PEARSON EDEXCEL A-LEVEL CHEMISTRY · 9CH0

CHEMISTRY



MARK SCHEME

TOPIC 7: MODERN ANALYTICAL TECHNIQUES I

SCORE	PERCENTAGE
/170	%

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Give the chemical shift you would expect for this peak.

(1)

.....

(iv) Explain why, in high resolution nmr, the peak due to the hydrogens of the 2-methyl group in 2-hydroxy-2-methylbutanoic acid is a singlet.

(1)

.....

.....

(d) Molecules of 2-hydroxy-2-methylbutanoic acid react together to form a condensation polymer.

Draw a **displayed** formula for this polymer, showing two repeating units.

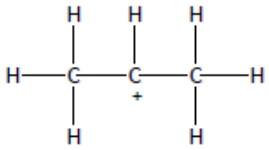
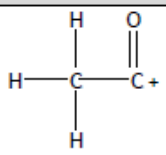
(2)

(Total for question = 18 marks)

Mark Scheme

Q1.

Question Number	Acceptable Answers	Additional Guidance	Mark
(i)	(identify the peak at the) highest/largest *m/z* value	Allow Peak (furthest) to the right/last peak on the spectrum Do not award the mark for "largest peak" / "highest peak" Ignore "parent ion" / molecular ion peak / References to *m/z* = 86	**(1)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(ii)	 (1)  (1)	Allow positive charge anywhere on structure Ignore open bonds Penalise non-displayed formulae once only Ignore brackets around the structure Penalise missing charge once only	(2)

Q2.

Question Number	Answer	Additional guidance	Mark
	spectrum 1 is methylbenzene, because • it contains an absorption at 2962 – 2853 cm^{-1} (1) • owing to alkyl C—H stretching (1)	Identification unqualified gains no marks	2

Q3.

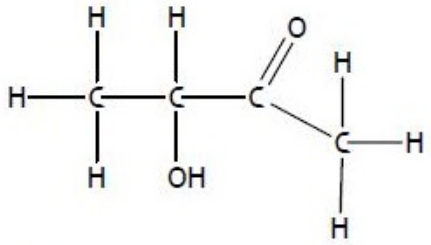
Question Number	Acceptable Answers	Reject	Mark
(a)(i)	C : H : O Mole ratio / mol $\frac{54.5}{12}$: $\frac{9.1}{1}$: $\frac{36.4}{16}$ **(1)** = 4.5417 : 9.1 : 2.275 = 1.996 : 4 : 1 = 2 : 4 : 1 C_2H_4O **(1)** Correct empirical formula of C_2H_4O, with or without working, scores **(2)**		**2**

Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	**First mark:** Any mention of **44** or of doubling C_2H_4O **(1)** **Second mark:** Any mention of **88 in the context of the mass spectrum** eg mentions 'molecular ion' / M^+ / heaviest peak / peak furthest to the right / annotation at 88 on the mass spectrum itself / highest $\frac{m}{z}$ value **(1)**	**88** obtained **just** by adding up the relative atomic masses in $C_4H_8O_2$ scores **(0)** for 2nd scoring point	**2**

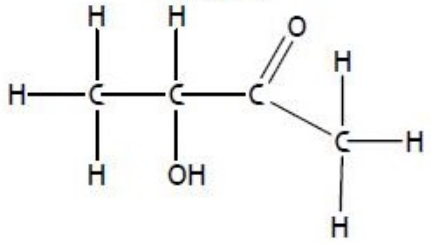
Question Number	Acceptable Answers	Reject	Mark
(b)	(Peak at 3500 cm^{-1}) **O—H** **(1)** Allow OH (Peak at 1700 cm^{-1}) **C=O** **(1)** **Penalise extra extension bond on an otherwise correct answer once only** (eg —O—H **and** —C=O scores (1)) **IGNORE** any names for the bonds suggested even if incorrect	—O—H / —OH C—O / —C=O / CO	**2**

