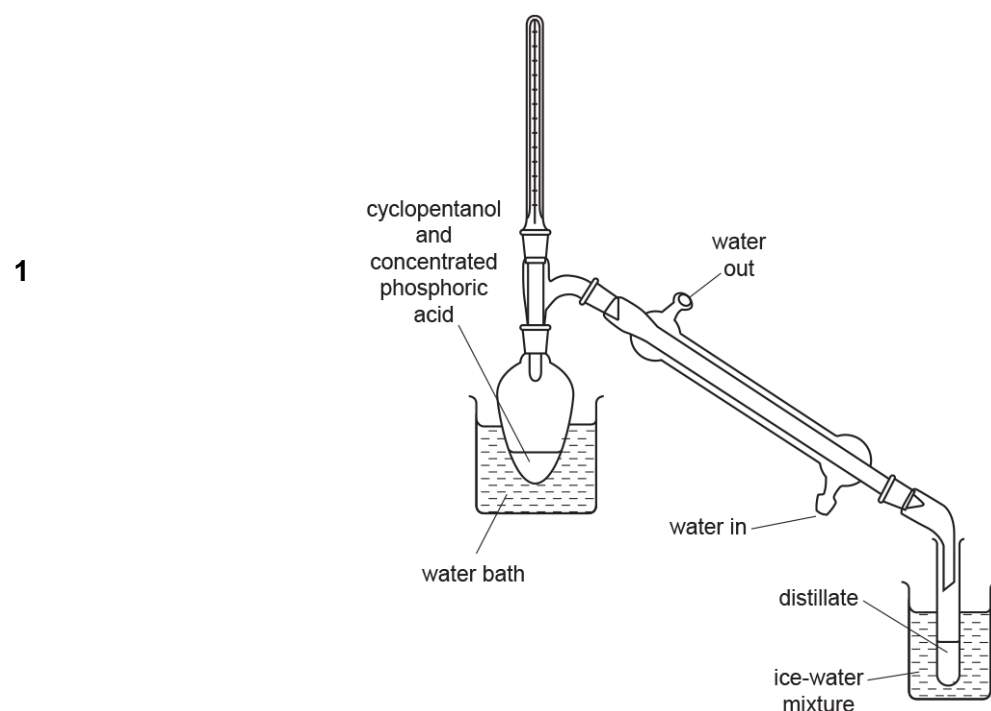


The expected percentage yield of cyclopentene is 64.0%.

Method

The student carries out the preparation using apparatus set up for distillation, as shown below.

The reaction mixture is heated gently, and a distillate containing impure cyclopentene is collected.

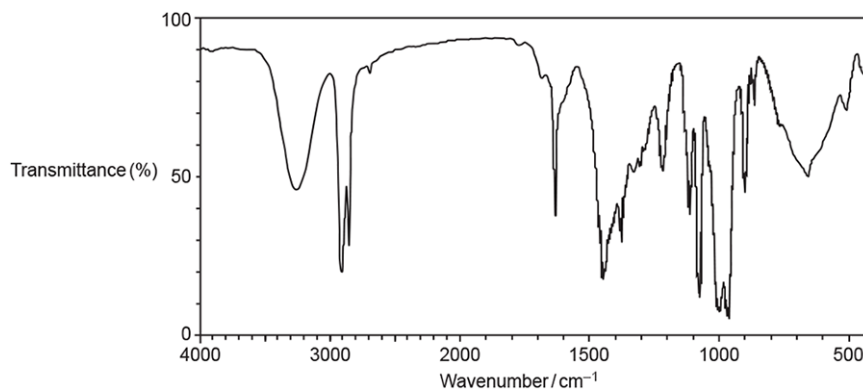


- 2
- The distillate has an aqueous layer and an organic layer.
The student purifies the cyclopentene from the distillate.



The organic layer in the distillate was analysed by IR spectroscopy.

The IR spectrum is shown below.



Explain how the IR spectrum of the organic layer suggests that cyclopentene has been formed and that the reaction is incomplete.

[2]

39. An organic compound **I** is analysed, using a combination of techniques. The analytical data is shown below.

Elemental analysis by mass

C, 56.69%; H, 7.09%; N, 11.02%; O, 25.20%

Mass spectrum

Molecular ion peak at $m/z = 127.0$



[6]

40. Which statement about absorption of radiation is correct?

- A Absorption of IR radiation can break covalent bonds, forming radicals.
- B Absorption of IR radiation causes covalent bonds to vibrate more.
- C Absorption of UV radiation is a major cause of global warming and climate change.
- D Absorption of UV radiation is used in modern breathalysers to measure ethanol in the breath.

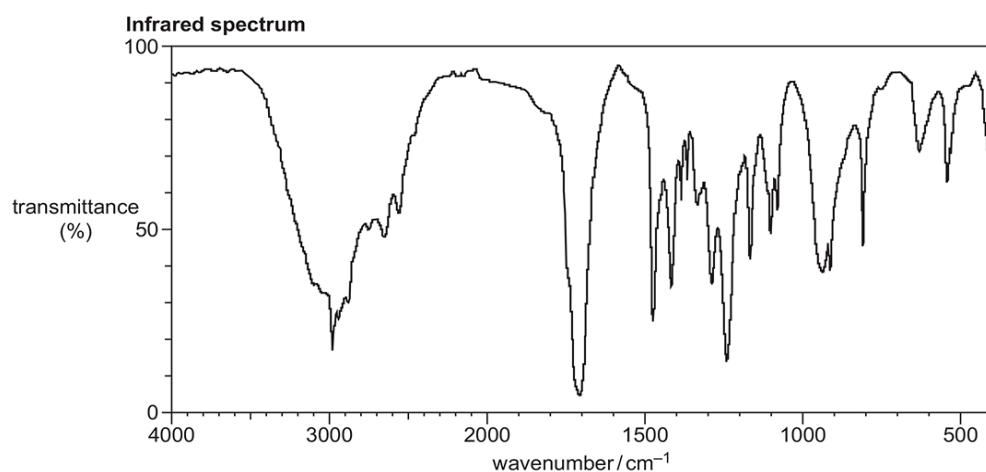
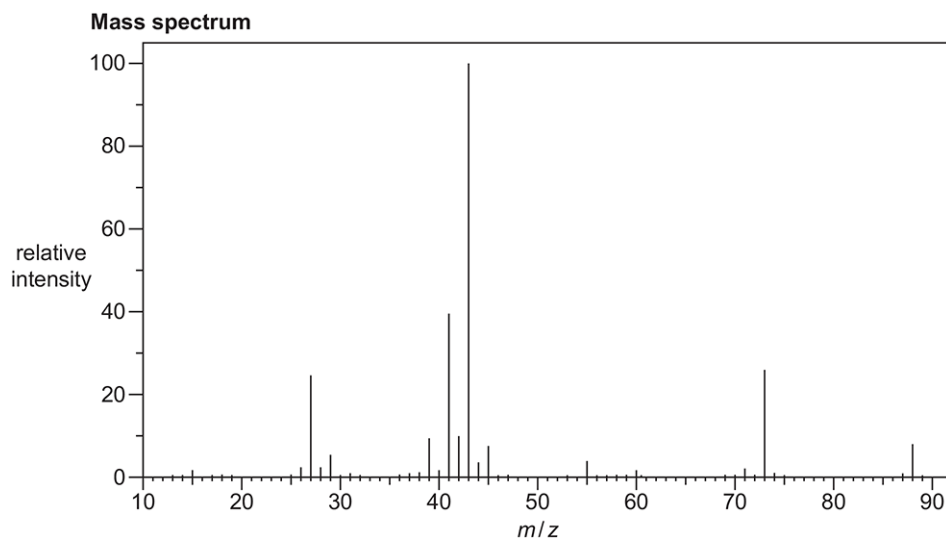
Your answer

[1]



41. An organic compound **E** contains C, H and O only.

The mass and infrared spectra of organic compound **E** are shown below.



Analyse this information to suggest **two** different possible structures for compound **E**.

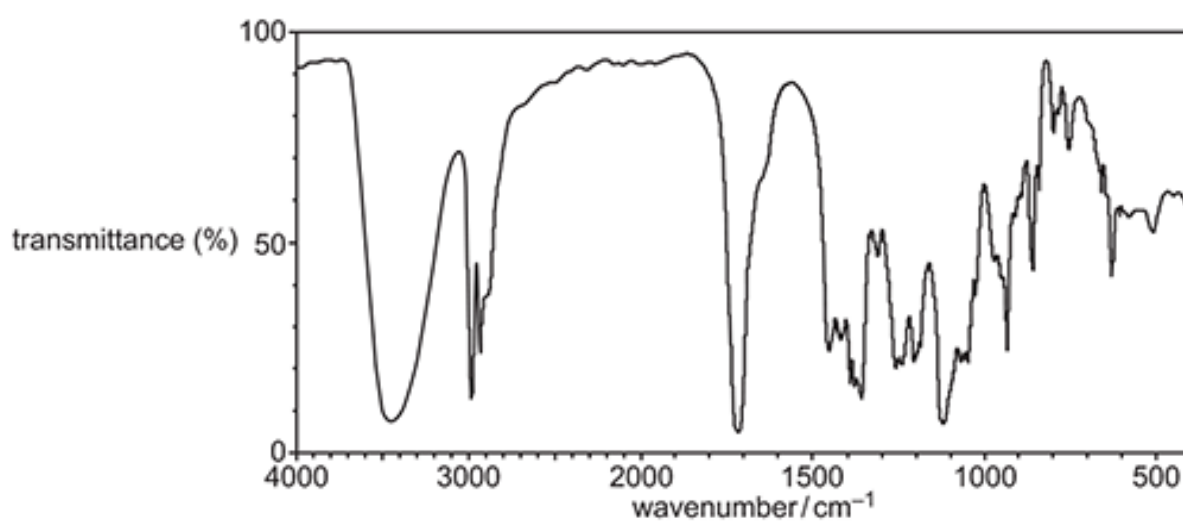
Explain your reasoning.



Structures	

[5]

42. Which compound could have produced the IR spectrum below?



- A $(\text{CH}_3)_2\text{CHCHO}$
- B $(\text{CH}_3)_2\text{CHCOOH}$
- C $\text{CH}_3\text{CH}(\text{OH})\text{CH}=\text{CH}_2$
- D $\text{CH}_3\text{COCH}(\text{OH})\text{CH}_3$

Your answer

[1]



43. Which peak would be in the mass spectrum of propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, but **not** in the mass spectrum of propanone, CH_3COCH_3 ?

- A $m/z = 15$
- B $m/z = 29$
- C $m/z = 43$
- D $m/z = 58$

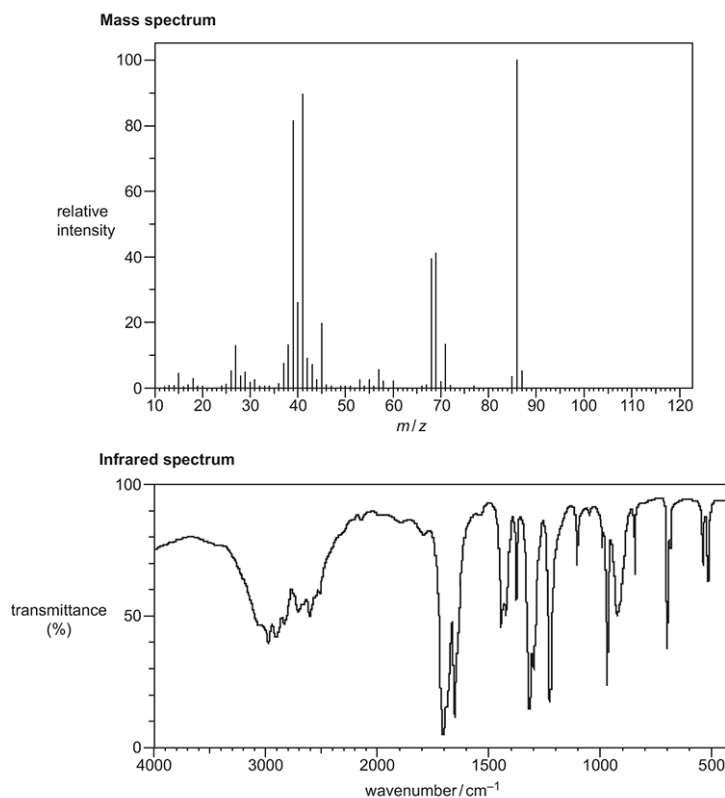
Your answer

[1]

44. * The organic compound **A** is unsaturated and is a *trans* stereoisomer.

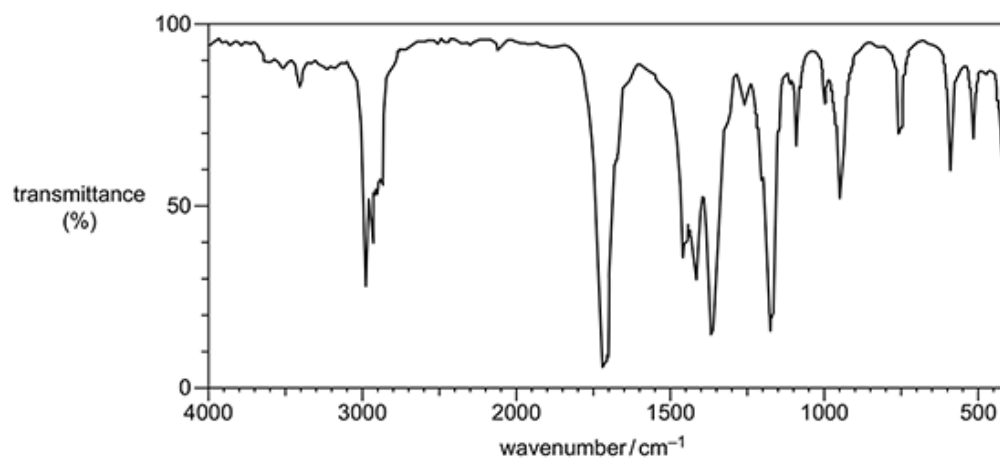
Compound **A** has the following composition by mass: C, 55.8%; H, 7.0%; O, 37.2%.

The mass spectrum and the infrared spectrum of compound **A** are shown below.





45. Which organic compound could have produced the infrared spectrum below?



- A $\text{CH}_3\text{COCH}_2\text{CH}_3$
- B $\text{CH}_3\text{CH}_2\text{CHOHCH}_3$
- C $\text{CH}_3\text{COCH}_2\text{CH}_2\text{OH}$
- D $\text{CH}_3\text{CH}_2\text{COOH}$

Your answer

[1]

46. Which alcohol is likely to have fragment ions at $m/z = 15$, 29 **and** 43 in its mass spectrum?

A	
B	
C	
D	

Your answer

[1]



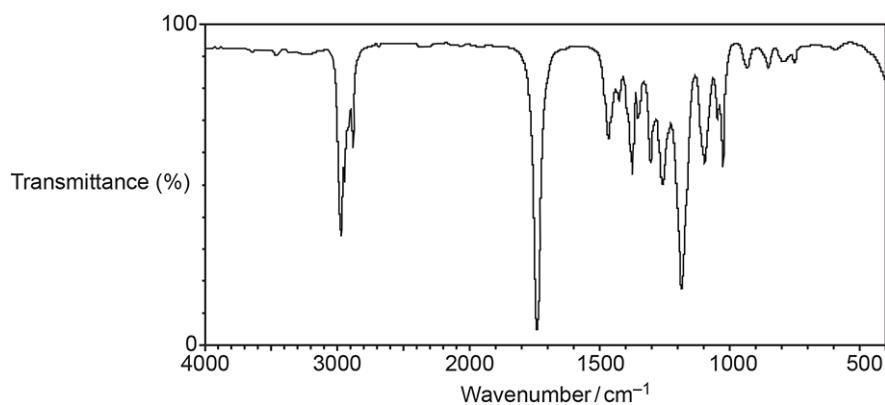
47. Which statement about absorption of radiation is correct?

- A Infrared radiation can result in the breakdown of the ozone layer.
- B Ultraviolet radiation can cause some polymers to photodegrade to benefit the environment.
- C Ultraviolet radiation is linked to global warming.
- D Ultraviolet radiation is used in modern breathalysers to measure ethanol in the breath.

Your answer

[1]

48. The infrared spectrum of an organic compound is shown below.



Which compound could have produced this spectrum?

- A $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{OH}$
- B $\text{CH}_3\text{COOCH}_2\text{CH}_3$
- C $\text{H}_2\text{NCH}_2\text{COOCH}_3$
- D $(\text{CH}_3)_2\text{CHCONH}_2$

Your answer

[1]



49. This question is about unsaturated hydrocarbons.

Compounds **B** and **C** are **branched** hydrocarbons that are structural isomers of C_6H_{12} .

Compounds **B** and **C** both have stereoisomers.

- Compound **B** has *cis* and *trans* isomers but does **not** have optical isomers.
- Compound **C** has optical isomers but does **not** have *cis* and *trans* isomers.

i. What is meant by the term **structural isomers**?

[1]

ii. What is meant by the term **stereoisomers**?

[1]

iii. Draw structures for the *cis* and *trans* isomers of the branched hydrocarbon **B**.

<i>cis</i> isomer	<i>trans</i> isomer

[2]



- iv. Draw 3D structures for the optical isomers of compound **C**.

Optical isomers	

[2]

- v. Compounds **D** and **E** are two more structural isomers of C_6H_{12} .

Compounds **D** and **E** do **not** show stereoisomerism.

Table 16.1 shows NMR and infrared (IR) spectral data for **D** and **E**.

	Number of peaks in 1H NMR spectrum	Number of peaks in ^{13}C NMR spectrum	IR peak at $1620-1680\text{ cm}^{-1}$
D	1	1	No
E	1	2	Yes

Table 16.1

Draw the structures of **D** and **E** and explain how the spectral data in **Table 16.1** provides evidence for the structures.

