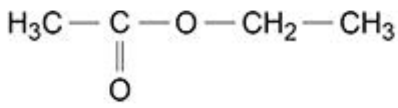
Q1.

Which statement does **not** support the suggestion that an unknown organic compound is



A Its ^{1}H NMR spectrum has 3 peaks with an integration ratio of 2:3:3

B Its ^{13}C NMR spectrum has 3 peaks.

C Its infrared spectrum has an absorption at 1735 cm^{-1}

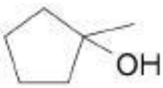
D It has 36.36% by mass of oxygen and 9.09% by mass of hydrogen.

(Total 1 mark)

Q2.

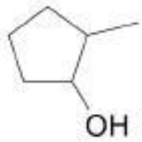
This question is about the structural isomers shown.

P

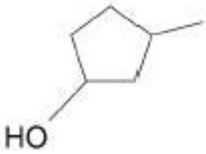


Q

R

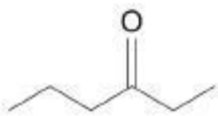


S



T

U



(a) Identify the isomer(s) that would react when warmed with acidified potassium dichromate(VI).

State the expected observation when acidified potassium dichromate(VI) reacts.

Isomer(s) ____

Expected observation ______________________________________

____

(2)

(b) Identify the isomer(s) that would react with Tollens' reagent.

State the expected observation when Tollens' reagent reacts.

Isomer(s) ______________________________

Expected observation ______________________________

____

(2)

(c) Separate samples of each isomer are warmed with ethanoic acid and a few drops of concentrated sulfuric acid. In each case the mixture is then poured into a solution of sodium hydrogencarbonate.

Identify the isomer(s) that would react with ethanoic acid.

Suggest a simple way to detect if the ethanoic acid reacts with each isomer.

Give a reason why the mixture is poured into sodium hydrogencarbonate solution.

Isomer(s) ______________________________

Suggestion ______________________________

____

____

Reason ______________________________

____

(3)

(d) State the type of structural isomerism shown by isomers **P**, **Q**, **R** and **S**.

____

(1)

(e) Describe fully how infrared spectra can be used to distinguish between isomers **R**, **S** and **T**.
Use data from **Table A** in the Data Booklet in your answer.

____

____

____

____

____

____

(4)

(f) State why mass spectrometry using electrospray ionisation is **not** a suitable method to distinguish between the isomers.

____

____

(1)

(Total 13 marks)

Q3.

Some compounds with different molecular formulas have the same relative molecular mass to the nearest whole number.

(a) A dicarboxylic acid has a relative molecular mass of 118, to the nearest whole number.

Deduce the molecular formula of the acid.

Molecular formula ___________________________________

(3)

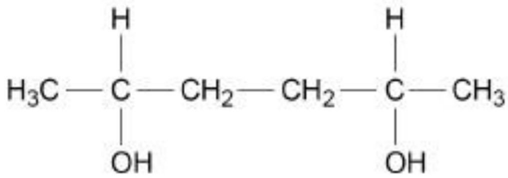
(b) A student dissolved some of the dicarboxylic acid from part (a) in water and made up the solution to 250 cm^3 in a volumetric flask.
In a titration, a 25.0 cm^3 sample of the acid solution needed 21.60 cm^3 of 0.109 mol dm^{-3} sodium hydroxide solution for neutralisation.

Calculate the mass, in g, of the dicarboxylic acid used.
Give your answer to the appropriate number of significant figures.

Mass ____________________ g

(4)

(c) Compounds with molecular formula $C_6H_{14}O_2$ also have a relative molecular mass of 118 to the nearest whole number. These include the diol shown.



Deduce the number of peaks in the ¹H NMR spectrum of this diol.

___

(1)

(d) Draw the structure of a different diol also with molecular formula $C_6H_{14}O_2$ that has a ^{1}H NMR spectrum that consists of two singlet peaks.

