[9]

1

Mark schemes

Q1.	
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(a)	Tick in carbonyl box only	1
(b)	Peak at 2220-2260 cm ⁻¹ (for C≡N) disappears If both C≡N disappears and N-H appears without wavenumbers scores 1	M1
	Peak at 3300-3500 cm ⁻¹ (for N-H) appears	M2
	Fingerprint region different	M3
(c)	Integration ratio 2:2:3 If no link between delta value and oxygen and chlorine, then can award 1 mark for correct explanation of splitting of all 3 peaks	M1
	Peak at 3.95 triplet (integration 2) CI-CH $_2$ next to CH $_2$	M2
	Peak at 3.65 triplet (integration 2) O-CH ₂ next to CH ₂ If no explanation of splitting, then can award 1 mark for 3 correct links between delta value and oxygen and chlorine M1	М3
	Peak at 3.35 singlet (integration 3) O-CH $_3$ no adjacent H	M4
	Structure CH ₃ -O-CH ₂ CH ₂ CI	M5

Q2.

В

Q3.

(a)

	Its ¹³ C NMR spectrum has 3 peaks.	
		[1]
M1	Q, R, S, T	
	M1 Allow the mark for candidates who correctly	

M2	(Orange solution) turns green	
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name or draw the isomers.

		Independent	1	
(b)	M1	т		
		As above	1	
	M2	Silver mirror	-	
	1112	Allow grey/black ppt		
			1	
(c)	M1	P, Q, R, S		
		As above	1	
			1	
	M2	Sweet smelling (liquid)	1	
		—	-	
	М3	To react with (remove excess) acid / neutralise Allow easier to identify the smell		
		Allow easier to identify the smell	1	
(d)	Posit	ion		
()		Allow positional		
			1	
(e)	M1	R & S have an <u>O-H alcohols</u> peak at <u>3230-3550</u> cm⁻¹		
		Allow value within the range	1	
	MO	$T_{has} = 0$ neck at 1690 1750 cm ⁻¹		
	M2	T has <u>C=O</u> peak at <u>1680-1750</u> cm⁻¹	1	
	М3	R & S (unique) fingerprint region or below 1500 cm ⁻¹		
			1	
	M4	Compare to a database / known spectra (and look for an exact		
	mato	h)	1	
			T	
(f)	All ha	ve the same <i>M</i> ^r <i>Allow</i>		
		same (molecular) ion M/Z peak		
		same molecular formula		
			1	[40]
				[13]
4.				
(a)	M1 N	lamed carbonate / hydrogencarbonate / bicarbonate (or Mg / Na)		

Q4.

M1 Named carbonate / hydrogencarbonate / bicarbonate (or Mg / Na) Allow any correct chemical test. Allow name or formula of suitable reagent in M1

M2 No (visible/observed) reaction/change/effect

(b)

1 M3 effervescence / bubbles (of gas) / fizzing If no reagent or incorrect reagent in M1, CE = 0 and no marks for M2 or M3 In M3 ignore reference to name/formula of correct gas, but penalise reference to name/formula of incorrect gas In M3 allow reference to limewater going cloudy as an alternative Penalise incorrect formula of correct reagent (or incomplete reagent) in M1, but mark on for M2 and M3 Where there is no reaction, ignore "nothing (happens)" or "no observation" 1 OR M1 universal indicator M2 neutral / no change / pH7 M3 orange / red / pH < 7 / acidic If use of named alcohol in M1, allow no reaction for M2 and sweet smell for M3 Allow use of other suitable indicators (e.g. litmus) M1 Tollens' (reagent) OR ammoniacal silver nitrate OR a description of making Tollens' 1 M2 No (visible/observed) reaction/change or stays colourless 1 M3 silver mirror or black solid / precipitate 1 OR M1 Fehling's (solution) or Benedict's solution M2 no (visible/observed) reaction/change or stays blue M3 red solid / precipitate (credit orange or brown) OR M1 acidified potassium dichromate or K₂Cr₂O₇/H₂SO₄ or K₂Cr₂O₇/H⁺ or acidified K₂Cr₂O₇ M2 no (visible/observed) reaction/change or stays orange