D	E



[4]

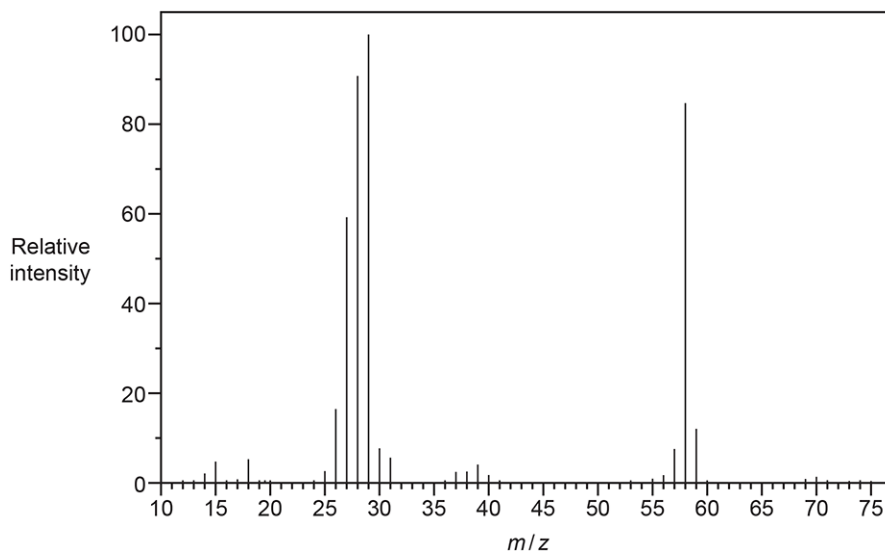
50. A student is provided with two unknown carbonyl compounds, **F** and **G**.

The compounds are analysed and found to have identical percentage compositions by mass:

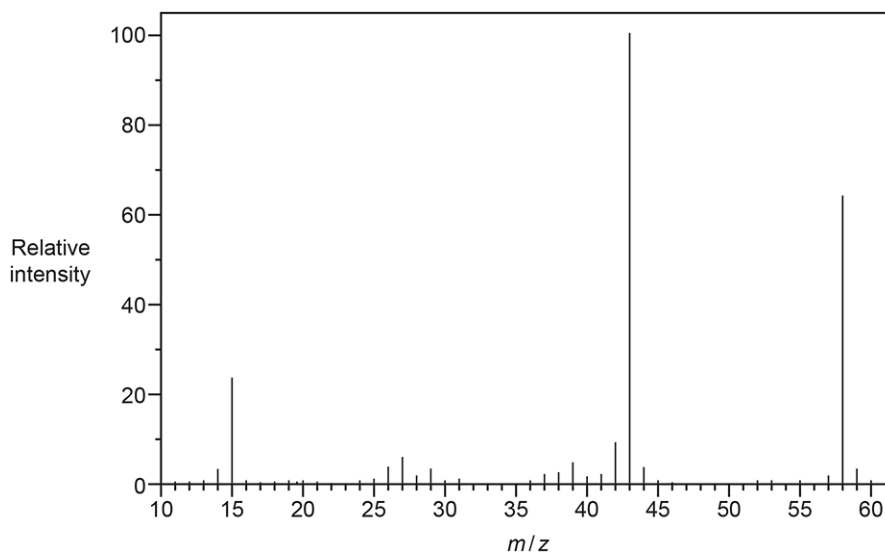
C: 62.07%; H: 10.34%; O: 27.59%

The mass spectra of the two compounds are shown below.

Mass spectrum of F



Mass spectrum of G





Use the results to identify the structures of the two compounds.

Include relevant peaks present in the mass spectrum of each compound.

F	G

[4]



51. Which ester is most likely to produce a mass spectrum with a fragment ion at $m/z = 43$?

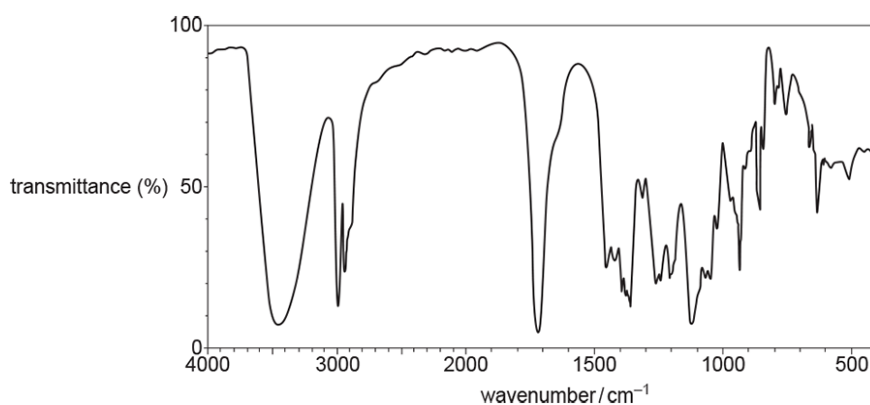
A	$\begin{array}{c} \text{OH} \quad \text{O} \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{O}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$
B	$\text{HO}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3$
C	$\begin{array}{c} \text{OH} \quad \text{O} \\ \quad \\ \text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{C}-\text{O}-\text{CH}_3 \end{array}$
D	$\begin{array}{c} \text{OH} \quad \text{O} \\ \quad \\ \text{CH}_3\text{CH}_2-\text{C}-\text{C}-\text{O}-\text{CH}_2\text{CH}_2\text{OH} \\ \\ \text{CH}_3 \end{array}$

Your answer

[1]



52. The infrared spectrum of an organic compound is shown below.



Which compound could have produced this spectrum?

A	
B	
C	
D	

Your answer

[1]



53. An unknown organic compound is analysed.

The results are shown below.

Addition of 2,4-DNP

No visible change

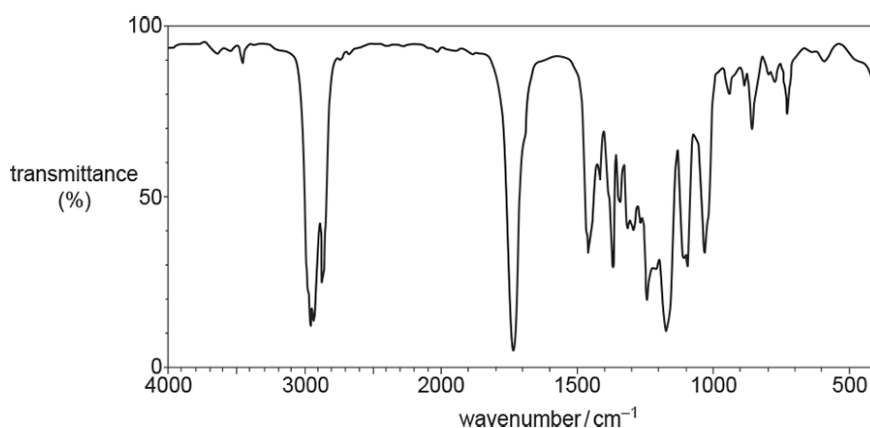
Elemental analysis by mass

C, 66.63%; H, 11.18%; O, 22.19%

Mass spectrum

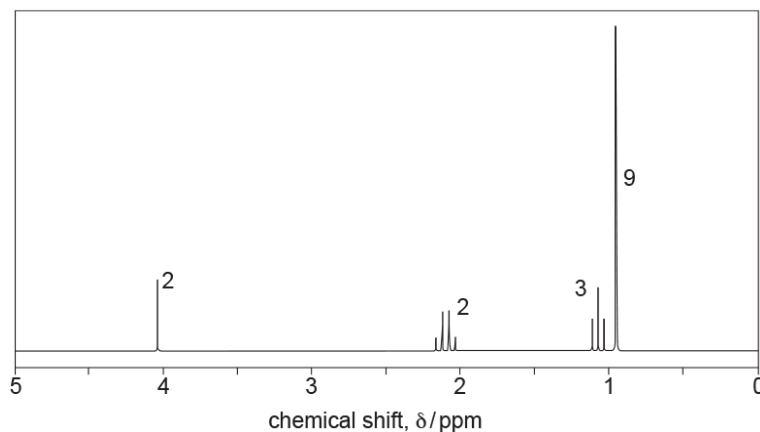
Molecular ion peak at $m/z = 144.0$

IR spectrum



Proton NMR spectrum

The numbers by each peak are the relative peak areas.





55. Pentan-2-ol and pentan-3-ol are structural isomers with the molecular formula $C_5H_{12}O$ and $M_r = 88$.

The isomers can be distinguished from the fragment ions in their mass spectra.

Which fragment ion would you expect to be present in only **one** of these isomers?

- A $m/z = 29$
- B $m/z = 45$
- C $m/z = 59$
- D $m/z = 73$

Your answer

[1]

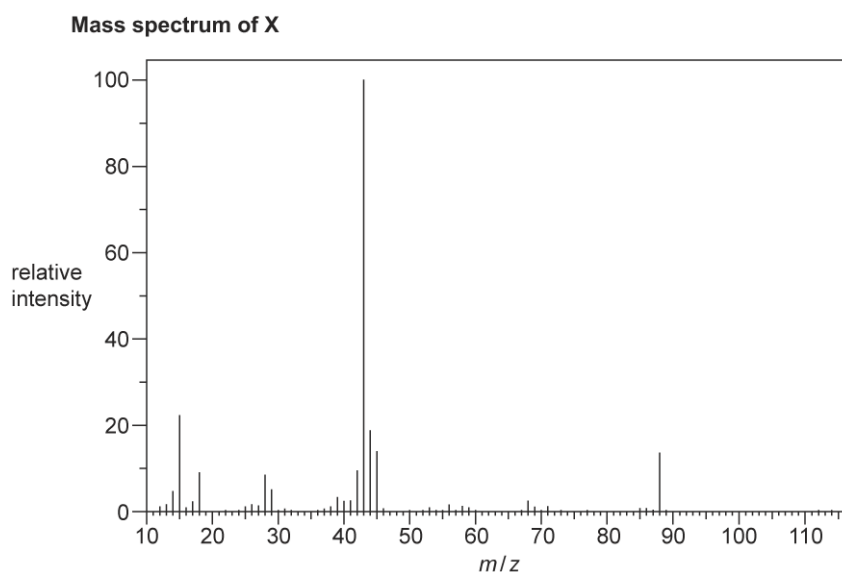
56. Compound **X** is an organic compound with **two** functional groups.

Compound **X** has the percentage composition by mass:

C, 40.91%; H, 4.54%; O, 54.55%.

Compound **X** does **not** decolourise bromine water.

A scientist analyses compound **X** using mass spectrometry and infrared spectroscopy.





57. Which statement about infrared radiation (IR) is **not** correct?

- A Absorption of IR by molecules such as CO₂, H₂O and CH₄ has been linked to global warming.
- B IR causes CFC molecules to produce chlorine radicals that initiate ozone breakdown in the upper atmosphere.
- C IR causes some covalent bonds to vibrate more and absorb energy.
- D IR is used in modern breathalysers to detect ethanol.

Your answer

[1]

58. An alcohol CH₃CH₂CH(CH₃)OH produces a mass spectrum.

The mass spectrum contains a large fragment ion at $m/z = 45$.

What is the possible identity of this fragment ion?

- A CH₂CHOH⁺
- B CH₂CH₂OH⁺
- C CH₃CHOH⁺
- D CH₃CH₂CH⁺

Your answer

[1]

59. Which statement gives a valid scientific reason for global warming?

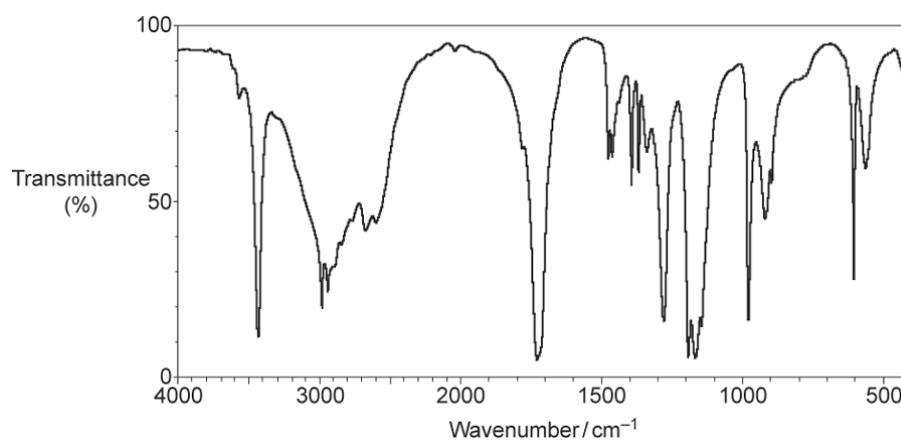
- A Infrared radiation causes bonds in CH₄ molecules to vibrate more.
- B Infrared radiation causes O₂ molecules to vibrate more.
- C Ultraviolet radiation causes bonds in CO₂ to vibrate more.
- D Ultraviolet radiation causes bonds in CFC molecules to break.

Your answer

[1]



60. Which compound could have produced the IR spectrum shown below?



- A HOCH_2CHO
- B $\text{CH}_3\text{CH}_2\text{COOH}$
- C $\text{CH}_3\text{CH}_2\text{COOCH}_3$
- D $(\text{CH}_3)_2\text{C}(\text{OH})\text{COOH}$

Your answer

[1]

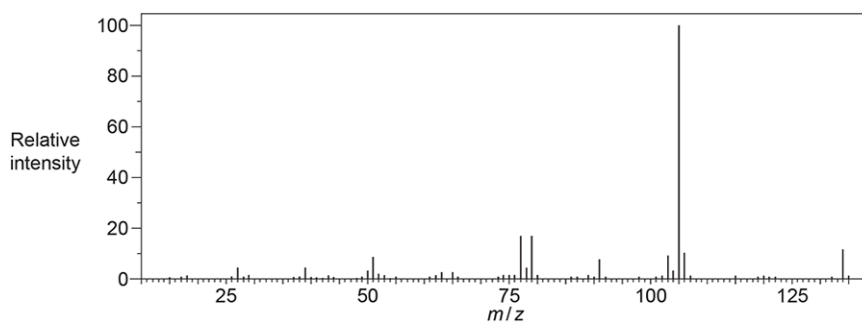


61. Analysis of an unknown organic compound **J** produces the following results.

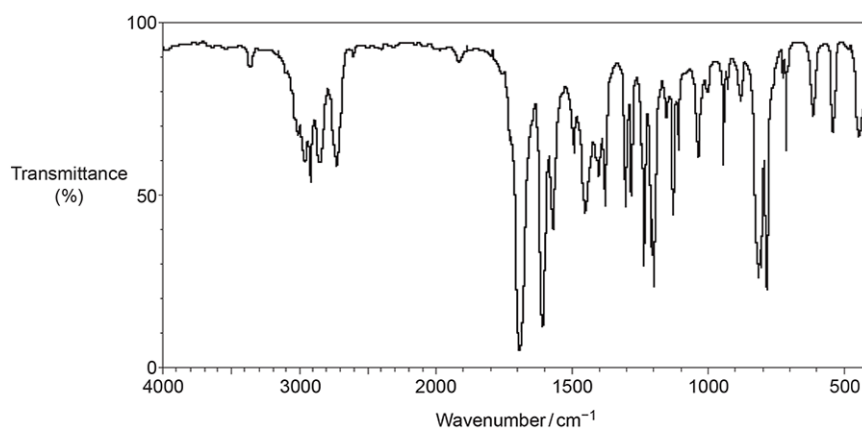
Elemental analysis by mass of compound **J**

C, 80.60%; H, 7.46%; O, 11.94%

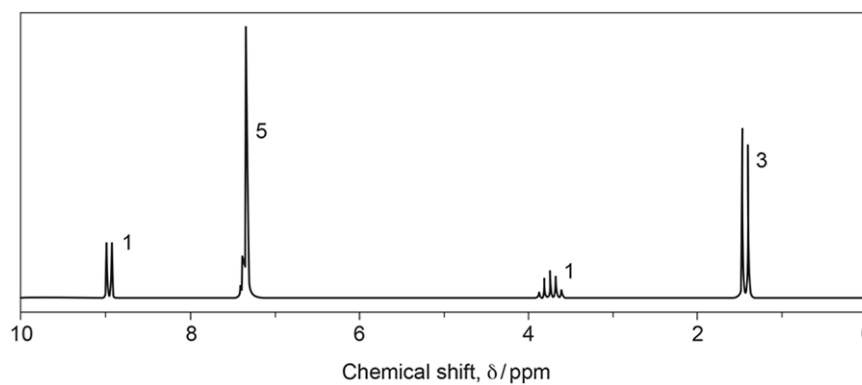
Mass spectrum of compound **J**



IR spectrum of compound **J**



Proton NMR spectrum of compound **J**





Mark scheme

Question	Answer/Indicative content	Marks	Guidance
1	<p>(broad) peak at 3300–3600 (cm⁻¹) for O–H (therefore A or C) (1)</p> <p>molar ratio: C : H : O</p> $\frac{78.94}{12.0} : \frac{10.53}{1.0} : \frac{10.53}{16.0} \text{ OR } 6.58 : 10.53$ <p>(1)</p> <p>10 : 16 : 1 OR C₁₀H₁₆O, therefore C (1)</p>	3	<p>allow 3200–3600 cm⁻¹</p> <p>ignore references to the peak at ~2900 for C–H</p> <p>allow annotation of the spectrum to identify the bond responsible for the peak instead of quoting the wavenumber.</p> <p>Conclusion may also follow from empirical formula followed by IR data.</p>
	Total	3	
2	<p>I = C₄H₁₀⁺ (1)</p> <p>II = C₃H₇⁺ (1)</p> <p>III = C₂H₅⁺ (1)</p> <p>C₃H₇⁺ could be CH₃CH₂CH₂⁺ or CH₃CHCH₃⁺</p> <p>OR</p> <p>C₃H₇⁺ could be from CH₃CH₂CH₂CH₃ or CH₃CH(CH₃)₂ (1)</p> <p>CH₃CH₂⁺ could only be from CH₃CH₂CH₂CH₃ (1)</p>	5	<p>THROUGHOUT:</p> <p>if any charge is missing, do not allow 1st formula but allow subsequent formulae by ecf</p> <p>allow + charge anywhere</p>
	Total	5	
3	<p><i>* Please refer to the marking instruction point 10 for guidance on how to mark this question.</i></p> <p>(Level 3)</p> <p>Candidate provides a method for identifying the alcohols AND provides all supporting evidence from IR spectrum AND gives details of reagents and conditions and correct equations.</p> <p><i>The explanation is detailed and well structured. The information is clearly supported by details of reactions and evidence of oxidation product.</i></p>	6	<p>Indicative scientific points may include</p> <p>Identification of alcohols</p> <p>Based on recognition of alcohols as primary, secondary and tertiary (stated or implied by method). Basic procedure involves reflux followed by use of IR to identify different oxidation products.</p> <p>Reactions</p> <ul style="list-style-type: none"> stated reagents (H⁺/Cr₂O₇²⁻ and conditions (reflux)) equations using [O] including structural formulae <p>CH₃CH₂CHOHCH₃ + [O] →</p>