(1)

(e) The dicarboxylic acid in part **(a)** and the isomers of $C_6H_{14}O_2$ in parts **(c)** and **(d)** all have a relative molecular mass of 118

State why the dicarboxylic acid can be distinguished from the two diols by high resolution mass spectrometry using electrospray ionisation.

___

___

___

(1)

(Total 10 marks)

Q4.

Four compounds, all colourless liquids, are

- butan-2-ol
- butanal
- butanone
- 2-methylpropan-2-ol

Two of these compounds can be identified using different test-tube reactions.

Describe these **two** test-tube reactions by giving reagents and observations in each case. Suggest how the results of a spectroscopic technique could be used to distinguish between the **other** two compounds.

____

(Total 6 marks)

Q5.

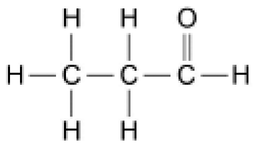
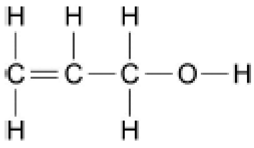
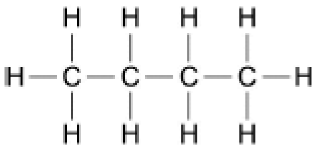
Which compound forms a molecular ion with a different precise molecular mass from the other three?

A	butanone	○
B	cyclobutanol	○
C	dimethylpropane	○
D	methylpropanal	○

(Total 1 mark)

Q6.

The compounds in the table all have a relative molecular mass of 58.0

Name	Propanal	Prop-2-en-1-ol	Butane
Structure			

(a) Explain why determining the precise relative molecular mass of propanal and prop-2-en-1-ol by mass spectrometry could not be used to distinguish between samples of these two compounds.

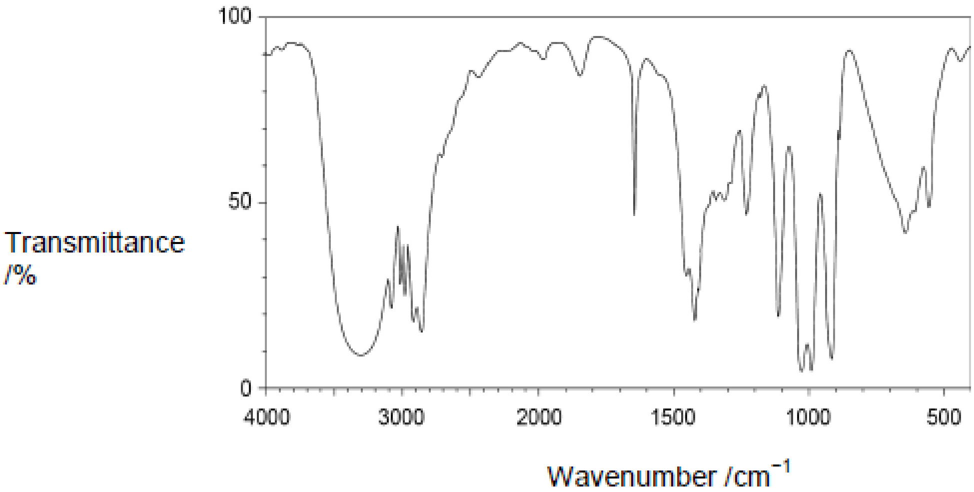
____

____

____

(2)

(b) The infrared spectrum of one of these three compounds is shown below.



Use the spectrum to identify the compound.
State the bond that you used to identify the compound and give its wavenumber range.
You should only consider absorptions with wavenumbers greater than 1500 cm^{-1}.

Compound ____

Bond used to identify compound ____________________________________

Wavenumber range of bond used to identify compound _______________ cm^{-1}

(2)

(c) Predict the relative boiling points of these three compounds from the highest to the lowest boiling points.