M3 (orange to) green solution or goes green

OR

M1 acidified potassium manganate(VII) or KMnO₄/H₂SO₄ *OR* KMnO₄/H⁺ *OR* acidified KMnO₄

M2 no (visible/observed) reaction/change or stays purple

M3 (purple to) colourless solution OR goes colourless

Allow any correct chemical test. If no reagent or incorrect reagent in **M1**, **CE** = **0** and no marks for **M2** or **M3**

Allow name or formula of suitable reagent in **M1** Penalise incorrect formula of correct reagent in **M1**, but mark on for **M2** and **M3**

For Tollens' reagent: for **M1** ignore either $AgNO_3$ or $[Ag(NH_3)_2^+]$ or "the silver mirror test" on their own, or "Tolling's reagent", but mark **M2** and **M3**; for **M3** allow silver precipitate/deposit

For Fehling's/Benedict's solution: for **M1** Ignore Cu²⁺(aq) or CuSO₄ or "Fellings" on their own, but mark **M2** and **M3**

For acidified potassium dichromate(VI): if "dichromate" or "(potassium) dichromate(IV)" or incorrect formula or no acid, penalise **M1** but mark **M2** and **M3**; for **M3** ignore dichromate described as "yellow" or "red".

For acidified potassium manganate(VII): If "manganate" or "(potassium manganate(IV)" or incorrect formula or no acid, penalise **M1** but mark **M2** and **M3**.

Credit alkaline / neutral KMnO₄ for possible full marks but **M3** gives <u>brown precipitate</u> or solution goes <u>green</u>

Where there is no reaction, ignore "nothing (happens)" or "no observation"

[6]

[1]

Q5. B

4-hydroxybutanone

Q6.

(a) Must be a single test-tube reaction

If incorrect reagent then no marks

M1 Reagent: acidified potassium dichromate $OR K_2Cr_2O_7/H_2SO_4 OR K_2Cr_2O_7/H^+ OR$ acidified $K_2Cr_2O_7$

For acidified potassium dichromate: if "dichromate" or "(potassium) dichromate(IV)" or incorrect formula or no acid, penalise **M1** but mark on - ignore dichromate described as "yellow" or "red".

1

1

M2-1-ol (orange to) green solution OR goes green

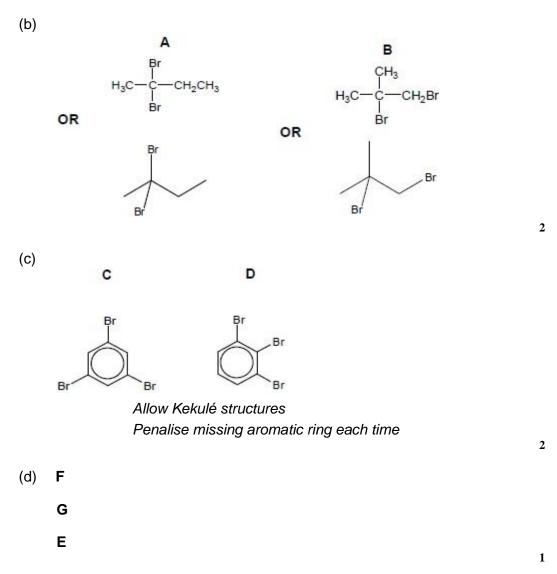
M3-2-ol no (visible/observed) reaction/change or NVR or stays orange

OR

M1 Reagent: acidified potassium manganate(VII) or KMnO₄/H₂SO₄ *OR* KMnO₄/H⁺ *OR* acidified KMnO₄

M2....-1-ol (purple to) colourless solution OR goes colourless

M3....-2-ol no (visible/observed) reaction/change or stays purple
 For acidified potassium manganate(VII): If "manganate" or "(potassium manganate(IV)" or incorrect formula or no acid, penalise M1 but mark on
 Credit alkaline / neutral KMnO4 for possible full marks but M2 gives brown precipitate or solution goes green



[8]

1

Q7.