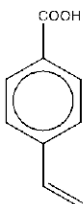
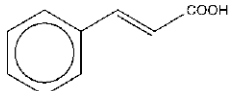
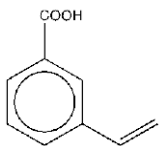
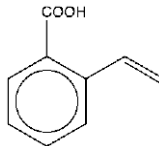


			(5–6 marks)		$\text{CH}_3\text{CH}_2\text{COCH}_3 + \text{H}_2\text{O}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + 2[\text{O}] \rightarrow$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{H}_2\text{O}$ <p>Identification of oxidation product</p> <ul style="list-style-type: none"> IR: carboxylic acid from broad OH absorption and C=O IR: carbonyl / ketone from C=O and no OH tertiary alcohol from lack of C=O and OH peak in IR <p>OR no colour change in reflux.</p>																
			<p>(Level 2) Candidate provides a basic method AND provides some supporting evidence from IR spectrum AND gives details of reagents and conditions with some attempt at equations.</p> <p><i>The explanation has some structure. The information is supported by some details of reactions and evidence from IR spectrum.</i></p> <p>(3–4 marks)</p> <p>(Level 1) Candidate attempts to describe a basic method AND gives some supporting evidence from IR spectrum OR details of reagents and conditions with some attempt at equations.</p> <p><i>The explanation is basic and lacks structure. The information is supported by limited evidence from the reactions and oxidation products and would not lead to identification.</i></p> <p>(1–2 marks)</p> <p>No response or no response worthy of credit.</p> <p>(0 marks)</p>																		
			Total	6																	
4			<p>Use of elemental analysis data</p> <table border="1"> <thead> <tr> <th></th> <th>C</th> <th>H</th> <th>O</th> </tr> </thead> <tbody> <tr> <td>%</td> <td>46.1</td> <td>7.7</td> <td>46.2</td> </tr> <tr> <td>mol</td> <td>3.84</td> <td>7.7</td> <td>2.89</td> </tr> <tr> <td>ratio</td> <td>1.33</td> <td>2.66</td> <td>1</td> </tr> </tbody> </table>		C	H	O	%	46.1	7.7	46.2	mol	3.84	7.7	2.89	ratio	1.33	2.66	1	5	
	C	H	O																		
%	46.1	7.7	46.2																		
mol	3.84	7.7	2.89																		
ratio	1.33	2.66	1																		



	<p>atom ratio with calculation empirical formula = C₄H₈O₃</p> <p>IR spectrum (very) broad absorption 2500–3300 cm⁻¹ (COOH) AND absorption 1640–1750 cm⁻¹ (C=O) absorption 3450 cm⁻¹ (alcohol –OH)</p> <p>Identification</p> <p>conclusion from data: compound contains –COOH and –OH (empirical formula confirms no other C=O than in COOH) in place of the previous chlorine-containing groups</p> $ \begin{array}{c} \text{H} \quad \text{OH} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{CH}_3 \\ \quad \\ \text{H} \quad \text{COOH} \end{array} $		<p>ALLOW any values given within ranges given on Data Sheet</p> <p>ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous</p>
	Total	5	
5	<p>* Please refer to the marking instruction point 10 for guidance on how to mark this question.</p> <p>Level 3 (5–6 marks) Structure correct AND Analysed all ¹H NMR signals with at least two supporting statements made.</p> <p><i>The analysis is clear and logically structured. The supporting statements are relevant to the correct structure drawn.</i></p> <p>Level 2 (3–4 marks) Structure has correct molecular formula AND C=O AND OH but in incorrect positions AND Analysed at least three ¹H NMR signals with one or two supporting statements made.</p> <p><i>The analysis is presented with some structure. The supporting statements</i></p>	6	<p>Indicative scientific points may be included:</p> <p>Structure</p> <p>L =</p> <p>¹H NMR spectrum</p> <p>δ = 3.8 ppm, triplet, 2H CH₂—CH₂—O</p> <p>δ = 3.7 ppm, singlet, 1H O—H</p> <p>δ = 3.1 ppm, triplet, 2H CH₂—CH₂C=O</p> <p>δ = 2.7 ppm, septet, 1H (CH₃)₂CHC=O</p> <p>δ = 1.0 ppm, doublet, 6H (CH₃)₂CH</p> <p>Supporting statements δ = 3.7 ppm lost after D₂O, indicating —OH δ = 213 ppm in ¹³C NMR but no δ = 9–10 ppm in ¹H NMR so ketone, not aldehyde M_r(C₃H₆O) = 58 116/58 = 2 → C₆H₁₂O₂</p>



		<p>are in the most-part relevant to the structure drawn.</p> <p>Level 1 (1–2 marks) Structure has correct molecular formula AND C=O OR OH but in incorrect positions. AND Analysed at least two ^1H NMR signals with no or one supporting statements made.</p> <p><i>The analysis is basic and communicated in an unstructured way. The relationship of the supporting evidence to the structure may not be clear.</i></p> <p>0 marks No response or no response worthy of credit.</p>		
		Total	6	
6		A	1	
		Total	1	
7		<p>Electrophilic substitution means benzene ring</p> <p>Electrophilic addition means alkene / C=C</p> <p>Isomer of $\text{C}_9\text{H}_8\text{O}_2$ containing C=C, benzene ring AND COOH Correct isomer:</p> <div style="display: flex; align-items: center; justify-content: center;">  OR  </div> <p>justification in terms of number of carbon environments</p>	5	<p>Concluded using data provided and conclusions from 1st two marks.</p> <p>ALLOW 1 mark for:</p> <div style="display: flex; align-items: center; justify-content: center;">  OR  </div> <p>(does not gain final justification mark)</p>
		Total	5	
8		<p>Molecular formula for G: 2 marks</p>	7	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES ETC</p> <p>ALLOW mass of C = 0.558×86 or 48 AND mass of H = 0.07×86 or 6 AND mass of O =</p>



<p style="text-align: right;">$\frac{55.8}{12.0} : \frac{7.0}{1.0} : \frac{37.2}{16.0}$</p> <p>Mole ratio C : H : O = $\frac{55.8}{12.0} : \frac{7.0}{1.0} : \frac{37.2}{16.0}$</p> <p>OR 4.65 : 7.0 : 2.33 / 2.325 OR 2 : 3 : 1 OR C₂H₃O ✓</p> <p>Molecular formula of G C₄H₆O₂ ✓</p> <p>Mass spectrum for G: 2 marks</p> <p>Peak X or peak 41 indicates C₃H₅⁺ ✓</p> <p>Peak Y or peak 45 indicates COOH⁺ ✓</p> <p>Infrared for G: 1 marks</p> <p>Peak at 1640–1750 cm⁻¹ indicates presence of C=O AND Peak at 2500–3300 cm⁻¹ (indicates the presence of) –OH group linked carboxylic acid / COOH QWC ✓</p> <p>Structure of G: 2 marks</p> <p>Correct structure:</p> <div style="text-align: center;"> </div> <p>✓✓</p> <p>1 mark for one of the following structures of C₄H₆O₂:</p> <p>H₂C = CH—CH₂—COOH OR H₃C—CH = CH—COOH</p>	<p>0.372 x 86 = 32</p> <p>+ charge required for each response ALLOW one mark if both formulae are correct but with no charge/incorrect charge</p> <p>ALLOW any possible fragments that contain C, H and / or O that have the correct mass. E.g. Peak X indicates C₂OH⁺, Peak Y indicates C₂H₅O⁺ Unfeasible fragments are not allowed e.g. C₃H₉⁺ (too many H atoms)</p> <p>LOOK ON THE SPECTRUM for labelled absorbance which can be given credit Candidates must link absorbance to bond in order to gain the mark</p> <p>ALLOW 1700 cm⁻¹</p> <p>For 2500–3300 cm⁻¹, ALLOW 2900 cm⁻¹ or any stated wavenumber with range 2500–3300 cm⁻¹ ALLOW wavenumber range up to 2400–3500 cm⁻¹</p> <p>ALLOW structural, skeletal or displayed formula.</p> <p>DO NOT ALLOW ECF from incorrect molecular formula</p> <p>Examiner's Comments</p> <p>This question allowed the candidates to demonstrate their understanding of the more complex aspects of the course and use their problem-solving skills to tie together the all of the evidence.</p> <p>The calculation of the empirical formula was completed well and most candidates were able to determine the molecular formula of G.</p> <p>Many of the more able candidates were able to identify one, if not both, of the ions responsible</p>
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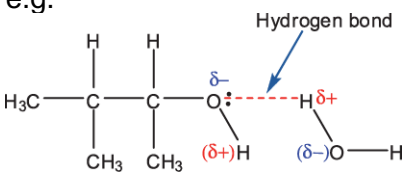


		<p>OR</p>		<p>for peaks X and Y in the mass spectrum. A number of candidates were able to show correct fragments but omitted the positive charge. Candidates should be reminded to include the correct charge when suggesting particles responsible for peaks in mass spectra.</p> <p>The majority of candidates were able to recognise the characteristic absorptions in the IR spectrum. The strongest responses attributed these peaks to the appropriate bonds and deduced that G was a carboxylic acid.</p> <p>Two marks were available for the structure of G. The most able candidates were able to interpret all the information and provide the correct branched carboxylic acid. Some candidates recognised that the number of hydrogen atoms present suggested the presence of a carbon- carbon double bond, but suggested a straight chain compound. Other candidates provided a cyclic carboxylic acid. These two approaches were awarded one mark. The most common incorrect structure seen for G was butanoic acid.</p>
		Total	7	
9		Carboxylic acids have a broad O-H absorption at 2500–3300 (cm ⁻¹) (which ketones do not)	1	
		Total	1	
10	i	<p>bond vibrates (more) OR bond bends (more) OR bond stretches (more) ✓</p>	1	<p>BOND essential</p> <p>IGNORE molecule vibrates / rotates Assume "It" refers to the molecule and is insufficient DO NOT ALLOW any reference to bond breaking</p> <p>DO NOT ALLOW a stated bond if not present in C and F e.g. C–O, C–H not present</p> <p>Examiner's Comments</p> <p>Most candidates identified that IR radiation would cause the bonds within the molecule to vibrate. However, there were many examples of vague responses such as 'they vibrate'.</p>

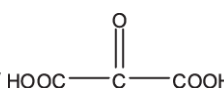


				Candidates are advised identify the subject of their statement and avoid the use of words such as 'they' and 'it' in their responses.
		ii	C_3C^+ ✓ CF_2C^+ ✓	<p>ALLOW 1 mark for C_3C AND CF_2C <i>i.e. no + charge used</i></p> <p>ALLOW 1 mark for C_3C^- AND CF_2C^- <i>i.e. — charge used on both</i></p> <p>Examiner's Comments</p> <p>The majority of candidates identified the formulae of the two ions, although not all candidates specified the correct charge. Candidates should be aware that fragmentation in a mass spectrometer produces positive ions.</p>
		Total		3
1 1	a		<p>QWC: Evidence of the IR absorption at 1720 (cm^{-1}) for presence of C=O / carbonyl group ✓</p> <p>QWC: No carboxylic acid OH absorption in IR OR no peak between 2500–3300 cm^{-1} AND so J is a secondary alcohol OR so K is a ketone ✓</p> <p>Alcohol J</p> $ \begin{array}{c} \text{OH} \quad \text{H} \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{CH}_3 \\ \quad \\ \text{H} \quad \text{CH}_3 \quad \checkmark\checkmark \end{array} $ <p>Compound K Structure of a carbonyl compound that could be obtained from alcohol J ✓</p>	<p>6</p> <p>ANNOTATE ANSWER WITH TICKS AND CROSSES ETC</p> <p>LOOK ON THE SPECTRUM for labelled peaks which can be given credit BOTH IR at ~ 1720 (cm^{-1}) AND C=O required ALLOW ranges from <i>Data Sheet</i>, i.e. C=O within range 1640–1750 cm^{-1};</p> <p>IGNORE any reference to C-O absorption For structures of J and K, ALLOW correct structural OR displayed OR skeletal formula OR mixture of the above IGNORE any names given for J and K</p> <p>ALLOW 1 mark for the structure of an alcohol with the molecular formula $C_5H_{12}O$ DO NOT ALLOW pentan-1-ol (<i>primary and unbranched</i>) or 2-methylbutan-2-ol (<i>branched but tertiary</i>)</p> <p>DO NOT ALLOW any marks for J and K if more than one structure is given for J</p> <p>Note: 'sticks' in either J and / or K will lose only 1 mark</p> <p>ALLOW 1 mark for:</p> $ \begin{array}{c} \text{O} \quad \text{H} \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{CH}_3 \\ \quad \quad \\ \quad \quad \text{CH}_3 \end{array} $



	<p>Equation Balanced equation for conversion of J to K ✓ e.g. $\text{CH}_3\text{CHOHCH}(\text{CH}_3)_2 + [\text{O}] \rightarrow \text{CH}_3\text{COCH}(\text{CH}_3)_2 + \text{H}_2\text{O}$</p>		<p>IF a structure is not given for J</p> <p>NOTE: structures for J and K could be awarded from the equation, even if not labelled.</p> <p>ALLOW molecular formulae in equation i.e. $\text{C}_5\text{H}_{12}\text{O} + [\text{O}] \rightarrow \text{C}_5\text{H}_{10}\text{O} + \text{H}_2\text{O}$ DO NOT ALLOW equations that form a carboxylic acid</p> <p>Examiner's Comments</p> <p>This question discriminated well and most candidates were able to score at least one mark, by identifying the C=O peak in the IR spectrum provided. The most able candidates gave succinct responses that included both the correct structures of J and K as well as a balanced equation. In addition, they included reference to the absence of a carboxylic acid O-H peak in the IR spectrum concluding that K must be a ketone. This marking point was missed by a large proportion of the cohort and often a branched primary alcohol for J and corresponding aldehyde for K were suggested. Some candidates incorrectly identified the C—H peak in the spectrum as an O—H and suggested that K was a carboxylic acid.</p>
b	<p>Labelled diagram showing at least one H-bond between alcohol molecule and water ✓ e.g.</p> 	1	<p>IF diagram is not labelled ALLOW Hydrogen bonds / H bonds from text</p> <p>Diagram should include role of an O lone pair and dipole charges on each end of H bond.</p> <p>IGNORE alcohol R group, even if wrong</p> <p>ALLOW structural OR displayed OR skeletal formula OR mixture of the above</p> <p>Examiner's Comments</p> <p>The majority of candidates were able to draw a diagram to show the hydrogen bond between an alcohol and water. However, a significant proportion lacked the accuracy required at this level and failed to show the role of the lone pair. It was also common to see responses that omitted the relevant dipoles. The question asked for the inclusion of relevant dipoles and lone pairs and candidates are advised to</p>



				double check diagrams to ensure these key features are not neglected.
		Total	7	
1 2	a	<p>Mole ratio C : H : O is 3.33 : 6.67 : 3.33 ✓</p> <p>Empirical formula is CH₂O ✓</p> <p>Molecular formula is C₃H₆O₃ AND use of 90 OR 3 + 30 ✓</p>	3	<p>ALLOW $\frac{40.00}{12.0}, \frac{6.67}{1.0}, \frac{53.33}{16.0}$</p> <p>ALLOW mass of C = 0.400 × 90 or 36 AND mass of H = 0.06677 × 90 or 6 AND mass of O = 0.5333 × 90 or 48</p> <p>Examiner's Comments</p> <p>Almost all candidates were able to correctly calculate the empirical formula of L. Although the majority also deduced the correct molecular formula, not all included their working. A small, but significant, proportion of candidates omitted this part of the question. Candidates are advised to show all working when required.</p>
	b	<p>Evidence of carboxylic acid (1 mark) IR: 1550–1800 cm⁻¹ AND C=O / carbonyl AND 2300–3700 cm⁻¹ AND O–H in carboxylic acid ✓</p> <p>Evidence of alcohol (1 mark)</p> <p>(broad) 3200–3700 cm⁻¹ linked to O–H in alcohol OR (is a primary) alcohol as oxidised (to a COOH) OR is an alcohol as it forms a carboxylic acid OR is an alcohol as water is eliminated. ✓</p> <p>Identifications (2 marks)</p>	5	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES ETC</p> <p>LOOK ON THE SPECTRUM for labelled peaks which can be given credit</p> <p>ALLOW ranges from <i>Data Sheet</i>: C=O within range 1640–1750 cm⁻¹; (broad) O–H within range 2500–3300 cm⁻¹ (broad) O–H within range 3200–3550 cm⁻¹</p> <p>For ALL structures: ALLOW correct structural OR skeletal OR displayed formula OR mixture of the above</p> <p>IGNORE names</p> <p>FOR M: ALLOW 1 mark for  ✓</p>



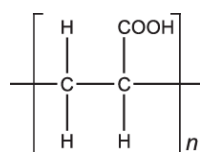
	<p>L:</p> $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{HO}-\text{C}-\text{C}-\text{COOH} \\ \quad \\ \text{H} \quad \text{H} \end{array} \quad \checkmark$ <p>M:</p> $\begin{array}{c} \text{H} \\ \\ \text{HOOC}-\text{C}-\text{COOH} \\ \\ \text{H} \end{array} \quad \checkmark$ <p>Equation (1 mark) $\text{C}_3\text{H}_6\text{O}_3 + 2[\text{O}] \rightarrow \text{C}_3\text{H}_4\text{O}_4 + \text{H}_2\text{O} \quad \checkmark$</p>		<p>AS ECF from L as either</p> $\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \\ \quad \quad \\ \text{HO}-\text{C}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{H} \quad \text{H} \end{array} \quad \text{OR} \quad \begin{array}{c} \text{H} \quad \text{OH} \\ \quad \\ \text{HO}-\text{C}-\text{C}-\text{C}=\text{O} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ <p>Equation: $\text{C}_3\text{H}_6\text{O}_3 + 4[\text{O}] \rightarrow \text{C}_3\text{H}_2\text{O}_5 + 2\text{H}_2\text{O} \quad \checkmark$ </p> <p>ALLOW correct structural OR displayed OR skeletal formula OR mixture of the above in equation</p> <p>Examiner's Comments</p> <p>This question allowed candidates to demonstrate their knowledge and problem solving skills to tie together all the evidence provided. It was common to see candidates identify the ranges of the characteristic peaks for a carboxylic acid in the IR spectrum but a significant proportion did not identify the relevant bond that each peak referred to. Many candidates interpreted the flowchart given at the start of the question to comment on the presence of an alcohol group in L, and using their molecular formula from part (a), deduced structures for both L and M. The strongest candidates were also able to provide a correctly balanced equation for the formation of M. The most common incorrect structure for L was 1,3-dihydroxypropanone, however, error carried forward marks were awarded to candidates who provided the corresponding dicarboxylic acid as the oxidation product M.</p>
C	<p>Monomer N: (1 mark)</p> $\begin{array}{c} \text{H} \quad \text{COOH} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array} \quad \checkmark$	4	<p>For ALL structures: ALLOW correct structural OR skeletal OR displayed formula OR mixture of the above</p> <p>IGNORE names</p> <p>ALLOW 1 mark for either</p>



Polymer P: (1 mark)

Section showing at least one repeat unit of a polymer formed from **N** with side links ✓

e.g.