Justify this order in terms of intermolecular forces.

(6)
(Total 10 marks)

Q7.

Butane and propanal are compounds with M_r = 58.0, calculated using data from your Periodic Table.

(a) A mass spectrometer can be used to distinguish between samples of butane and propanal.

The table shows some precise relative atomic mass values.

Atom	Precise relative atomic mass
^{1}H	1.00794
^{12}C	12.00000

(i) Use data from the table to show that, to 3 significant figures, a more accurate value for the M_r of butane is 58.1

(1)

(ii) State why the precise relative atomic mass quoted in the table for the ^{12}C isotope is exactly 12.00000

____

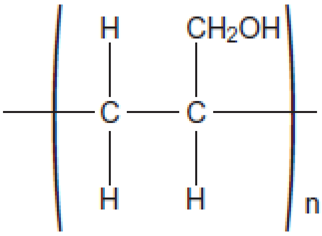
____

(1)

(b) Draw a **displayed formula** for the organic product that is formed when propanal is oxidised by warm Tollens' reagent.

(1)

(c) Prop−2−en−1−ol is an isomer of propanal and can be polymerised to form a polymer represented by the following structure.



(i) Draw the structure of prop−2−en−1−ol.

(1)

(ii) Deduce the type of polymerisation that results in the formation of this polymer from prop−2−en−1−ol.

____

(1)

(iii) There are two functional groups in prop−2−en−1−ol. Each of these functional groups contains a bond with a characteristic absorption range in the infrared spectrum.

Use **Table A** on the Data Sheet to suggest a bond and its absorption range for each of the two functional groups.

Bond 1 ____________ Absorption range _________________________

Bond 2 ____________ Absorption range _________________________

(2)

(d) Compound **X** is another isomer of propanal. The infrared spectrum of **X** shows an absorption in the range 1680−1750 cm^{-1}.

(i) Draw the structure of **X**.

(ii) Which of the following, **A**, **B**, **C** or **D**, represents the type of isomerism shown by **X** and propanal?

Write the correct letter, **A**, **B**, **C** or **D**, in the box.

A chain isomerism
B E−Z isomerism
C functional group isomerism
D position isomerism

(1)
(Total 9 marks)

Q8.

The manufacture of food grade phosphoric acid for use in cola drinks begins with the production of pure white phosphorus from the mineral fluoroapatite, $Ca_5F(PO_4)_3$

(a) Complete the following equation for the manufacture of phosphorus.

$$....Ca_5F(PO_4)_3 + 9SiO_2 + ...C \longrightarrow 9CaSiO_3 + CaF_2 + ...CO + ...P$$

(1)

(b) As the phosphorus cools, it forms white phosphorus, P_4

Give the oxidation state of phosphorus in each of the following.

P_4 ______________________________

H_3PO_4 ______________________________

(2)

(c) Fertiliser grade phosphoric acid is manufactured from sulfuric acid and calcium phosphate.
Use the following precise relative atomic mass data to show how mass spectrometry can be used to distinguish between pure sulfuric acid (H_2SO_4) and pure phosphoric acid (H_3PO_4) which both have M_r = 98 to two significant figures.

Atom	Precise relative atomic mass
^{1}H	1.00794
^{16}O	15.99491
^{31}P	30.97376
^{32}S	32.06550

____

____

____

(1)

(d) Concentrated phosphoric acid is used as a catalyst in the hydration of propene to form the alcohol $CH_3CH(OH)CH_3$ as the main organic product.
The industrial name for this alcohol is isopropyl alcohol.

(i) State the meaning of the term *catalyst*.

____

____

____

(1)

(ii) State the meaning of the term *hydration*.

____

____

____

(1)

(iii) Write an equation for the hydration of propene to form isopropyl alcohol.
Give the IUPAC name for isopropyl alcohol.

Equation ____

IUPAC name ____

(2)

(Total 8 marks)

Mark schemes

Q1.