(a) <u>Cyclopentanone</u>

Allow cyclopentan -1-one but no other numbers Ignore spaces, commas and hyphens

	is marked using Levels of Response. Refer to the Mark uctions for Examiners for guidance.
l evel 3	All stages are covered and each stage is generally correct and virtually complete.
5-6 marks	Answer is well structured with no repetition or irrelevant points. Accurate and clear expression of ideas with no errors in use of technical terms.
Level 2	All stages are covered but stage(s) may be incomplete or may contain inaccuracies OR two stages are covered and are generally correct and virtually complete.
3-4 marks	Answer shows some attempt at structure Ideas are expressed with reasonable clarity with, perhaps, some repetition or some irrelevant points.
	Some minor errors in use of technical terms
Level 1 1-2 marks	Two stages are covered but stage(s) may be incomplete or may contain inaccuracies OR only one stage is covered but is generally correct and virtually complete.
	Answer includes isolated statements and these are presented in a logical order.
	Answer may contain valid points which are not clearly linked.
	Errors in the use of technical terms.
0 marks	Insufficient correct chemistry to gain a mark.

Indicative Chemistry content

Stage 1: boiling points

- 1a) Y has a higher bp
- 1b) Y has H-bonds between molecules and X has dip-dip imf
- 1c) More energy required to overcome H-bonds

Mention of covalent bond breaking loses 1c

Stage 2: ¹³C NMR

- 2a) Both have 3 peaks/absorptions in their ¹³C NMR
- 2b) **X** has peaks at 20-50 **OR** 190-220ppm
- 2c) Y has peaks at 50-90 OR 90-150ppm

(Ignore peaks at 5-40ppm - present in both)



Q8. B

[1]

Q9.

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		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		
Level 2 3-4 marks	All three stages are covered but the explanations of each stage may be incomplete or may contain	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	deduction Stage 3 Uses spectroscopy to distinguish two compounds. 3a suitable		

	inaccuracies			spectroscopy to distinguish these two compounds (if spectroscopy included)	technique 3b data that will distinguish compounds
Level 1 1-2 marks	Two stages covered but the explanations of each stage may be incomplete or may contain inaccuracies	One stage covered and explanation is generally correct and virtually complete	•	Chemical tests reagents and observations are complete and correct (if awarded level 1 for one chemical 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			

Possible test tube reactions

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

Possible spectroscopic methods for a pair

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*)

[1]

Q10.	
Α	
	[1]
Q11.	
С	

Q12.

This question is marked using Levels of Response. Refer to the Mark Scheme Instructions for Examiners for guidance.

Level 3 (5 – 6 marks)

All stages are covered and each stage is generally correct and virtually complete.

Answer is communicated coherently and shows a logical progression from Stage 1 to Stages 2 and 3 to distinguish all the compounds with results for all remaining compounds stated.

Describing subsequent organic test on product (unnecessary) - limits to lower mark in level

Level 2 (3 – 4 marks)

All stages are covered but stage(s) may be incomplete or may contain inaccuracies

OR two stages are covered and are generally correct and virtually complete. Answer is communicated mainly coherently and shows a logical progression from Stage 1 to Stages 2 and 3.

Describing subsequent organic test on product (unnecessary) - limits to lower mark in level

Level 1 (1 – 2 marks)

Two stages are covered but stage(s) may be incomplete or may contain inaccuracies OR only one stage is covered but is generally correct and virtually complete.

Answer includes isolated statements but these are not presented in a logical order.

Level 0 (0 marks)

Insufficient correct chemistry to gain a mark.

Indicative chemistry content

Stage 1: An initial test to separate into two groups (2 groups of 2 OR 1 group of 3 and 1 group of 1)

Stage 2: A second test to distinguish within a group or to separate into two further groups

Stage 3: A third test leads to a set of results/observations which distinguishes between all 4 compounds

Tests must include reagent and observation which identifies compound(s)

-COOH

- a) NaHCO₃ / Na₂CO₃ (or correct alternative)
- b) effervescence /gas turns limewater milky
- c) K and /or M but not L and/or N

-OH and -CHO

- d) acidified K₂Cr₂O₇
- e) solution turns green
- f) K and/or L and/or N but not M

-CHO

- g) Fehlings OR Tollens
- h) red ppt OR silver mirror
- i) N only but not K and/or L and/or M