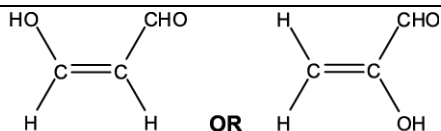
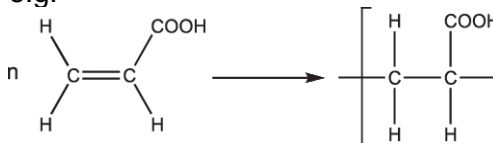
Repeat units (1 mark)

$n = 10000/72 = 139$ ✓

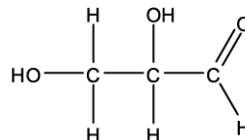
Equation (1 mark)

Balanced equation for formation of P from **N** ✓

e.g.



AS ECF from L:



For P: **ALLOW ECF** from an alkene with molecular formula $\text{C}_3\text{H}_4\text{O}_2$

ALLOW one or more repeat units but has to have a whole number of repeat units

ALLOW repeat unit with no brackets and absence of n

MUST be a whole number.

ALLOW 138 OR 140

For equation, **ALLOW** molecular OR structural OR skeletal OR displayed formulae OR mixture of the above
e.g. **ALLOW** $n\text{C}_3\text{H}_4\text{O}_2 \rightarrow (\text{C}_3\text{H}_4\text{O}_2)_n$

n on LHS can be at any height to the left of formula

AND n on the RHS must be a subscript (essentially below the side link if displayed / skeletal formula is used)

ALLOW use of calculated value for n in equation

e.g. $139\text{C}_3\text{H}_4\text{O}_2 \rightarrow (\text{C}_3\text{H}_4\text{O}_2)_{139}$

Examiner's Comments

This was a very demanding question and the strongest candidates were able to identify both **N** and **P** in addition to calculating the number of repeat units the polymer. However, not all included the polymerisation equation. Some



				<p>candidates who were unable to deduce a correct structure for L in part (b) approached this part as a 'fresh start'. Using both the molecular formula from (a) and the information in the flowchart worked out the molecular formula of N and built a response from there.</p>
			Total	12
1 3		i	<p>Compound B AND M⁺ / molecular ion peak (at m/z) = 124 ✓</p>	<p>1</p> <p>ALLOW Mr = 124 IGNORE compound B because m/z = 124 ALLOW C₇H₈O₂⁺ = 124 OR C₇H₈O₂ = 124 ALLOW peak at (m/z =) 109 due to HOC₆H₄O⁺ ALLOW peak at (m/z =) 109 due to loss of CH₃ IGNORE reference to other peaks in the spectrum</p> <p>Examiner's Comments</p> <p>This question was well answered. The majority of candidates focussed on the different molar masses of the compounds and many referred to the M⁺ peak or molecular ion peak of compound B.</p>
		ii	<p>Compound (B) is less soluble in the stationary phase / liquid</p>	<p>1</p> <p>ORA Answer refers to the first compound to emerge from the column ALLOW compound (B) is more soluble in mobile phase / gas ALLOW compound interacts less with stationary phase / liquid OR compound interacts more with mobile phase / gas IGNORE compound adsorbs less IGNORE compound is not very soluble (comparison needed) IGNORE volatility OR reactivity</p> <p>Examiner's Comments</p> <p>Relatively few creditworthy responses were seen here. The specification describes chromatography as an analytical technique that separates components in a mixture between a mobile phase and a stationary phase. Many candidates referred to differences in solubility or the strength of interactions without linking this to a particular phase in the column.</p>
			Total	2
1 4		i		<p>1</p> <p>ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above</p>



			<p>as long as unambiguous</p> <p>Examiner's Comments</p> <p>The majority scored this mark for the structure of glutamic acid.</p>																				
	ii		<p>ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous</p> <p>ALLOW a cyclic amide with a 3 membered ring</p> <p>ALLOW</p> <p>OR a structure obtained by condensation of a glutamic acid molecule with the first cyclic amide</p> <p>Examiner's Comments</p> <p>Marks were awarded for a variety of structures and although few candidates scored both marks here, examiners were impressed by the excellent attempts to produce workable cyclic structures.</p>																				
		Total	3																				
1 5		<p><i>Please refer to marking instructions on page 4 of mark scheme for guidance on how to mark this question.</i></p> <p>Level 3 (5–6 marks)</p> <p>A comprehensive description with all three scientific points explained thoroughly. C identified as a carboxylic acid containing four carbon atoms linked to the peak in the mass spectrum at 43.</p> <p><i>The explanation makes use of all the evidence including the secondary</i></p>	<p>6</p> <p>LOOK ON THE SPECTRA for labelled peaks. Indicative scientific points may include:</p> <p>1. Molecular formula</p> <table border="1"> <thead> <tr> <th>Element</th> <th>% mass</th> <th>Ar</th> <th>moles</th> <th>ratio</th> </tr> </thead> <tbody> <tr> <td>C</td> <td>54.5</td> <td>12</td> <td>4.54</td> <td>2</td> </tr> <tr> <td>H</td> <td>9.1</td> <td>1</td> <td>9.1</td> <td>4</td> </tr> <tr> <td>O</td> <td>36.4</td> <td>16</td> <td>2.28</td> <td>1</td> </tr> </tbody> </table> <ul style="list-style-type: none"> empirical formula = C₂H₄O molecular ion peak <i>m/z</i> or Mr = 88 	Element	% mass	Ar	moles	ratio	C	54.5	12	4.54	2	H	9.1	1	9.1	4	O	36.4	16	2.28	1
Element	% mass	Ar	moles	ratio																			
C	54.5	12	4.54	2																			
H	9.1	1	9.1	4																			
O	36.4	16	2.28	1																			



	<p><i>carbocation in justifying the correct structure of C.</i></p> <p>Level 2 (3–4 marks) Attempts all three scientific points but explanations may be incomplete. OR Explains two scientific points thoroughly with few omissions.</p> <p><i>The analysis is clear and includes some interpretation of IR and MS peaks.</i></p> <p>Level 1 (1–2 marks) A simple explanation based on at least two of the main scientific points. OR Explains one scientific point thoroughly with few errors.</p> <p><i>The analysis is communicated in an unstructured way and includes interpretation of peaks from IR OR MS spectrum</i></p> <p>0 marks – No response worthy of credit.</p>	<ul style="list-style-type: none"> molecular formula = $C_4H_8O_2$ <p>2. Infrared spectrum</p> <ul style="list-style-type: none"> peak at 2500-3500 (cm^{-1}) is O–H peak at 1630-1820 (cm^{-1}) is C=O C is a carboxylic acid <p>ALLOW stated values within the ranges above IGNORE references to C–O peaks</p> <p>3. Identifying the carboxylic acid</p> <ul style="list-style-type: none"> ($CH_3CH_2CH_2COOH$ OR (CH_3)₂CHCOOH) Mass spectrum peak at $m/z = 43 = C_3H_7^{+}$ secondary carbocation: $CH_3C^+HCH_3$ compound C: (CH_3)₂CHCOOH <div style="text-align: center;"> </div> <p>IGNORE name of carboxylic acid if structure given</p> <p>Examiner's Comments</p> <p>The final question on the paper was a six mark level of response question which required candidates to identify a molecule from a range of data. Most candidates were able to process the percentage composition data to arrive at an empirical formula but less able candidates then failed to use the data from the mass spectrum to arrive at the molecular formula. Candidates were generally able to use the infrared spectrum to identify the presence of –OH and C=O and could link this to the carboxyl functional group. The best candidates were able to identify the peak in the mass spectrum at 43 and to link this to a $C_3H_7^+$ fragment which led to the assumption that the carboxylic acid was butanoic acid. Many outstanding candidates were able to discuss the peak at 43 being that of a branched chain secondary carbocation and linked this to the correct branched product. Some answers were unstructured and disorganised and candidates</p>
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				<p>Examiner's Comments</p> <p>In general the attempts at this question were good, and the majority of candidates chose to show the fragments as displayed formulae. A common incorrect response for the fragment that gave rise to peak I was $\text{CH}_3\text{CH}_2\text{C}$. Some candidates failed to show the positive charge on each fragment, although this was less common than in previous sessions.</p>
		Total	4	
1 7	a	<p>Empirical / molecular formula 3 marks Mole ratio C : H : Br is 2.44 : 5.70 : 0.814 ✓</p> <p>(Empirical formula) = $\text{C}_3\text{H}_7\text{Br}$ ✓</p> <p>QWC (Molecular formula) = $\text{C}_3\text{H}_7\text{Br}$ AND relative mass linked to 150 evidence ✓</p> <p>Structural isomers 2 marks $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ ✓ $\text{CH}_3\text{CHBrCH}_3$ ✓</p>	5	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES</p> <p>ALLOW $\frac{29.29}{12.0} : \frac{5.70}{1.0} : \frac{65.01}{79.9}$</p> <p>Evidence could include a calculation of the relative mass of $\text{C}_3\text{H}_7\text{Br}$ as 122.9 linking to M_r being less than 150</p> <p>ALLOW correct structural OR displayed OR skeletal formula OR mixture of the above (as long as unambiguous)</p> <p>DO NOT ALLOW missing H atom(s) in a displayed formula for one structure but ALLOW missing H atoms in subsequent structure</p> <p>Note: structures from an incorrect molecular formula will be credited on their merits. Please consult TL for advice on how to mark the subsequent parts of this question</p> <p>Examiner's Comments</p> <p>Calculation of empirical formula has always been a strength of candidates at this level. Consequently the vast majority were able to deduce the structures of the two isomers correctly. A significant number of candidates failed to secure full marks as they did not link the M_r of the empirical formula with the information about the M_r of the isomers being less than 150. Some candidates tried to use the value of 150 to determine the formula of C and D, ultimately ending up with an incorrect</p>

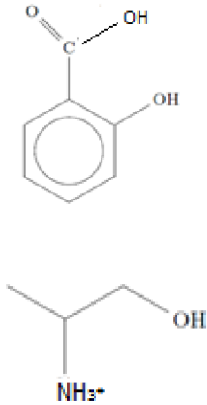


				answer. However, error carried forward marks were allowed through subsequent parts of this question where appropriate.
	b	i	<p>Infrared for G 2 marks</p> <p>1700 cm⁻¹ AND C=O/carbonyl group ✓</p> <p>(broad) 2300–3600 cm⁻¹ AND O–H in carboxylic acid ✓</p> <p>Structures 3 marks</p> <p>CH₃CH₂CH₂OH ✓</p> <p>CH₃CHOHCH₃ ✓</p> <p>CH₃CH₂COOH ✓</p> <p>Equation for formation of G 1 mark</p> <p>C₃H₈O + 2[O] → C₃H₆O₂ + H₂O ✓</p>	6
				<p>ANNOTATE ANSWER WITH TICKS AND CROSSES</p> <p>LOOK ON THE SPECTRUM for labelled peaks which can be given credit</p> <p>ALLOW ranges from <i>Data Sheet</i>: C=O within range 1640–1750 cm⁻¹; (broad) O–H within range 2500–3300 cm⁻¹</p>
				<p>ALLOW correct structural OR displayed OR skeletal formula OR mixture of the above (as long as unambiguous)</p> <p>ALLOW CH₃CH₂CO₂H for carboxylic acid</p> <p>IGNORE names</p> <p>IGNORE labels</p> <p>DO NOT ALLOW missing H atom(s) in a displayed formula for one structure but ALLOW missing H atoms in subsequent structures</p>
				<p>ALLOW correct structural OR displayed OR skeletal formula OR mixture of the above in equation</p> <p>Examiner's Comments</p> <p>Candidates were well prepared for a structural determination question and examiners were encouraged by the number of high quality of responses to this question. Most candidates were able interpret the key peaks in the IR spectrum and identified the O–H bond of a carboxylic acid and C=O bond accurately. Most candidates identified all three structures correctly. Only the strongest responses included a correct equation for the formation of</p>



					<p>G by oxidation of E. Many responses failed to include this and others often had H₂ as the inorganic product. Candidates are advised to revise oxidation reactions of alcohols thoroughly as it is often the case that incorrect equations are frequently seen in responses to exam questions.</p>												
		ii	<p>2 marks for correct ester.</p> <p>CH₃CH₂COOCH(CH₃)₂ ✓✓</p> <p>Award 1 mark for: CH₃CH₂COOCH₂CH₂CH₃</p> <p>OR Ambiguous ester: CH₃CH₂COOC₃H₇ ✓</p>	2	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES</p> <p>ALLOW correct structural OR displayed OR skeletal formula OR mixture of the above (as long as unambiguous)</p> <p>ALLOW C₂H₅CO₂CH(CH₃)₂</p> <p>IF there is one bond and its H missing from the correct ester award 1 mark</p> <p>Examiner's Comments</p> <p>Most candidates were able to show the structure of the ester formed from propanoic acid (G and propan-2-ol (F) correctly. Some candidates used the incorrect alcohol, propan-1-ol (E) and such responses received only one of the two marks available.</p>												
			Total	13													
1 8	a	i	<p>¹H NMR spectrum for 2-aminopropan-1-ol</p> <table border="1"> <thead> <tr> <th>Chemical shift, δ/ppm</th> <th>Relative peak area</th> <th>Splitting pattern</th> </tr> </thead> <tbody> <tr> <td>0.8 – 2.0</td> <td>3</td> <td>doubl</td> </tr> <tr> <td>2.3 – 3.0</td> <td>1</td> <td>multip</td> </tr> <tr> <td>3.3 – 4.2</td> <td>2</td> <td>doubl</td> </tr> </tbody> </table> <p>✓✓✓</p>	Chemical shift, δ/ppm	Relative peak area	Splitting pattern	0.8 – 2.0	3	doubl	2.3 – 3.0	1	multip	3.3 – 4.2	2	doubl	3	<p>One mark for each correct row</p> <p>ALLOW δ values as a range or a value within the specified range.</p> <p>ALLOW δ values +/- 0.2 ppm.</p> <p>ALLOW a response that implies a splitting into two for a doublet etc.</p> <p>ALLOW sextet/hextet/six (or more than 5) as alternative to multiplet</p> <p>Relative peak area = CH / 3H etc. penalise once</p> <p>Examiner's Comments</p> <p>Although it could be argued that this question tested the same skill three times, the full range of marks was awarded and errors were seen in the chemical shift, relative peak area and splitting pattern. Fully correct responses included either a chemical shift value within the range specified on the data sheet or a range that matched the one given on the data sheet.</p>
Chemical shift, δ/ppm	Relative peak area	Splitting pattern															
0.8 – 2.0	3	doubl															
2.3 – 3.0	1	multip															
3.3 – 4.2	2	doubl															

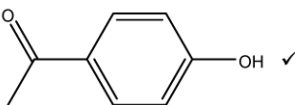
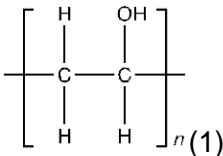


				<p>Examiner's Comments</p> <p>Generally well answered but incorrect functional groups included carbonyl and amine.</p>
	ii		2	<p>ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above</p> <p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>ALLOW + on N or H i.e. NH_3^+ or NH_3^+Cl^- ALLOW NH_3^+Cl^-</p> <p>Examiner's Comments</p> <p>Many candidates were able to score one mark for this question but the amine group was often not protonated and it was surprisingly common to see the amine group as NH_2^+.</p>
		Total	10	
19		<p>m/z molecular ion peak = 60 ✓</p> <p>Alcohol A identified as $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ OR $\text{CH}_3\text{CHOHCH}_3$ ✓</p> <p>Peak X identified as CH_2OH^+ AND Alcohol A identified as $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ✓</p>	3	<p>ALLOW labelling on spectrum</p> <p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>DO NOT ALLOW CH_3O^+</p>
		Total	3	
20		B	1	<p>Examiner's Comments</p> <p>Just over half of the candidates identified the correct alcohol. The common incorrect answer was C.</p>
		Total	1	