B

Its ^{13}C NMR spectrum has 3 peaks.

[1]

Q2.

(a) **M1** Q, R, S, T

M1 Allow the mark for candidates who correctly name or draw the isomers.

1

M2 (Orange solution) turns green

Independent

1

(b) **M1** T

As above

1

M2 Silver mirror

Allow grey/black ppt

1

(c) **M1** P, Q, R, S

As above

1

M2 Sweet smelling (liquid)

1

M3 To react with (remove excess) acid / neutralise

Allow easier to identify the smell

1

(d) Position

Allow positional

1

(e) **M1** R & S have an O-H alcohols peak at 3230-3550 cm^{-1}

Allow value within the range

1

M2 T has C=O peak at 1680-1750 cm^{-1}

1

M3 R & S (unique) fingerprint region or below 1500 cm^{-1}

1

M4 Compare to a database / known spectra (and look for an exact match)

1

(f) All have the same M_r

Allow
same (molecular) ion M/Z peak
same molecular formula

1

[13]

Q3.

(a) $(COOH)_2 = C_2H_2O_4 = 90$ **M1**

$118 - 90 = 28$ OR C_2H_4 **M2**

$C_4H_6O_4$ **M3**

Must be molecular formula
*Structural formula can score **M1** & **M2***

(b) Amount NaOH = $(21.60 \times 10^{-3}) \times 0.109$

$= 2.3544 \times 10^{-3}$ mol

***M1** for answer (to 3sfs min)* **M1**

Amount H_2A in 25 cm^{-3} = 1.177×10^{-3} mol

M2** = 0.5 × **M1 **M2**

Amount H_2A in 250 cm^{-3} = 1.177×10^{-2} mol

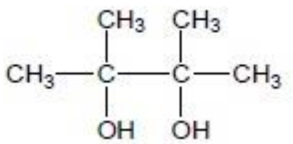
***M3** = **M2** × 10* **M3**

Mass = 1.39 g (Must be 3sf)

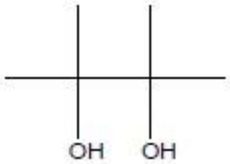
***M4** = answer to (**M3** × 118) and must be 3sf* **M4**

(c) 4 or four **1**

(d)



OR



1

(e) The precise (relative molecular) masses are <u>different</u> or wtte

Allow M_r are different to 2 or more or several dp
Ignore different molecular formula
Ignore accuracy
Penalise fragments

1

[10]

Q4.

This question is marked using levels of response. Refer to the Mark Scheme Instructions for Examiners for guidance on how to mark this question.

	How to choose the level		**Requirements for communication for higher mark**	**Stages**
Level 3 5-6 marks	All three stages are covered and explanation of each stage is generally correct and virtually complete – **leads to all four compounds being distinguished**		• Answer communicates whole process coherently with logical progression • Chemical tests (appear to) start with all compounds rather than selected compounds • Chemical tests reagents and observations are complete and correct • Chemical tests leave two compounds to be distinguished by spectroscopy • Enough detail is given about the spectroscopy to distinguish these two compounds	**Stage 1** Carries out a test-tube reaction to identify a compound (or to split the compounds into two groups). 1a reagent 1b observation with correct deduction **Stage 2** Carries out a second test-tube reaction to identify a second compound. 2a reagent 2b observation with correct deduction **Stage 3** Uses spectroscopy to distinguish two compounds. 3a suitable technique 3b data that will distinguish compounds
Level 2 3-4 marks	All three stages are covered but the explanations of each stage may be incomplete or may contain inaccuracies	Two stages covered and explanations are generally correct and virtually complete	• Answer is mainly coherent • Chemical tests reagents and observations are complete and correct • Enough detail is given about the spectroscopy to distinguish these two compounds (if spectroscopy included)	
Level 1 1-2 marks	Two stages covered but the explanations of each stage may be incomplete or may contain	One stage covered and explanation is generally correct and virtually	• Chemical tests reagents and observations are complete and correct (if awarded level 1 for one chemical	

	inaccuracies	complete	test stage) • Enough detail is given about the spectroscopy to distinguish these two compounds (if spectroscopy included)	
0 marks	Nothing valid to warrant a mark			