-Br

- j) Silver nitrate
- k) cream ppt
- I) L and/or N but not K and/or M

Isolated tests on individual compounds - max LEVEL 2 Isolated tests not linked to any compound – max LEVEL 1 Penalise observation if deduction wrong, but allow observation if deduction incomplete

Alternative tests

-СООН	-СООН	-OH only		
 a) named alcohol & H₂SO₄ b) sweet smell (of ester) c) K and /or M but not L and/or N 	 a) named indicator b) correct colour c) K and /or M but not L and/or N 	 m) named carboxylic acid & H₂SO₄ n) sweet smell (of ester) o) K and/or L but not M and /or N 		

			н н₃с—с—соон он	СН ₃ H ₃ C—С—СН ₂ ОН Br	сн ₃ н ₃ с—с—соон н	СН ₃ H ₃ C—С—СНО Br
	Test	Tests for	к	L	М	N
a)	NaHCO ₃ / Mg / Indicator	КМ	√	×	\checkmark	x
d)	$K_2Cr_2O_7 / H^+$	KLN	\checkmark	\checkmark	X	\checkmark
g)	Fehlings / Tollens	N	×	×	×	✓
j)	AgNO₃ see Note *	LN	×	\checkmark	×	\checkmark
a)	named alcohol &	КM	\checkmark	×	\checkmark	X

H ₂ SO ₄					
m) named carboxylic acid & H ₂ SO ₄	ΚL	\checkmark	\checkmark	X	×

Note * allow NaOH then HNO_3 , $AgNO_3$ as one test; but treat NaOH, $AgNO_3$ without acid as incomplete, so can mark on.

[6]

Q13. C			
			[1]
Q14. A			
			[1]
Q15.			
(a)	Si		
	1×A01	1	
(b)	S	1	
	R	1	
	Q	1	
(c)	(Isomer T)		
	signals due to OH (alcohol) at 3230-3350 <u>and</u> C=O at 1680-1750	1	
	OH and C=O (functional groups) separated in molecule. Allow not a carboxylic acid.		
	(Isomer U)	1	
	(only) signal for OH (alcohol) at 3230–3350	1	
	2 × OH groups present / diol / OH & cyclo(ether) structure.		

	Allow OH but not C=O.	1	
	(Isomer V)		
	signals due to OH (acid) at 2500–3000 (and C=O at 1680–1750)		
	carboxylic acid group / -COOH present.	1 1	
(d)	2:2:2:3:3 Any order.	1	
(e)	(The quartet at δ =3.5 is for a CH ₂ group) next to $-O-CH_2 OR$ shifted significantly downfield by electronegative O	1	
	(is a quartet) because of an adjacent CH_3 group / couple with 3 adjacent protons	1	
	(singlet at δ =2.2 is for a CH ₃ group) attached to $-C - CH_3$ OR shifted downfield by electronegative C=O	1	
	(is a singlet) because there are no adjacent protons / no coupling.	1	
(f)	$CH_{3}-CH_{2}-O-CH_{2}-CH_{2}-CH_{3}$ $Allow 1 mark for:$ $CH_{3}-O-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{3}$	2	[17]
Q16. IR			

Extended response

Absorption at 3360 cm⁻¹ shows OH alcohol present Deduction of correct structure without explanation scores maximum of 4 marks as this does not show a clear, coherent line of reasoning.

M1

1

NMR

There are 4 peaks which indicates 4 different environments of hydrogen Maximum of 6 marks if no structure given OR if coherent logic not displayed in the explanations of how two of OH, CH ₃ and CH ₂ CH ₃ are identified.			
	M2	1	
The integration ratio = 1.6 : 0.4 : 1.2 : 2.4			
The simplest whole number ratio is 4 : 1 : 3 : 6			
The singlet (integ 1) must be caused by H in OH alcohol			
The singlet (integ 3) must be due to a CH_3 group with no adjacent H			
Quartet + triplet suggest CH ₂ CH ₃ group			
Integration 4 and integration 6 indicates two equivalent CH ₂ CH ₃ groups			
CH ₂ CH ₃ H ₃ COH CH ₂ CH ₃			

1 [8]

M8