2 1		A	1	<p>Examiner's Comments Fewer than half the candidates obtained the correct alcohol (A). The common incorrect answer was C.</p>
		Total	1	
2 2	a	<p>Empirical formula</p> <p>Mole Ratio C : H : O = 5.88 : 5.92 : 1.47 ✓</p> <p>Empirical formula = C₄H₄O ✓</p> <p>Molecular formula Molecular formula = C₈H₈O₂ AND</p> <p>Evidence of 136 in working or from labelled peak in spectrum ✓</p>	3	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES</p> <p>ALLOW $\frac{70.58}{12.0} : \frac{5.92}{1.0} : \frac{23.50}{16.0}$</p> <p>ALLOW 4:4:1 if linked to C:H:O</p> <p>Alternative method for 3 marks:</p> <p>C: $\frac{136 \times 70.58/100}{12.0} = 8$</p> <p>H: $\frac{136 \times 5.92/100}{1.0} = 8$</p> <p>O: $\frac{136 \times 23.50/100}{16.0} = 2$</p> <p>Examiner Comments The empirical formula was correctly calculated by all but the weakest candidates. The final mark was more difficult to obtain as it required evidence that the molar mass had been determined from the mass spectrum and used in establishing the molecular formula.</p>
	b	<p>Functional groups</p> <p>Phenol AND ketone ✓</p> <p>Explanation Links phenol to (weak) acidity AND no reaction with Na₂CO₃ (so not carboxylic acid) ✓</p> <p>Links 2,4-DNP(H) or Brady's reagent observation to carbonyl AND</p> <p>Tollens' reagent observation (so not an aldehyde) ✓</p>	3	<p>DO NOT ALLOW any other functional groups for first marking point. ALLOW identity of functional groups in the explanation if not stated on functional group prompt line.</p> <p>ALLOW "aldehyde or ketone" in place of carbonyl</p> <p>Examiner Comments Many candidates were able to suggest that the compound contained a ketone but found it more difficult to indicate the presence of phenol. Approximately 20% of the entry obtained all three marks. When explaining the presence of the ketone some failed to indicate that the 2,4-DNP test indicated that the compound must contain a carbonyl and just</p>



				focused on the lack of reactivity with Tollens'. Answers suggesting the molecule contained a ketone as no reaction was observed with Tollens' did not gain credit when no reference to carbonyl was seen. Those who recognised the presence of a phenol explained that the only acidic functional group that does not react with sodium carbonate is a phenol.
	c	<p>Carbon NMR analysis</p> <p>Peaks between 110–160 ppm are the (four) aromatic (carbon environments) ✓</p> <p>Compound contains a C=O between 190 – 200 ppm</p> <p>AND</p> <p>Compound contains a C-C at 20 – 30 ppm ✓</p> <p>Structure</p> 	3	<p>ALLOW peaks to be identified by:</p> <ul style="list-style-type: none"> • Peaks labelled on spectrum • Peaks indicated on a chemical structure • Peaks indicated from within text <p>Note: If identifying aromatic peaks from the spectrum all four peaks should be indicated. ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>Examiner Comments</p> <p>When interpreting a carbon-13 NMR spectrum, candidates should be advised to fully label any peaks. Many candidates failed to indicate the presence of four aromatic peaks yet produced a structure containing a benzene ring. In some cases candidates did not link their answer to part (a) of the question giving structures that did not match their molecular formula.</p>
		Total	9	
2 3		<p>It increases / causes / contributes to global warming</p> <p>OR C–H bonds vibrate OR absorb IR ✓</p>	1	<p>ALLOW it is a greenhouse gas / increases temp</p> <p>IGNORE ozone, radicals OR acid rain</p> <p>Examiner's Comment:</p> <p>Most candidates were awarded this straightforward mark for stating that methane is a greenhouse gas. A common error was depletion of the ozone layer.</p>
		Total	1	
2 4	i		1	



	ii	<p>Evidence against ethenol: No infrared absorption between 3200 and 3600 cm^{-1} from O–H (1)</p> <p>Evidence for isomer: Infrared absorption between 1640 and 1750 cm^{-1} indicates C=O (1) Mass spectrum: fragmentation peak at $m/z = 29$ suggests CHO^+</p> <p>ii OR fragmentation peak at $m/z = 15$ suggests CH_3 (1)</p> <p>Identification: Ethanal / CH_3CHO (1)</p>	4																					
				ignore molecular ion peak at m/z confirms molecular mass of 44 g mol^{-1}																				
		Total	5																					
2 5		<p><i>Please refer to the marking instructions on page 5 of the mark scheme for guidance on how to mark this question.</i></p> <p>Level 3 (5-6 marks) A comprehensive description including most of the evidence to justify the correct structure of F (accept <i>cis</i> or <i>trans</i>). <i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i></p> <p>Level 2 (3-4 marks) The candidate attempts all three scientific points, but explanations are incomplete. OR Explains two scientific points thoroughly with few omissions. AND an attempt at a feasible structure based on deduction from correct molecular formula <i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i></p> <p>Level 1 (1-2 marks) The correct empirical formula AND a simple description based on</p>	6	<p>LOOK AT THE SPECTRA for labelled peaks Indicative scientific points may include:</p> <p>Empirical formula</p> <ul style="list-style-type: none"> empirical formula = $\text{C}_4\text{H}_6\text{O}$ <table border="1"> <thead> <tr> <th>element</th> <th>% mass</th> <th>Ar</th> <th>moles</th> <th>ratio</th> </tr> </thead> <tbody> <tr> <td>C</td> <td>68.6</td> <td>12</td> <td>5.72</td> <td>4</td> </tr> <tr> <td>H</td> <td>8.6</td> <td>1</td> <td>8.60</td> <td>6</td> </tr> <tr> <td>O</td> <td>22.8</td> <td>16</td> <td>1.43</td> <td>1</td> </tr> </tbody> </table> <p>IR and spectra and molecular formula</p> <ul style="list-style-type: none"> infrared absorption; 1630–1820 cm^{-1}, due to C=O (aldehyde/ketone/carbonyl group) molar mass = 70 g mol^{-1} (mass spectrum molecular ion peak $m/z = 70$) molecular formula = $\text{C}_4\text{H}_6\text{O}$ <p>Functional groups, structure and stereochemistry</p> <ul style="list-style-type: none"> alkene / C=C aldehyde / $-\text{CHO}$ (C_3H_5^+ fragment) mass spectrum; peak at 41 due to C_3H_5^+ (loss of CHO) <i>E/Z</i> or <i>cis-trans</i> isomer: <i>E/Z</i> or <i>cis-trans</i> isomer: 	element	% mass	Ar	moles	ratio	C	68.6	12	5.72	4	H	8.6	1	8.60	6	O	22.8	16	1.43	1
element	% mass	Ar	moles	ratio																				
C	68.6	12	5.72	4																				
H	8.6	1	8.60	6																				
O	22.8	16	1.43	1																				



	<p>at least one of the main scientific points.</p> <p>OR</p> <p>The candidate explains one scientific point thoroughly with few omissions.</p> <p><i>There is an attempt at a logical structure with a line of reasoning.</i></p> <p><i>The information is in the most part relevant.</i></p> <p>0 No response or no response marks worthy of credit.</p>	<div data-bbox="933 212 1117 369"></div> <p data-bbox="1005 414 1045 448"><i>cis</i></p> <div data-bbox="1244 212 1428 369"></div> <p data-bbox="1252 392 1428 470"><i>trans (correct structure)</i></p> <p data-bbox="869 571 1189 604"><u>Examiner's Comments</u></p> <p data-bbox="869 638 1484 1467">This question was a good discriminator. Most candidates were able to deduce the empirical formula and the C=O peak on the IR spectrum. However, many mistook the C-H peaks around 3000 cm⁻¹ for an alcohol O-H peak or assumed from the empirical formula that it was an alcohol so made the spectra 'fit' their hypothesis. At AS, the exposure of candidates to IR and MS spectra is not as comprehensive as in the second year of A Level and this was evident. There was very little annotation of the spectra and candidates should be encouraged to do this as it is helpful to them in their deductions (and to the examiners for crediting marks). Analysis of the IR spectrum was much more detailed than the mass spectrum. Most candidates just referred to the molecular ion peak and made no attempt, or an incorrect attempt, at discerning the peak at 41. Those that did quickly realised what the structure was and gained 5 or 6 marks. Some candidates, despite ascertaining that a <i>trans</i> stereoisomer should be drawn, drew the <i>cis</i> version instead.</p> <p data-bbox="869 1500 1029 1534">Exemplar 5</p>
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In the mass spectrum, the peak with the greatest relative intensity is caused by the loss of a functional group from the molecular ion of compound F.

Determine the structure of compound F.

Explain your reasoning and show your working.

C : H : O = $\frac{68.6}{12} : \frac{8.6}{1} : \frac{22.8}{16}$

= $5.716 : 8.6 : 1.425$

= $4.011 : 6.03 : 1$

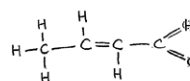
Empirical formula of compound F is C_4H_6O .

The M_r peak on the mass spectrum has an m/z value of 70, so the molecular mass of compound F is 70 g mol^{-1} .

So the molecular formula of compound F is C_4H_6O .

The infrared spectrum shows an absorbance peak at in the range $1630-1820 \text{ cm}^{-1}$, indicating the presence of a $C=O$ bond. There is no absorbance peak in the range $2500-3300 \text{ cm}^{-1}$, so there is no O-H bond, so compound F is not a carboxylic acid. Compound F is an aldehyde.

The mass spectrum shows a fragmentation peak at 41 m/z , indicating the presence of a $CH_2CH_2^+$ fragment from the loss of a CHO functional group. Compound F is an aldehyde. It is a *trans* isomer, so the hydrogens attached to the carbons on the double bond are opposite each other.



This candidate has very logically worked through all the information provided and has come up with the correct structure from the deductions.

Exemplar 6

Explain your reasoning and show your working.

C : H : O

$\frac{68.6}{12} : \frac{8.6}{1} : \frac{22.8}{16}$

= $5.716 : 8.6 : 1.425$

= $4.0 : 6.0 : 1$

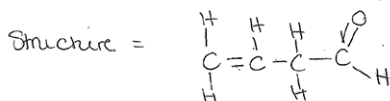
empirical formula = C_4H_6O

$M_r = (12 \times 4) + (6 \times 1) + (16) = 70$

$F M_r = 70 \rightarrow$ molecular formula = C_4H_6O

Peak at $29 \rightarrow$ CHO } mass spectrum
 Peak at $41 \rightarrow H_2C = CH_2$

IR Spectrum \rightarrow Peak at $1630-1820$ indicates the presence of a $C=O$ group
 \rightarrow Peak at $1620 \rightarrow 1630$ indicates the presence of a $C=C$ group.



Like most candidates, the crucial information about F being a *trans* isomer was not picked up so they drew the double bond in the wrong place.

Total

6



2 6		B	1	<p><u>Examiner's Comments</u></p> <p>Most candidates correctly identified B as the compound after labelling the O-H and C≡N peaks in the spectrum.</p>
		Total	1	
2 7		C	1	<p><u>Examiner's Comments</u></p> <p>Most candidates were able to identify C as the fragment responsible for the peak at $m/z = 43$. A number of different approaches were used. Some candidates determined the mass of each fragment shown while others drew the structures to see which were likely to be formed from $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$.</p>
		Total	1	
2 8		<p><i>Please refer to the marking instructions on page 5 of this mark scheme for guidance on how to mark this question.</i></p> <p>Level 3 (5–6 marks) Compound is a structure of $\text{C}_6\text{H}_{12}\text{O}_3$ that is consistent with splitting pattern and chemical shifts in NMR spectrum. AND Comprehensive reasoning with most of the data analysed.</p> <p><i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i></p> <p>Level 2 (3–4 marks) Compound has a feasible chemical structure that is consistent with the splitting pattern in NMR spectrum but may have incorrect molecular formula. AND Reasoning provided with some of the data analysed.</p> <p><i>There is a line of reasoning presented with some structure. The information presented is relevant</i></p>	6	<p>Indicative scientific points:</p> <p><u>Empirical and Molecular Formula</u></p> <p>• $\text{C} : \text{H} : \text{O} = 54.54/12 : 9.10/1 : 36.36/16$ $4.545 : 9.10 : 2.273$ $2 : 4 : 1$</p> <p>• Empirical formula = $\text{C}_2\text{H}_4\text{O}$</p> <p>• uses $m/z = 132.0$ to determine molecular formula as $\text{C}_6\text{H}_{12}\text{O}_3$</p> <p><u>$^1\text{H}$ NMR analysis</u></p> <p>Spectrum:</p> <ul style="list-style-type: none"> • $\delta = 4.0$ ppm, quartet, 1H, $\text{CH}_3\text{-CH-O}$ • $\delta = 1.3$ ppm, singlet, 6H, $(\text{CH}_3)_2\text{-C}$ • $\delta = 1.2$ ppm, doublet, 3H, $\text{CH}_3\text{-CH-}$ <p>Without D_2O:</p> <ul style="list-style-type: none"> • Peak at 11.0 ppm COOH or OH • peak at 3.6 ppm OH <p>Note: Data Sheet shows O-H chemical shift can occur around 11.0 ppm</p>



and supported by some evidence.

Level 1 (1–2 marks)

Correct determination of empirical formula and/or molecular formula.

OR

Analyses most of the NMR data.

OR

Attempts to determine empirical formula and/or molecular formula

AND analyses some of the NMR data.

There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.

0 marks

No response or no response worthy of credit.

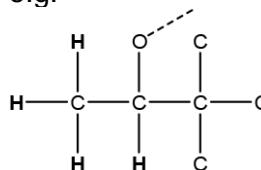
Structure

ALLOW any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous

Contains

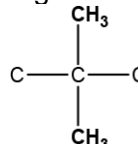
- region that gives doublet and quartet

e.g.

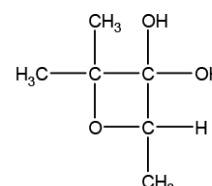
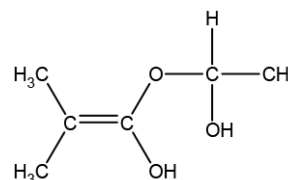
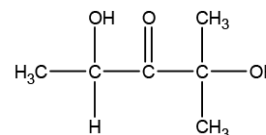
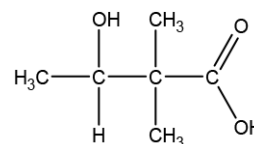


- region that gives singlet

e.g.



Examples of structures consistent with splitting and chemical shift in NMR





Note: there may be other possible structures that are consistent with the splitting pattern and chemical shifts in NMR – if an alternative structure is seen, please contact your team leader

Examiner's Comments

Most candidates were able to determine the empirical and molecular formula of the unknown compound. A number of excellent and clear responses were seen, where the NMR data was explained, including interpretation of the additional peaks observed without D₂O. However many candidates were unable to suggest a structure that matched their NMR interpretation. Some candidates used the quartet, doublet and singlet to suggest a structure that would give rise to this splitting pattern, but which was not consistent with the chemical shifts, see Exemplar 12. Such responses received a level 2 mark (3-4). Stronger responses were able to use all the data to suggest a correct structure. The most common was CH₃CH(OH)C(CH₃)₂COOH although other viable structures, including CH₃CH(OH)COC(CH₃)₂OH, were also seen. Examiners were impressed with the problem solving ability shown by candidates and a significant proportion of responses were credited six marks.

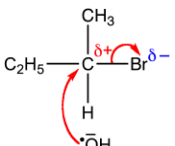
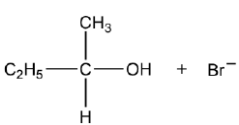
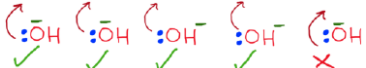
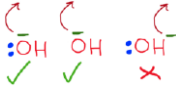

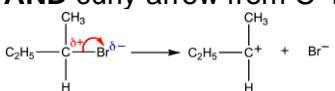
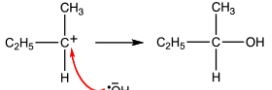
Exemplar 12



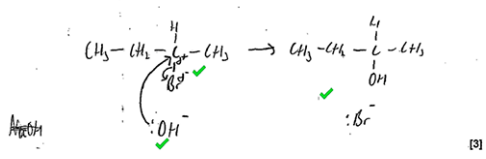
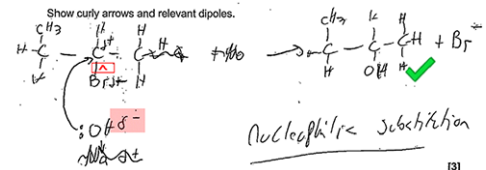
				<p>C H O 54.54 9.10 36.36 12 1 16 empirical formula = C₅H₈O 4.545 9.10 2.2725 Mr = 44 2 4 1 132 = 3 44</p> <p>molecular formula = C₅H₈O × 3 = C₁₅H₂₄O₃ peak at 1.2 ppm = alk HC-R. It's a doublet so adjacent carbon has 1 H. peak integral of 3 → CH₃ peak at 1.3 ppm = HC-R. Singlet so adjacent C has no protons. Integral of 6 = (CH₂)₂ Peak at 4 ppm indicative of HC=O. Quartet so adjacent C has 3 protons. Integral of 1 = CH</p> <p>Additional answer space if required. D₂O at 11 ppm = -C(=O)OH and 3.5 ppm indicative of HC=O. M.f. = C₆H₁₂O₃</p>
		Total	6	
2 9		D	1	<p>Examiner's Comments</p> <p>Overall, candidates answered this question well with many selecting the correct response</p>

This logically presented Level 2 response uses the elemental analysis and mass spectrum data to determine the correct empirical and molecular formula of the unknown compound. The peaks in the NMR spectrum are analysed in detail, with a clear explanation of the splitting patterns. A comment about the two additional peaks observed when the spectrum is run without D₂O is also provided. The response concludes with a structure of C₆H₁₂O₃ that would show a singlet, doublet and quartet in its ¹H NMR spectrum. However, this structure is not consistent with the chemical shift values shown in the spectrum provided. In particular this structure would produce a quartet between 2.0–2.9 ppm, rather than at 4.0 as in the spectrum shown. Consequentially this response does not achieve Level 3. When tackling questions of this type candidates are advised to check that a proposed structure would produce peaks in the correct region of the NMR spectrum to ensure it is totally consistent with the data analysed.



				of D. From scripts, successful candidates drew vertical lines to isolate likely fragments.
		Total	1	
3				
0	i	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES</p> <p>-----</p> <p>--</p> <p>Curly arrows 2 marks</p> <p>curly arrow from OH⁻ to C atom of C-Br bond ✓</p> <p>dipole shown on C-Br bond, C^{δ+} and Br^{δ-},</p> <p>AND curly arrow from C-Br bond to Br atom</p>  <p>IGNORE incorrect R groups for curly arrow marks</p> <p>IGNORE presence of Na⁺/Na but OH⁻ needed i.e. Na⁺OH⁻; NaOH⁻ can be allowed with correct use of curly arrow</p> <p>-----</p> <p>--</p> <p>Products 1 mark</p> <p>correct organic product AND Br⁻ ✓</p>  <p>IGNORE presence of Na⁺ but Br⁻ needed</p>	<p>1st curly arrow must</p> <ul style="list-style-type: none"> go to the C of C-Br AND start from, OR be traced back to any point across width of lone pair on O of OH⁻  <ul style="list-style-type: none"> OR start from - charge on O of ⁻OH ion  <p>(Lone pair NOT needed if curly arrow shown from O⁻)</p> <p>2nd curly arrow must start from, OR be traced back to, any part of C-Br bond and go to Br</p>  <p>-----</p> <p>ALLOW S_N1 mechanism for 2 curly arrow marks</p> <p>First mark Dipole shown on C-Br bond, C^{δ+} and Br^{δ-}, AND curly arrow from C-Br bond to Br atom</p>  <p>Second mark Curly arrow from OH⁻ AND to correct carbocation</p>  <p>Use curly arrow criteria in guidance above</p> <p>Examiner's Comments</p> <p>As with 25(a)(i), this question rewarded the well-prepared candidate. The large number of proposed mechanisms showed little resemblance to the accepted mechanism for nucleophilic substitution. Mechanisms were often seen showing curly arrows going in the wrong direction and between the wrong bonds and atoms, charges and dipoles were often incorrect, and partial charges used where full</p>	