<u>Possible test tube reactions</u> **Tollens' reagent [or Fehling's / Benedict's]** Identifies butanal – silver mirror (or black ppt) [or orange/brick/red ppt with Fehling's] (No reaction with other compounds) **Acidified potassium dichromate** Reacts with butanal and butan-2-ol – goes green (No reaction with other compounds) **Sodium** *(not on specification but may be mentioned)* Reacts with butan-2-ol and 2-methylpropan-2-ol – fizzes (No reaction with other compounds) Examples of incomplete/incorrect reagents include "Tolling's solution", no acid with potassium dichromate, wrong oxidation state for Cr in potassium dichromate if stated. Examples of incomplete/incorrect observations include silver precipitate with Tollens', green ppt with acidified potassium dichromate	**<u>Possible spectroscopic methods for a pair</u>** **IR (infra-red) spectroscopy** If different functional groups: need to identify wavenumber and bond of key functional group signal (e.g. (alcohol) O-H 3230-3550 or C=O 1680-1750 (cm^{-1})). If same functional group, need idea of using fingerprint region to look for match to known compounds / comparing region to samples in a database **Mass spectrometry** If different, can use different M_r values with values of M_r given butanone 72(.0), 2-methylpropan-2-ol = 74(.0), butan-2-ol = 74(.0), butanal = 72(.0) If compounds have same M_r, then would have to use idea that fragmentation patterns would be different *(not on specification but may be mentioned)*

[6]

Q5.

C

[1]

Q6.

(a) M1 have the same molecular formula
or are C_3H_6O
or both have the same number/amount of each type of atom or same amount of each element
or are isomers

Not just the same atoms;

1

M2 identical / exactly the same / same precise (relative) molecular mass / formula mass / M_r

Same (relative) molecular mass / formula mass / M_r is NOT enough got score M2

Allow same accurate (relative) molecular mass / formula mass / M_r

Ignore reference to number of decimal places

1

(b) M1 prop-2-en-1-ol

Must refer to this compound clearly by name or structure (not to alcohol alone); ignore minor slips in name/structure

1

M2 O(-)H (alcohol) and 3230–3550 (cm^{-1}), or C=C and 1620–1680 (cm^{-1})

Marked independently from M1

Could score from bond labelled on correct signal on spectrum

Allow any value within these ranges

If additional incorrect signals given penalise M2

Ignore signals below 1500 cm^{-1} and C-H signals

1

(c) (i) Determine the level by looking at the chemical content. (**NB** - If there is clear breakage of covalent bonds then max level 2 (max 3 marks).

(ii) The mark within that level is then determined by looking at how coherent and logical the answer is and by use of terminology; start at the higher mark and penalise poor terminology/explanation; examples of terminology that would reduce the mark to the lower one:

- reference to van der Waals 'bonds' or dipole-dipole 'bonds in relevant compounds that are being credited
- uncertainty about whether hydrogen bonds are the O-H bonds within or are forces/bonds between molecules (if the alcohol is being credited)
- use of 'vdw' or 'dip-dip' unless these terms 'van der Waals' for 'dipole-dipole' have been used elsewhere in answer (note that IMF and H-bond would not be penalised)

(iii) If the answer does not achieve level 1, then 1 mark maximum could be scored for any correct point from the list of indicative content

Level 3

- **Relative order** of boiling points of **all three** compounds
- Strongest intermolecular force of **all three** compounds identified
- Answer explains this coherently and logically and uses correct terminology for all **three** compounds

5-6 marks

Level 2

- **Relative** boiling points of **two** compounds correctly compared
- Strongest intermolecular force for these **two** compounds correctly identified
- Answer explains this coherently and logically and uses correct terminology for **these two** compounds

3-4 marks

Level 1

- **One** compound with the **highest** or **lowest** boiling point is correctly identified
- Strongest intermolecular force for that **one** compound identified
- Answer explains this coherently and logically and uses correct terminology for **this one** compound
- Allow 1 mark for individual correct point from indicative content on the right if no other mark scored

1-2 marks

Level 0

None of the indicative chemistry content given.