	<p>i.e. $\text{Na}^+\text{Br}^-/\text{NaBr}^-$ can be allowed</p> <p>BUT NaBr does NOT show Br^-</p> <p>NOTE: curly arrows can be straight, snake-like, etc. but NOT double headed or half headed arrows</p>		<p>charges were required.</p> <p>Two exemplars are shown. The first exemplar shows clear curly arrows, the role of the lone pair and all charges correct. The second exemplar shows a typical muddled response. Although the curly arrow from the hydroxide ion has been accurately drawn, the hydroxide ion has a partial charge rather than a - charge. There is also no curly arrow showing breaking of the C–Br bond. The only mark available is for the correct organic product and a Br^- ion.</p> <p>Some mechanisms were so poor that it was impossible to credit many candidates with any marks. Writing mechanisms is an important skill in organic chemistry and it is recommended that candidates learn and practice their writing.</p> <p>Exemplar 7</p> <p>(b) An alcohol can be prepared by hydrolysing the haloalkane $\text{C}_2\text{H}_5\text{CHBrCH}_3$ with aqueous sodium hydroxide.</p> <p>(i) Outline the mechanism for this reaction. Show curly arrows and relevant dipoles.</p>  <p>Exemplar 8</p> <p>(b) An alcohol can be prepared by hydrolysing the haloalkane $\text{C}_2\text{H}_5\text{CHBrCH}_3$ with aqueous sodium hydroxide.</p> <p>(i) Outline the mechanism for this reaction. Show curly arrows and relevant dipoles.</p> 
ii	<p>Disappearance of</p> <p>peak at $500\text{--}800\text{ cm}^{-1}$ OR C–Br peak ✓</p> <p>Appearance of</p> <p>peak at $3200\text{--}3600\text{ cm}^{-1}$ OR alcohol O–H peak</p>	2	<p>ALLOW value within range $500\text{--}800\text{ cm}^{-1}$</p> <p>ALLOW value within range $3200\text{--}3600\text{ cm}^{-1}$</p> <p>DO NOT ALLOW responses that only describe the spectrum shown</p> <p>Examiner's Comments</p>



					This part discriminated very well with able candidates identifying that the absorption for the C–Br bond would disappear, with a new peak appearing for the alcohol O–H bond. A significant number of candidates did not seem to understand what was required, with many interpreting the spectrum as that of the alcohol, rather than predicting how the spectrum would change during the reaction. A common error was to interpret the absorption for a C–H bond at $\sim 3000\text{ cm}^{-1}$ as that of an O–H bond.
			Total	5	
3 1			A	1 (AO2.5)	<p><u>Examiner's Comments</u></p> <p>Candidates found this part difficult. Less than half the candidates selected the correct option A, with 'B' being the main distractor. From annotations on scripts, successful candidates often drew rings around parts of the structures which helps in identifying parts of a structure that might fragment.</p>
			Total	1	
3 2			D	1 (AO1.1)	<p><u>Examiner's Comments</u></p> <p>Less than half the candidates correctly chose option D. This part discriminated well, with less able candidates selecting the incorrect A and C in similar amounts. A small number of candidates selected B.</p>
			Total	1	
3 3			B	1 (AO2.5)	<p><u>Examiner's Comments</u></p> <p>Able candidates selected option B, identifying that the O–H peak matches an alcohol rather than carboxylic acid from the wavenumbers. Many candidates opted for option A, the carboxylic acid, which would have a much broader O–H peak with slightly lower wavenumber range. Annotations were common on the spectrum and a sizeable number labelled the C–H peak with O–H, a clear misconception which was also mentioned in the report for H032/01 from June 2018.</p>
			Total	1	
3 4	a	i	Molecular mass ✓	1(AO1.1)	<p>IGNORE 'relative'</p> <p>IGNORE 'molecular ion' alone, answer must relate to mass</p>



				<p>ALLOW M_r / molar mass</p> <p>Examiner's Comments</p> <p>This was generally well answered. The most common incorrect answer was atomic mass.</p>
		ii	<p>Y: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^+$ ✓</p> <p>Z: $\text{CH}_3\text{CH}_2\text{CH}_2^+$ ✓</p> <p><i>If positive charge is missing but the structures of Y AND Z are correct, award one mark</i></p>	<p>2(AO3.2 x2)</p> <p>FOR ONE MARK ALLOW $\text{C}_5\text{H}_{11}^+$ AND C_3H_7^+</p> <p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>Examiner's Comments Most students gained one mark on this question as they omitted the + sign or wrote the molecular formula instead of the structural formula.</p>
	b	i	<p style="text-align: right;">✓</p>	<p>1(AO1.1)</p> <p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>Examiner's Comments This was well answered by most candidates</p>
		ii	<p>Similarity</p> <p>Both have a peak at ($m/z =$) 198 (X) OR 71 (Y) OR 29 ✓</p> <p>Difference</p> <p>2-iodo-2-methylbutane has no peak at ($m/z =$) 43 (Z) ✓</p>	<p>2(AO3.2 x2)</p> <p>ALLOW same molecular ion peak / M_r</p> <p>IGNORE statements where no specific ion peak is suggested e.g. "different ion peaks"</p> <p>Examiner's Comments Most candidates answered the similarity part correctly, many wrote vague answers to the difference and were not specific. A common error focused on the peak at $m/z = 71$, very few recognised that the Z peak at 43 would not be present for 2-iodo-2-methylbutane</p>
			Total	6
3 5			C	<p>1 (AO2.6)</p> <p>Examiner's Comments From the working on the scripts, the best approach was to reduce the options down to A and C, the two with a molecular mass of 102. The best candidates then identified option C as the one with a CH_3CH_2 group for 29. Option A was the key distractor.</p>
			Total	1



3 6	i	<p>FIRST CHECK ANSWER ON THE ANSWER LINE If answer = 35.48 (to 2 DP) award 2 marks</p> $\frac{(35 \times 75.76) + (37 \times 24.24)}{100}$ <p>OR 35.4848</p> <p>OR 35.485 ✓</p> <p>= 35.48 (to 2 DP) ✓</p>	2 (AO1.2x 2)	<p>For 1 mark: ALLOW ECF → to 2 DP if:</p> <ul style="list-style-type: none"> • %s used with wrong isotopes ONCE <p>OR</p> <ul style="list-style-type: none"> • transposed decimal places for ONE % <p>AND</p> <ul style="list-style-type: none"> • calculated Ar is between 35 and 37
	ii	<p>$m/z = 72$: $^{35}\text{Cl}^{37}\text{Cl}$ OR Contains chlorine-35 AND chlorine-37 ✓</p> <p>m/z values: 70 AND 74 ✓</p>	2 (AO3.1) 2 (AO3.2)	<p><u>Examiner's Comments</u></p> <p>This was a high demand question and only the highest scoring answers identified that the peak at 72 was caused by a chlorine molecule containing the chlorine-35 and chlorine-37 isotopes shown in the supplied mass spectrum. Very few candidates went on to predict further peaks with m/z values of 70 (from $^{35}\text{Cl}^{35}\text{Cl}$) and 74 (from $^{37}\text{Cl}^{37}\text{Cl}$). There was little pattern in the incorrect responses, suggestion that many were guesses.</p>
		Total	4	
3 7		<p><i>Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.</i></p> <p>Level 3 (5–6 marks) The candidate gives thorough explanations of both spectra, and correctly identifies X and Y with a correct equation.</p> <p><i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i></p> <p>Level 2 (3–4 marks) The candidate attempts all three scientific points but explanations are incomplete.</p>	6 (AO2.5x 1) (AO3.1x 2) (AO3.2x 3)	<p>Indicative scientific points</p> <p>LOOK AT THE SPECTRA for labelled peaks Mass Spectrum</p> <ul style="list-style-type: none"> • M^+ or molecular ion of 86 • $m/z = 43$ shows CH_3CO^+ OR C_3H_7^+ <p>IR Spectrum</p> <ul style="list-style-type: none"> • IR shows no broad absorption at 2500–3300 cm^{-1} so no O–H bond AND not a carboxylic acid • IR shows absorption at 1700 cm^{-1} for C=O bond OR indicates a ketone/aldehyde present <p>Identification and Equation</p> <ul style="list-style-type: none"> • X must be a secondary alcohol, since refluxing a secondary alcohol with acidified potassium dichromate (VI)



		<p>OR Explains two scientific points thoroughly with few omissions. AND Attempts a feasible structure based on deduction from correct M_r. <i>There is a line of reasoning presented with some structure.</i> <i>The information presented is relevant and supported by some evidence</i></p> <p>Level 1 (1–2 marks) The candidate gives a simple description based on at least two of the main scientific points. OR Gives a thorough description and explanation of one of the scientific points.</p> <p><i>There is an attempt at a logical structure with a line of reasoning.</i> <i>The information is in the most part relevant.</i></p> <p>0 marks <i>No response or no response worthy of credit.</i></p>		<p>forms a ketone OR primary alcohol → carboxylic acid AND tertiary alcohol would not be oxidised.</p> <ul style="list-style-type: none"> X is $(\text{CH}_3)_2\text{CHCHOHCH}_3$ OR compound E OR 3-methylbutan-2-ol Y is $(\text{CH}_3)_2\text{CHCOCH}_3$ OR 3-methylbutan-2-one <p><i>Equation</i> $(\text{CH}_3)_2\text{CHCHOHCH}_3 + [\text{O}] \rightarrow (\text{CH}_3)_2\text{CHCOCH}_3 + \text{H}_2\text{O}$</p> <p><u>Examiner's Comments</u></p> <p>* This was a challenging problem-solving question, relying on candidates to make use of all of the information provided to determine the structure. Very few candidates made no attempt at all at this question.</p> <p>The most common error was incorrectly identifying the peak at 3000 cm^{-1} as O-H from a carboxylic acid, despite it being indicated on the data sheet that this would be a broad peak. It suggested that candidates were not familiar with looking at spectra and understanding what data it gave. Candidates should also be reminded when answering these types of question that they should give the structures, not just molecular formulae, where possible.</p>
		Total	6	
3 8		<p>C=C/alkene peak in region $1620\text{--}1680\text{ cm}^{-1}$ ✓</p> <p>O–H/alcohol peak in region $3200\text{--}3600\text{ cm}^{-1}$ ✓</p>	<p>2 (AO3.2x 2)</p>	<p>LOOK ON THE SPECTRUM for labelled peaks which can be given credit</p> <p>IGNORE references to C-O at 1000 cm^{-1}</p>
		Total	2	
3 9		<p><i>Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.</i></p> <p>Level 3 (5–6 marks) Structure I has a viable chemical structure of $\text{C}_6\text{H}_9\text{NO}_2$ which has the key features consistent with spectral data AND</p>	<p>6 (AO3.1x 4) (AO3.2x 2)</p>	<p>Indicative scientific points: <u>Empirical and Molecular Formulae</u></p> $\begin{array}{cccc} \text{C} & : & \text{H} & : & \text{N} & : & \text{O} \\ = & \frac{56.69}{12.0} & : & \frac{7.09}{1.0} & : & \frac{11.02}{14.0} & : & \frac{25.20}{16.0} \\ \text{OR} & 4.72 & : & 7.09 & : & 0.787 & : & 1.575 \\ = & 6 & : & 9 & : & 1 & : & 2 \end{array}$ <ul style="list-style-type: none"> Empirical formula = $\text{C}_6\text{H}_9\text{NO}_2$ $m/z = 127.0$ and empirical formula mass (127) used to determine molecular formula as $\text{C}_6\text{H}_9\text{NO}_2$



Most of the data analysed

There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.

Level 2 (3–4 marks)

Compound I has a viable chemical structure of C₆H₉NO₂ with most of the key features consistent with spectral data

AND

Some of the spectral data analysed.

There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.

Level 1 (1–2 marks)

Correct determination of empirical formula and/or molecular formula.

OR

Analyses some of the IR and NMR data.

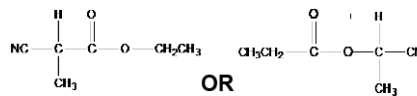
OR

Analyses most of the NMR data.

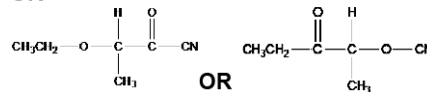
There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.

0 marks No response or no response worthy of credit.

Structures of compound I



OR



ALLOW any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous

Key features

- C \equiv N
- C=O in aldehyde, ketone, ester, amide, acid anhydride
- CH₃ group that would give a doublet
- CH₃ group that would give a triplet
- CH₂ group that would give a quartet

¹H NMR and IR analysis

¹H NMR spectrum

- $\delta = 4.2$ ppm, quartet, 2H CH₃-CH₂-O
- $\delta = 2.9$ ppm, quartet, 1H CO-CH-CH₃
- $\delta = 1.7$ ppm, doublet, 3H CO-CH-CH₃
- $\delta = 1.3$ ppm, triplet, 3H CH₃-CH₂

IR spectrum

- peak at 1750 (cm⁻¹) is C=O
- peak at 2280 (cm⁻¹) is C \equiv N

ALLOW ranges from *Data Sheet*
IGNORE references to C–O peaks

Examiner's Comments

Candidates achieving Level 2 had most of the key features, e.g. CN, C=O bond and a methyl group but did not consider the splitting patterns seen in the NMR. Most candidates could correctly work out the empirical and molecular formula but then did not use their analysis of the NMR and IR data to suggest a structure. This limited their response to Level 1. The IR spectrum had no O-H peak from an alcohol or carboxylic acid, but candidates often included these groups in their suggested structures.



		Total	6																					
4 0		B	1 AO1.1																					
		Total	1																					
4 1		<p>Mass spectrum: $M = 88$ ✓</p> <p>IR: Peak at 1630-1820 (cm^{-1}) is C=O ✓ Peak at 2500–3500 (cm^{-1}) is O–H AND carboxylic acid ✓</p> <p>Structures</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> $\begin{array}{ccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{O} \\ & & & & & & & // \\ \text{H} & - \text{C} & - & \text{C} & - & \text{C} & - & \text{C} \\ & & & & & & & \backslash \\ & \text{H} & & \text{H} & & \text{H} & & \text{OH} \end{array}$ ✓ </div> <div style="text-align: center;"> $\begin{array}{ccccccc} & \text{H} & & \text{CH}_3 & & & & \\ & & & & & & & \\ \text{H} & - \text{C} & - & \text{C} & - & \text{C} & & \\ & & & & & & & \\ & \text{H} & & \text{H} & & & & \end{array}$ ✓ </div> </div>	<p>ALLOW stated values within stated ranges</p> <p>ALLOW 'acid O–H</p> <p>IGNORE references to C–O peaks</p> <p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p>																					
		Total	5																					
4 2		D	1 (AO2.5)																					
		Total	1																					
4 3		B	1 (AO2.1)																					
		Total	1																					
4 4		<p>Level 3 (5-6 marks) A comprehensive description including most of the evidence to justify the correct structure of A (accept <i>cis</i> or <i>trans</i>).</p> <p><i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i></p> <p>Level 2 (3–4 marks)</p>	<p>6 (AO 3.1 × 3) (AO 3.2 × 3)</p>	<p>LOOK AT THE SPECTRA for labelled peaks Indicative scientific points may include:</p> <p>Empirical formula • empirical formula = $\text{C}_2\text{H}_3\text{O}$</p> <table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <thead> <tr> <th>element</th> <th>%mass</th> <th>A_r</th> <th>moles</th> <th>ratio</th> </tr> </thead> <tbody> <tr> <td>C</td> <td>55.8</td> <td>12</td> <td>4.65</td> <td>2</td> </tr> <tr> <td>H</td> <td>7.0</td> <td>1</td> <td>7.0</td> <td>3</td> </tr> <tr> <td>O</td> <td>37.2</td> <td>16</td> <td>2.325</td> <td>1</td> </tr> </tbody> </table>	element	%mass	A_r	moles	ratio	C	55.8	12	4.65	2	H	7.0	1	7.0	3	O	37.2	16	2.325	1
element	%mass	A_r	moles	ratio																				
C	55.8	12	4.65	2																				
H	7.0	1	7.0	3																				
O	37.2	16	2.325	1																				



	<p>Explains two scientific points thoroughly with few omissions. AND an attempt at a feasible structure with either a C=C OR COOH</p> <p><i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i></p> <p>Level 1 (1–2 marks) The correct empirical formula AND a simple description based on at least one of the main scientific points. OR Some aspects from two scientific points are given</p> <p><i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.</i></p> <p>0 marks No response or no response worthy of credit.</p>	<p><u>Spectra and molecular formula</u> Mass spectrum</p> <ul style="list-style-type: none"> • (molecular ion peak $m/z = 86$) • molar mass = 86 g mol^{-1} • molecular formula = $\text{C}_4\text{H}_6\text{O}_2$ <p>Infrared absorption;</p> <ul style="list-style-type: none"> • broad peak at $2500\text{--}3300 \text{ cm}^{-1}$, due to O–H in carboxylic acid, • peak at $1630\text{--}1820 \text{ cm}^{-1}$ due to C=O (peak at $1620\text{--}1680 \text{ cm}^{-1}$ due to C=C) <p>• <u>Functional groups, structure and stereochemistry</u></p> <ul style="list-style-type: none"> • alkene / C=C • carboxylic acid / –COOH • mass spectrum; peak at 41 due to loss of COOH • Correct structural formula: $\text{CH}_3\text{CH}=\text{CHCOOH}$ <p>i.e. <i>cis</i> OR <i>trans</i></p> <ul style="list-style-type: none"> • <i>trans</i> isomer indicates C=C bond with 2 different groups attached to both double bonded carbons • <i>trans</i>: common groups on opposite sides of double bond • Correct structure: <div style="text-align: center;"> </div> <p>NOTE: Correct <i>trans</i> assignment with</p>
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justification would be an example of a well-developed line of reasoning that is substantiated.

Examiner's Comments

About a third of candidates were given Level 3 for this question. The key to answering this style of question well is to make sure all the information provided is used and to avoid contradictory statements, e.g. "structure contains carboxylic acid from IR" but then not present in final structure drawn, or a structure that doesn't match the molecular formula given. A significant number of candidates did not include C=C despite being told in the question that it was "unsaturated and is a trans stereoisomer", plus the C=C bond is shown in the IR and molecular formula needed unsaturation. The M+1 peak did confuse some candidates who then tried to add an extra H to final structure. It is very important that any structure given is feasible in terms of bonding; many candidates gave structures with C with 5 bonds (with both C=C and C=O attached), limiting them to achieving only L1. Some candidates gave a *cis* structure rather than *trans*.

Other candidates ignored the O-H peak (from the carboxylic acid) in the IR spectrum, attributing this to a C-H bond as it was not as smooth or as prominent as they may have seen in other spectra. Some listed the bonds observed in the IR without linking to their position – this can easily be done by annotating the spectra.

Many candidates had messy answers with lots of rough working which was then not crossed out – this made their answer very confusing. Note that no marks were given for just the empirical formula calculation and some attempted to produce a structure from the empirical formula without determining the M_r from the M^+ peak in mass spectrum.

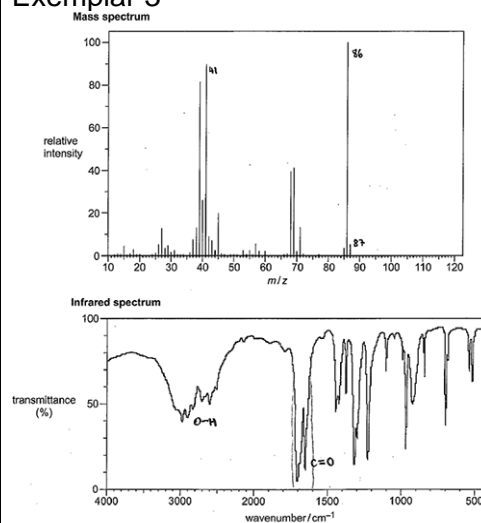


OCR support

We have put together a range of online resources to support teaching of organic chemistry:

<https://www.ocr.org.uk/qualifications/as-a-level-gce-chemistry-a-h032-h432-from-2015/deliveryguide/module-cam04-module-4-core-organic-chemistry/delivery-guide-cadq012-organicchemistry-as>

Exemplar 3



C	H	O	Empirical formula: C ₄ H ₆ O
65.4	7.0	27.2	
12	1	16	86
			43 = 2
4.85	7.0	27.25	
1.325	2.375	2.325	Molecular formula: C ₈ H ₁₂ O ₂
2	3	1	

Compound A has an empirical formula of C₄H₆O but the relative molecular mass is 86 so the molecular formula is C₈H₁₂O₂. It is a trans stereoisomer so it has a C=C double bond. Compound A has an O-H peak between 2500-3500 and a C=O peak between 1650-1820. Therefore it is a carboxylic acid. The most stable ion of compound A is ~~C₄H₅⁺~~ C₄H₅⁺ which has a m/z of 41. Therefore compound

A is:

This is an example of a good response which achieved L3 6 marks. Empirical and molecular formula are determined. Spectra have been annotated to aid their interpretation, but they have also included the key IR peaks as well as a MS fragment in their response. The correct structure for A is clearly drawn out. The response is clear and concise, with all information presented being relevant.



		Total	6	
4 5		A	1(AO2.5)	<p><u>Examiner's Comments</u></p> <p>Candidates found this question hard with many selecting C or D instead of the correct option, B. Candidates appeared to have assigned the C–H absorption at 3000 cm^{-1} to an O–H group (from an alcohol or carboxylic acid). Candidates should appreciate that this C–H absorption will be present in any organic compound possessing a C–H group (that is, nearly all organic compounds).</p>
		Total	1	
4 6		C	1(AO2.5)	<p><u>Examiner's Comments</u></p> <p>Compared to Question 19, candidates had more success with this question. Most drew out all the bonds in each structure, a good approach that should allow the candidate to identify the compound that would produce the three peaks.</p>
		Total	1	
4 7		B	1 (AO1.1)	<p><u>Examiner's Comments</u></p> <p>Candidates found this multiple choice question challenging. While some identified B as the correct answer, many candidates selected C.</p>
		Total	1	
4 8		B	1 (AO2.5)	<p><u>Examiner's Comments</u></p> <p>Most candidates correctly identified C as the compound after labelling the peaks in the spectrum.</p>
		Total	1	
4 9	i	<p>Same molecular formula AND Different structural formulae ✓</p> <p>OR</p> <p>Both have the molecular formula</p>	1 (AO1.1)	<p>Same formula is not sufficient</p> <p><i>(no reference to molecular)</i></p> <p>Different arrangement of atoms is not sufficient</p>



		<p>C_6H_{12} AND Different structural formulae ✓</p>		<p>(no reference to structure/structural)</p> <p>For 'structural formulae', ALLOW structure/displayed/skeletal formulae/functional groups</p> <p>DO NOT ALLOW any reference to spatial/space</p>												
	ii	<p>Same structural formula AND Different arrangement (of atoms) in space OR different spatial arrangement (of atoms) ✓</p>	<p>1 (AO1.1)</p>	<p>ALLOW structure/displayed/skeletal formula</p> <p>DO NOT ALLOW same empirical formula OR same general formula</p> <p>IGNORE same molecular formula</p> <p>Reference to <i>E/Z</i> isomerism or optical isomerism is not sufficient</p>												
	iii	<p>Correct identification of <i>cis</i> AND <i>trans</i> isomers of 4-methylpent-2-ene ✓✓</p> <table border="1" style="width: 100%; text-align: center;"> <tr> <td> </td> <td> </td> </tr> <tr> <td><i>cis</i> isomer</td> <td><i>trans</i> isomer</td> </tr> </table> <p style="text-align: center;">OR</p> <p>Identification of 3-methylpent-2-ene as <i>cis</i> AND <i>trans</i> isomers ✓✓</p> <table border="1" style="width: 100%; text-align: center;"> <tr> <td> </td> <td> </td> </tr> <tr> <td><i>cis</i> isomer</td> <td><i>trans</i> isomer</td> </tr> </table>			<i>cis</i> isomer	<i>trans</i> isomer			<i>cis</i> isomer	<i>trans</i> isomer	<p>2 (AO1.2) (AO2.5)</p>	<p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>C_3H_7 is not sufficient (could be unbranched)</p> <p>ALLOW one mark if <i>cis</i> AND <i>trans</i> isomers of 4-methylpent-2-ene are in the wrong boxes</p> <p>ALLOW the isomers of 3-methylpent-2-ene in either box</p> <table border="1" style="width: 100%; text-align: center;"> <tr> <td> </td> <td> </td> </tr> <tr> <td><i>cis</i> isomer</td> <td><i>trans</i> isomer</td> </tr> </table> <p><i>Ambiguity with cis/trans identification system</i></p> <p>ALLOW one mark for correct identification of <i>cis</i> AND <i>trans</i> isomers of unbranched C_6H_{12} e.g.</p>			<i>cis</i> isomer	<i>trans</i> isomer
<i>cis</i> isomer	<i>trans</i> isomer															
<i>cis</i> isomer	<i>trans</i> isomer															
<i>cis</i> isomer	<i>trans</i> isomer															

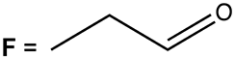
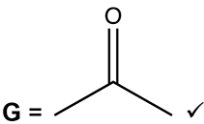


			<table border="1"> <tbody> <tr> <td> </td> <td> </td> </tr> <tr> <td><i>cis</i> isomer</td> <td><i>trans</i> isomer</td> </tr> </tbody> </table>			<i>cis</i> isomer	<i>trans</i> isomer
<i>cis</i> isomer	<i>trans</i> isomer						
iv	<p>Correct groups attached to chiral carbon of compound C seen once e.g.</p> <p>OR</p> <p>Two 3D structures of compound C that are mirror images with correct connectivity in both</p> <p>OR</p>	<p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>For C₂H₅–, ALLOW CH₃CH₂– For –CH=CH₂, ALLOW –C₂H₃ OR –CHCH₂</p> <p>For bond into paper accept:</p> <p>ALLOW two 3D structures with 2 groups swapped e.g.</p> <p>DO NOT ALLOW a bond angle of 180° e.g.</p>					
v	<table border="1"> <tbody> <tr> <td> </td> <td> </td> </tr> </tbody> </table>			<p>4 (AO2.5x 2) (AO2.2x 2)</p> <p>ALLOW 1 mark for structures if shown in wrong boxes.</p>			



		D	E		
		<p>Two of the following for D ✓</p> <p>All H are equivalent/in the same</p> <ul style="list-style-type: none"> • chemical environment/ the same type <p>All C are equivalent/ in the same</p> <ul style="list-style-type: none"> • chemical environment/ the same type • No C=C present <p>Two of the following for E ✓</p> <p>All H are equivalent/ in the same</p> <ul style="list-style-type: none"> • chemical environment/ the same type • 2 C environments • C=C present 			<p>CHECK table 16.1 for annotations that may be worthy of credit</p> <p>Examiner's Comments</p> <p>The majority of candidates were able to correctly define a structural isomer.</p> <p>This definition was well known by candidates with the majority of responses given the mark. Some candidates omitted the reference to structural formula.</p> <p>This question required candidates to link their knowledge of <i>cis</i> and <i>trans</i> isomers with branched hydrocarbons. Higher ability candidates were able to do this. The majority of candidates scored 1 mark for correctly drawing <i>cis</i> and <i>trans</i> isomers of an unbranched hydrocarbon.</p> <p>This question discriminated well. Candidates were required to identify the groups around a chiral carbon This question discriminated well. Candidates were required to identify the groups around a chiral carbon and then draw the two corresponding optical isomers. Incorrect responses frequently had incorrect connectivity around the chiral carbon, bond angles of 180° or 2D structures.</p> <p>Most candidates were able to correctly draw the structure of D and E. Many candidates did not explain their answers in terms of the number of different hydrogen and carbon environments or the presence/absence of a carbon-carbon double bond.</p>
		Total	10		
5 0		<p>Initial ratios</p> <p>C, $\frac{62.07}{12.0}$: H, $\frac{10.34}{1.0}$: O, $\frac{27.59}{16.0}$</p> <p>OR</p> <p>C, 5.1725 : H, 10.34 : O, 1.724</p>	<p>4 (AO1.2) (AO2.5) (AO3.2) (AO3.2)</p>	<p>CHECK spectra for annotations that may be worthy of credit</p>	



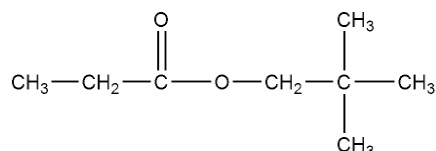
		<p>OR</p> <p>C, 3 : H, 6 : O, 1 ✓</p> <p>(Molecular formula =) C₃H₆O AND Evidence of 58 in working or from labelled peak in one of the spectra ✓</p> <p>For F evidence for fragment ion m/z=29 linked to CH₃CH₂(⁺) OR CHO(⁺) ✓</p> <p>F = </p> <p>AND</p> <p>G = </p>		<p>Mark can be awarded from a correct molecular formula</p> <p>IGNORE m/z=15 (as this is not unique) IGNORE m/z=43</p> <p>IGNORE incorrect fragments IGNORE charges on fragment ions</p> <p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>Examiner's Comments</p> <p>Most candidates were able to calculate the initial ratios and then use this to calculate the molecular formula, linking to the m/z peak at 58. The most common error seen was for the structures of F and G to be in the incorrect boxes, suggesting that candidates have not interpreted the fragment ions to work out F was the aldehyde.</p>
		Total	4	
5	1	B	1 (AO2.1)	
		Total	1	
5	2	C	1 (AO2.1)	<p>Examiner's Comments</p> <p>Many gained credit here but as A was the most common incorrect response it demonstrates the need to make sure candidates can recognise the difference between an alcoholic O-H and carboxylic acid O-H in IR.</p>
		Total	1	
5	3	Level 3 (5–6 marks)	6 (AO1.2 ×	Mark spectra page as SEEN Indicative scientific points:



	<p>Structure is either $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{C}(\text{CH}_3)_3$ OR $(\text{CH}_3)_3\text{CCH}_2\text{COOCH}_2\text{CH}_3$ AND Most of the data analysed.</p> <p><i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i></p> <p>Level 2 (3–4 marks) Structure is an ester of $\text{C}_8\text{H}_{16}\text{O}_2$ with some key features present AND Analyses some of the data from at least 3 of the scientific points.</p> <p><i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i></p> <p>Level 1 (1–2 marks) Attempts analysis from at least 2 of the scientific points.</p> <p><i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.</i></p> <p>0 mark No response or no response worthy of credit.</p>	<p>2) (AO3.1 × 2) 2) (AO3.2 × 2)</p>	<p><u>1. Empirical Formulae</u></p> <ul style="list-style-type: none"> $\text{C} : \text{H} : \text{O} = \frac{66.63}{12.0} : \frac{11.18}{1.0} : \frac{22.19}{16.0}$ $= 5.55 : 11.18 : 1.39$ $= 4 : 8 : 1$ Empirical formula = $\text{C}_4\text{H}_8\text{O}$ <p><u>2. Molecular Formulae</u></p> <ul style="list-style-type: none"> uses $m/z = 144.0$ to determine molecular formula as $\text{C}_8\text{H}_{16}\text{O}_2$ <p><u>3. Functional group</u> From IR,</p> <ul style="list-style-type: none"> → C=O from $\sim 1740 \text{ cm}^{-1}$ <p>IGNORE references to C–O peaks</p> <p>No reaction with 2,4-DNP</p> <ul style="list-style-type: none"> → no carbonyl/no ketone and aldehyde Likely to be an ester <p><u>4. ^1H NMR analysis</u></p> <ul style="list-style-type: none"> $\delta = 0.9$ ppm, singlet, 9H $-\text{C}(\text{CH}_3)_3$ $\delta = 1.2$ ppm, triplet, 3H CH_3CH_2- $\delta = 2.2$ ppm, quartet, 2H $\text{CH}_3\text{CH}_2\text{CO}$ $\delta = 4.1$ ppm, singlet, 2H $-\text{OCH}_2-$ <p><u>ALLOW</u> approximate values for chemical shifts.</p> <p><u>Structure</u> <u>ALLOW</u> any combination of skeletal OR structural OR displayed formula as long as <u>unambiguous</u></p> <p><u>Key features consistent with chemical shift data and relative peak areas</u></p> <ul style="list-style-type: none"> O-CH₂ C(CH₃)₃ CH₃CH₂C=O
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**Correct Structure**

- $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{C}(\text{CH}_3)_3$

**Examiner's Comments**

Most candidates were able to deduce the empirical and/or molecular formula of the organic compound. Analysis of the IR spectrum was also well attempted, but some candidates assumed the unknown was a carboxylic acid, attributing the sharp peak just below 3000 cm^{-1} to an OH group. Others misidentified the $\text{C}=\text{O}$ peak as a $\text{C}=\text{C}$ group suggesting alkene or arene structure. They were often led to this conclusion as they believed no precipitate with 2,4-DNP suggested no $\text{C}=\text{O}$ rather than no aldehyde or ketone.

Good analysis of the NMR data was crucial for deducing the correct ester. Some candidates opted to annotate the proton NMR spectrum, some produced tables and others gave written details for each peak. It was vital that they were able to interpret all information for each peak i.e. number of proton environments, the type of environment from chemical shift, the number of protons in each environment from relative peak areas and use of splitting patterns to find information about adjacent protons. Many tried to make the data fit their proposed structure rather than the other way round. Some suggested structures that were only partially consistent with the data such as $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOC}(\text{CH}_3)_3$ and were awarded Level 2. Others did not take full note of all the information provided, for example omitting the 2,4-DNP observations, giving the ketone $(\text{CH}_3)_3\text{COCH}_2\text{COCH}_2\text{CH}_3$ or not checking it



matched the molecular formula $\text{CH}_3\text{CH}_2\text{COOC}(\text{CH}_3)_3$ so only achieved Level 1.

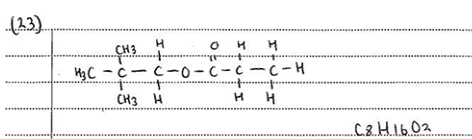
Candidates need to be encouraged to draw a structure as without they can only achieve a maximum of 2 marks despite some excellent analysis of the data. Conversely, it is not sufficient to just give a structure, candidates must give analysis of the data provided.

Exemplar 3

$\text{C } 66.63/12 \quad \text{H } 11.18/1 \quad \text{O } 22.19/16$
 $= 5.553 \quad 11.18 \quad 1.387$
 $= 4 : 8 : 1$
 empirical formula = $\text{C}_4\text{H}_8\text{O}$
 $\text{Mr} = 72$
 $144/72 = 2$ molecular formula = $\text{C}_8\text{H}_{16}\text{O}_2$
 because Mr = m/z peak which is easiest to find.
 IR spectrum: C=O peak at around 1700 cm^{-1}
 C-O peak at around 1300 cm^{-1}

shift	proton type	relative peak area	splitting	no adjacent protons	deductions
9.0	HC-O	2	singlet	0	$\text{O}=\text{C}-\text{O}$
2.1	HC-C=O	2	quartet	3	$\text{O}=\text{C}-\text{CH}_2-$
1.1	HC-R	3	triplet	2	$\text{CH}_2-\text{CH}_2-\text{H}$
0.9	HC-R	9	singlet	0	$\text{CH}_3-\text{C}-\text{CH}_3$

(continues on back page)



This is a good Level 3 6 mark response. As well as this clearly laid out analysis they also had details written on the question, e.g. no aldehyde or ketone due to no reaction with 2,4-DNP. This response has been selected due to the detailed analysis of NMR data that has been summarised in a table.