0 marks

Indicative chemistry content:

• Correct order (highest to lowest) = prop-2-en-1-ol > propanal > butane

• Prop-2-en-1-ol has hydrogen bonds

• Propanal has (permanent) dipole-dipole forces

• Butane has van der Waals' forces

• Strength of intermolecular forces:
hydrogen bonds > dipole-dipole > van der Waals

(Note - actual values for reference are prop-2-en-1-ol 97°C, propanal 46°C and butane −1°C)

[10]

Q7.

(a) (i) C_4H_{10}

M_r = 4(12.00000) + 10(1.00794)

= <u>58.07940</u> or <u>58.0794</u> or <u>58.079</u> or <u>58.08</u>

<u>and</u> **<u>58.1</u>**

Working is essential, leading to the final value of 58.1 which must be stated in addition to one of the four numbers underlined

1

(ii) <u>By definition</u>

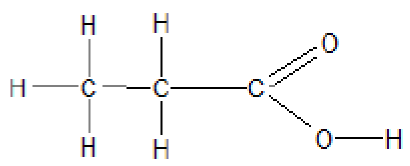
OR

The <u>standard</u> / <u>reference</u> (value / isotope)

Reference to ^{12}C alone is not enough

1

(b)



All bonds and atoms must be drawn

Give credit for the displayed formula for the anion

1

(c) (i) $H_2C = CHCH_2OH$

Any correct representation including correct use of "sticks".

Require the double bond to be shown

1

(ii) <u>Addition</u> (polymerisation)

ONLY this answer

1

(iii) **M1** **<u>C = C</u>** (in range) **<u>1620 to 1680</u>** (cm^{-1})

M2 **<u>O – H</u>** (in range) **<u>3230 to 3550</u>** (cm^{-1})

Award one mark for two correct ranges but a failure to draw out the C = C or O–H bonds

2

(d) (i) CH_3COCH_3

Any correct representation including correct use of "sticks"

1

(ii) C

1

[9]

Q8.

(a) **2**$Ca_5F(PO_4)_3$+ 9SiO_2 +**15**C9$CaSiO_3$ + CaF_2 +**15**CO + **6**P

1

(b) **M1** (P_4 =) **0**

M2 (H_3PO_4 =) **(+) 5**

Accept Roman numeral V for ***M2***

2

(c) H_2SO_4

Both numbers *required*

M_r = 2(1.00794) + 32.06550 + 4(15.99491)

= **98.06102 or 98.0610 or 98.061 or 98.06 or 98.1**

Calculations not required

<u>and</u>

H_3PO_4

M_r = 3(1.00794) + 30.97376 + 4(15.99491)

= **97.97722 or 97.9772 or 97.977 or 97.98 or 98.0**

1

(d) (i) A substance that <u>speeds up</u> a reaction OR <u>alters / increases the rate</u> of a reaction **AND** is <u>chemically unchanged at the end / not used up</u>.

Both ideas *needed*

Ignore reference to activation energy or alternative route.

1

(ii) The addition of water (**QoL**) to a molecule / compound

QoL- for the underlined words

1

(iii) **M1** $CH_3CH{=}CH_2 + H_2O$ $CH_3CH(OH)CH_3$

(C_3H_6)

*For **M1** insist on correct structure for the alcohol but credit correct equations using either C_3H_6 or double bond not given.*

M2 propan-2-ol

2

[8]