		Total	6	
5 4		C	1 (AO 2.5)	Examiner's Comments Less than half the candidates interpreted which compound could have produced the IR



				spectrum. Many wrote the functional groups present alongside each option and all four options were seen in the responses. It was expected that the presence of a C=O absorption at 1700 cm^{-1} would have led to A and B to be eliminated. Some thought that the peak at 3000 cm^{-1} was for the carboxylic acid O–H which diverted some away from the correct option, C.																				
		Total	1																					
5 5		B	1 (AO 2.6)	<p><u>Examiner's Comments</u></p> <p>Candidates found this question a little easier and, as with previous organic questions, the best route to success was to draw out the structures of the organic isomers. For mass spectrum fragmentation, this ensures that the molecules can visually be split up into possible fragments. So well over half the candidates correctly identified the possible fragments and the correct option, B.</p>																				
		Total	1																					
5 6		<p>Level 3 (5-6 marks) A comprehensive description including most of the evidence to justify the correct structure of X.</p> <p><i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated</i></p> <p>Level 2 (3-4 marks) Explains two scientific points with few omissions OR some aspects from all three</p> <p>AND an attempt at a feasible structure with either a C=O OR COOH</p> <p><i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i></p> <p>Level 1 (1-2 marks) Determines the correct empirical/molecular formula</p>	6	<p>LOOK ON THE SPECTRA for labelled peaks. Indicative scientific points may include:</p> <p><u>1. Empirical formula</u></p> <table border="1"> <thead> <tr> <th>Element</th> <th>%mass</th> <th>Ar</th> <th>moles</th> <th>ratio</th> </tr> </thead> <tbody> <tr> <td>C</td> <td>40.91</td> <td>12</td> <td>3.41</td> <td>3</td> </tr> <tr> <td>H</td> <td>4.54</td> <td>1</td> <td>4.54</td> <td>4</td> </tr> <tr> <td>O</td> <td>54.55</td> <td>16</td> <td>3.41</td> <td>3</td> </tr> </tbody> </table> <p>Empirical formula = $\text{C}_3\text{H}_4\text{O}_3$ ALLOW Alternative method using M_r of 88 i.e. $\text{C} = 88 \times (40.91/100) \times 12 = 3$ etc.</p> <p><u>2. Spectra and Molecular formula</u></p> <p>Mass spectrum</p> <ul style="list-style-type: none"> molecular ion peak m/z or $M_r = 88$ molecular formula = $\text{C}_3\text{H}_4\text{O}_3$ <p>IR</p>	Element	%mass	Ar	moles	ratio	C	40.91	12	3.41	3	H	4.54	1	4.54	4	O	54.55	16	3.41	3
Element	%mass	Ar	moles	ratio																				
C	40.91	12	3.41	3																				
H	4.54	1	4.54	4																				
O	54.55	16	3.41	3																				



OR

Some aspects from two scientific points are given

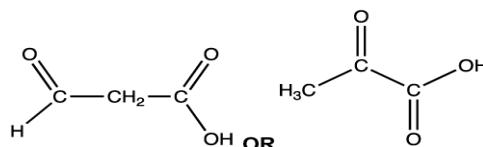
There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant

0 marks - No response worthy of credit.

- peak at 2500 to 3500 cm^{-1} is O-H
- peak at 1630 to 1820 cm^{-1} is C=O

3. Functional groups and structure of X

- **X** contains a carboxylic acid
- **X** doesn't decolourise Br_2 so no C=C bond
- Mass spectrum fragment peak(s) identified e.g.
 - $m/z = 43$ for CH_3CO^+
 - $m/z = 29$ CHO^+
 - $m/z = 15$ due to CH_3^+
- **Structure of X**



Aspects of the communication statement might typically have been met when evidence is presented in a logical and clear order making good use of all the evidence given.

Some points which may be seen where communication is good include:

- Easy to follow layout on empirical formula calculation
- Empirical formula is same as molecular formula i.e. not given as $\text{CH}_{1.33}\text{O}$
- IR peaks linked clearly to bond it refers to not just functional groups
- Positive charge given on MS fragments
- MS fragments plausible for the molecular formula determined.
- No additional irrelevant/incorrect information given

Examiner's Comments

Over a third of candidates achieved Level 3, gaining 5 or 6 marks. A correct structure (either aldehyde or ketone) alone was not enough to award Level 3 and candidates were expected to give a comprehensive description of how the



evidence helped them determine the structure.

The biggest challenge for many candidates was finding the correct empirical formula. The ratio worked out to 1:1.33:1 so many incorrectly rounded this to either 1:1:1 or 1:2:1, which meant they struggled to find a molecular formula that worked and added up to 88. Incorrect molecular formulas seen included $C_3H_3O_3$, which adds to 87 (often the extra H was just added to make it fit), or $C_4H_8O_2$, which does add to 88.

Most candidates could analyse the IR spectrum, identifying peaks corresponding to C=O or O-H. Candidates should identify bonds present before making conclusions about the functional groups.

Many were able to use mass spectra to determine the M_r value from the M^+ peak. Some did go on to make use of other peaks, identifying fragments and confirming whether the structure was an aldehyde or ketone depending on analysis. For example, CHO^+ at $m/z = 29$ suggests an aldehyde, or conversely CH_3^+ at $m/z = 15$ suggests a ketone.

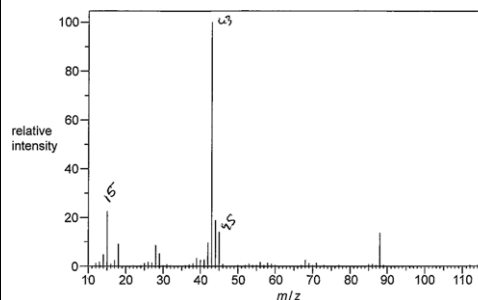
Candidates should always be encouraged to comment on all the data provided. This can be through good annotation of the spectra and notes added to the first page of the question. Many candidates didn't mention the evidence from the bromine test.

If candidates pieced together information to give a structure that is chemically feasible containing either a C=O or COOH group then they could achieve Level 2. Without a structure they were limited to Level 1.

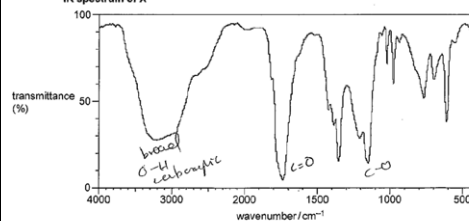
The most common incorrect structures seen included butanoic acid, 2-hydroxypropenoic acid or structures with $2 \times C=O$ and an alcohol OH.



Mass spectrum of X



IR spectrum of X



Empirical formulae:

	C	H	O
mass	40.91	4.54	54.65
M_r	12	1	16
moles	3.41	4.54	3.41
ratio	1	1.3	1

$$\text{CHO} = 29 \times 4 = 44 = \text{C}_2\text{H}_4\text{O}$$

Molecular formulae

$$m/z = 88 \text{ (molecular mass)} = 88$$



mass spectroscopy = (fragment ions)

$$m/z 15 = \text{CH}_3^+$$

$$m/z 43 = \text{C}_3\text{H}_7^+$$

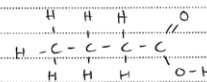
$$m/z 45 = \text{CH}_3\text{CH}_2\text{O}^+$$

IR spectroscopy

Extra answer space if required

shows a broad peak of key absorption at 2500-3300 suggesting O-H of carboxylic acid
shows an absorption at 1630-1820 for C=O of carboxylic acid, aldehyde etc.
C-O (1000-1300) carboxylic acid.

36) compound X




butanoic acid

This response achieved Level 2 - 4 marks. Despite a correct calculation for empirical formula, they rounded incorrectly to CHO. They then state that molecular formula is C4H8O2 which matches the M_r value determined from the mass spectrum but not their empirical formula. They demonstrated good analysis of the IR spectrum and have even looked at potential fragments from the mass spectrum. The response meets the Level 2 descriptor as



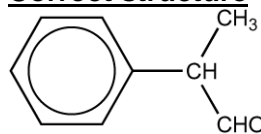
				they have a feasible structure with a COOH group and have some analysis of all three scientific points. The communication is good with a clearly laid out calculation and bonds identified from IR and MS fragments have a positive charge.
			Total	6
5 7			B	<p><u>Examiner's Comments</u></p> <p>Some candidates correctly chose option B, with the other options being chosen randomly. From the importance placed on the causes of global warming, it was interesting to see that many incorrectly chose option A.</p> <p>Note also the points made in Question 6 about underlining the word 'not'.</p>
			Total	1
5 8			C	<p><u>Examiner's Comments</u></p> <p>Most candidates first worked out the molecular mass of each fragment and annotated their scripts with this information, eliminating options A and C in the process. More successful responses than drew out the structure of the alcohol, to work out that only option C could have produced the fragment. This is evidence of good exam technique. Predictably, option B was the main distractor. This question discriminated well.</p>
			Total	1
5 9			A	<p><u>Examiner's Comments</u></p> <p>Most candidates gave the incorrect response D as their answer. Ultraviolet radiation does cause bonds in CFC molecules to break, and candidates may have been influenced by Question 8. However it is not a valid scientific reason for global warming. It suggests candidates may be confused about global warming verses the depletion of the ozone layer. This question was looking for candidates</p>



				<p>to link global warming to infrared active molecules i.e. C-H bond in methane. Just under a fifth of candidates gave the correct answer A.</p> <p> Misconception</p> <p>Many candidates believed there was a link between ultraviolet radiation and global warming. This is a topical issue so can be explored by looking at a range of resources including current news reports or exploring the United Nations resources.</p>
		Total	1	
60		D	1	<p><u>Examiner's Comments</u></p> <p>Many missed the separate O–H in alcohol and O–H in carboxylic acid peaks as it is unusual to see clearly defined peaks for both in an IR spectrum. Those who got D tended to annotate the spectrum, noting the sharp peak as O–H bond, as well as drawing out structures for each option. A was the most common incorrect response. It is good to remind candidates to look at all possible options before making a final decision.</p>
		Total	1	
61		<p><i>Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.</i></p> <p>Level 3 (5-6 marks) Structure is C₆H₅CHCH₃CHO AND Analyses data from all 3 scientific points</p> <p><i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i></p>	6	<p>LOOK ON THE SPECTRA for labelled peaks and mark as SEEN</p> <p>Indicative scientific points:</p> <p><u>1. Empirical (and Molecular) Formulae</u></p> <ul style="list-style-type: none"> $\begin{aligned} \text{C} : \text{H} : \text{O} &= \frac{80.60}{12.0} : \frac{7.46}{1.0} : \frac{11.94}{16.0} \\ &= 6.72 : 7.46 : 0.746 \\ &= 9 : 10 : 1 \end{aligned}$ Empirical formula = C₉H₁₀O <p><u>2. Mass spectrum and IR</u> Mass spectrum</p>



	<p>Level 2 (3-4 marks) Structure with most key features including O atom(s) AND Analyses data from at least 2 of the scientific points</p> <p><i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i></p> <p>Level 1 (1-2 marks) Attempts analysis from at least 2 of the scientific points</p> <p><i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.</i></p> <p>0 marks <i>No response or no response worthy of credit.</i></p>		<ul style="list-style-type: none"> uses $m/z = 134$ to give molecular formula: $C_9H_{10}O$ Any possible fragments: <ul style="list-style-type: none"> $m/z = 105$ $C_6H_5CHCH_3^+$ $m/z = 77$ $C_6H_5^+$ $m/z = 29$ CHO^+ <p>IR</p> <ul style="list-style-type: none"> $C=O$ from $\sim 1700\text{ cm}^{-1}$ Likely to be aldehyde or ketone $C=C$ (arenes) $\sim 1500\text{ cm}^{-1}$ <p>ALLOW Data Sheet ranges</p> <p>3. 1H NMR</p> <ul style="list-style-type: none"> $\delta = 1.4$ ppm, doublet, 3H CH_3CH- $\delta = 3.8$ ppm, quintet, 1H next to 4 adjacent H $\delta = 7.3$ ppm, singlet, 5H C_6H_5- $\delta = 9.0$ ppm, doublet, 1H $-CHCHO$ <p>ALLOW approximate values for chemical shifts</p> <p>Structure ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW correct Kekulé representation of benzene</p> <p>Key features</p> <ul style="list-style-type: none"> Benzene ring $C=O$ CH_3
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**Correct structure**

- (C₆H₅CHCH₃CHO)

Aspects of the **communication statement** being met might typically include:

- Structures given are feasible and unambiguous
- Easy to follow layout on empirical formula calculation
- Empirical formula is shown to be same as molecular
- IR peaks linked clearly to bond it refers to not just functional groups
- Positive charge given on MS fragments
- MS fragments plausible for the molecular formula determined
- Clear information for each NMR peak
- No additional irrelevant/incorrect information given

Examiner's Comments

This question was well-attempted by most candidates, with the majority of candidates gaining full marks or gaining 4 marks for a top Level 2 response.

Many candidates showed excellent recall of how to determine the correct empirical formula from the percentage composition data. Most then went on to use the m/z peak on the mass spectrum to confirm that the M_r was 134, and therefore the molecular formula was identical to the empirical formula. A few also made use of the mass spectrum to identify possible fragment ions including a correct positive charge.

Most candidates used the IR spectrum to identify a C=O bond and many also mentioned the absence of O-H or spotted C=C for arenes. Lower attaining candidates sometimes



incorrectly mentioned the presence of a carboxylic acid O-H despite the molecular formula only having 1 oxygen atom.

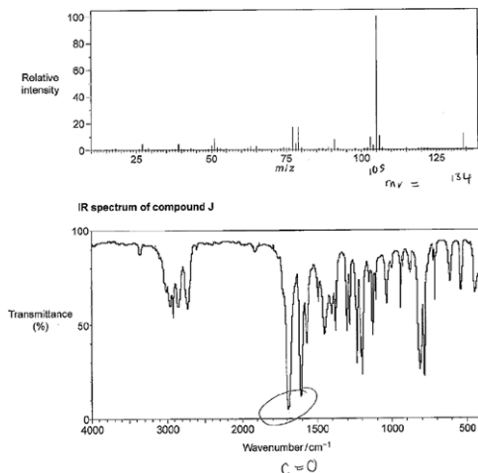
Many candidates annotated the NMR spectrum and/or presented their analysis clearly in a table format and were able to identify aldehyde and arene hydrogen environments. The best candidates had fragments built up alongside their NMR analysis clearly building them using chemical shift, integration ratios and splitting patterns. Those that struggled to interpret the splitting patterns correctly suggested incorrect structures but often with correct features so were still able to score Level 2, 4 marks. Some initially identified the multiplet peak at 3.8 ppm as being HC-O environment but many realised this did not fit the IR data. However, some changed other evidence to fit this, e.g. the peak at 9.0 ppm being an O-H rather than CHO and the IR having C=C only without C=O as well.

A large proportion of candidates were able to correctly determine the structure of compound J, recognising that the peak at 3.8 ppm was shifted up-field as adjacent to both the benzene ring and the aldehyde group. The data sheet refers to this: 'CH bonded to 'shifting groups' on either side, e.g. O-CH₂-C=O, may be shifted more than indicated above'.

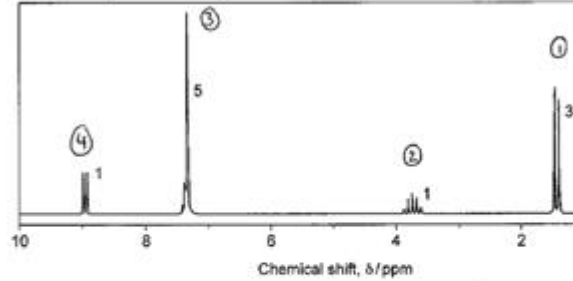
Several candidates who did not get the correct structure gave structures which were chemically unfeasible, e.g. with pentavalent carbons. Many candidates had several structures as part of working but did not always ensure their final structure was clearly highlighted.

A very small number of candidates received no credit for this question, as the majority were able to show analysis of 2 aspects, e.g. the calculation of empirical formula and labelling of IR or NMR spectra.

Exemplar 3



Proton NMR spectrum of compound J



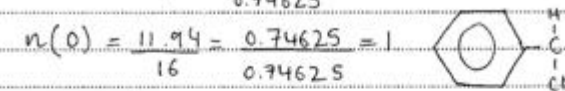
The numbers by the peaks are the relative peak areas. 4 protons

Determine the structure of compound J, showing all your reasoning.

elemental analysis:

$$n(C) = \frac{80.60}{12} = 6.71667 = 9$$

$$n(H) = \frac{7.46}{1} = 7.46 = 10 \quad C_9H_{10}O$$

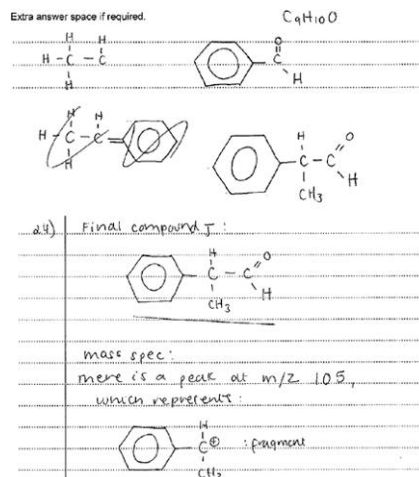


Infrared:

→ there's a peak at 1700 cm⁻¹, which rep C=O bond, which occurs between 1

H¹ NMR:

	ppm/ δ	n ^o of hydrogen	splitting	n ^o of protons on adjacent	
①	1.5	3	doublet	1	H ₃ C-CH
②	3.8	1	multiplet	4	HC-CH ₂ -CH ₃
③	7.3	5	doublet	0	⊙-CH
④	9.0	1	doublet	1	-C(=O)-H



Level 3, 6 marks

There is clear and detailed analysis throughout this response to determine the correct final structure for **J**. The empirical formula calculation shows how the empirical formula was determined. On the mass spectrum the annotation links to the M_r of 134 and at the end of the response they have identified the fragment responsible for the parent ion. The $C=O$ IR peak is labelled and described in the response. The NMR analysis is clear, with each peak being numbered and linked to a table which shows how the candidate has identified the hydrogens responsible for each peak as well as linking to neighbouring hydrogens from splitting patterns. The final compound is labelled as such to distinguish it clearly from other structures given, which were part of their problem solving to find a structure that fits all of the analysis they had completed.

Total

6