Question Number	Acceptable Answers	Reject	Mark
(c)(i)	**First mark:** (**X** is neutral) so not a (carboxylic) acid **(1)** **IGNORE** "**X** doesn't have a charge as it is neutral" / "**X** is not an alkali" / "**X** is not a base" **Second mark:** (**X** does not react with Tollens') so is **not** an aldehyde / is a ketone **(1)** **Third mark:** (**X** reacts with H^+ / $Cr_2O_7^{2-}$ so) is an alcohol /contains an OH (group) / contains R—OH / contains hydroxyl (group) **(1)** **IGNORE** 'not an acid' if this is deduced **solely** from the H^+ / $Cr_2O_7^{2-}$ information **Fourth mark:** a primary or a secondary (alcohol) **both needed** **OR** (**X** is) not tertiary (alcohol) **(1)** **Mark each point separately** **NOTE:** '**X** is a primary or a secondary alcohol' scores both the third and fourth marks **ALLOW** Correct formulae for the functional groups, instead of their names	**X** is an aldehyde scores **(0)** for this scoring point / **X** is not a ketone scores **(0)** for this scoring point	**4**

Question Number	Acceptable Answers	Reject	Mark
(c)(ii)	(primary or secondary) alcohol **and** ketone **NOTE** **BOTH names** are required here	Just 'hydroxyl for 'alcohol' and/or 'C=O /carbonyl' for ketone/	**1**

Question Number	Acceptable Answers	Reject	Mark
(d)	**MARKING ADVICE** Check answer for the suggested structure of X. If the correct structure is shown  Mark answer according to the following. However if no structure for **X** is shown or an incorrect structure for **X** is proposed, mark answer according to "COMMENTS" scheme below **MARKS CAN BE AWARDED FROM SUITABLY ANNOTATED FORMULAE FOR X.** **<u>First mark:</u>** Four different H / hydrogen / proton environments **(1)** **<u>Any five from following seven points</u>:** **Either** Application of the (n+1) rule to peak **J** (which is a quartet / splits into **four**) **or** application of the (n+1) rule peak **M** (which is a doublet / splits into **two**) **(1)** Any mention to explain **no** splitting for peak **L** as there is no H is attached to the adjacent carbon **(1)**	**Just** 'four different **chemical** environments'	**7**

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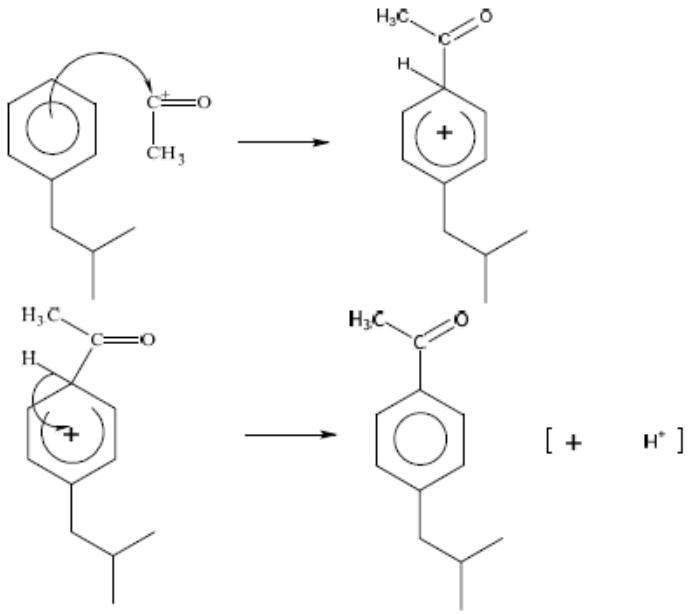
	Peak **L** (CH_3) next to C=O **(1)** Peak **M** (CH_3) next to CH **(1)** Peak **K** O**H** **(1)** Peak **J** (C**H**) next to CH_3 **(1)** Any **one** correct δ value quoted within ± 0.2 of the following chemical shifts: 1.4(**M**) or 2.2 (**L**) or 3.7(**K**) or 4.2 (**J**) (ppm) **(1)** **Final mark** (Compound **X** is) $CH_3CH(OH)COCH_3$ **NO** other compound allowed. **ACCEPT** any unambiguous formula, e.g. displayed formula **Peak J**  **Peak M** **Peak K** **Peak L** **ACCEPT** 3-hydroxybutan-2-one **(1)**	If any incorrect chemical shift **OR A RANGE** of chemical shifts is quoted, this scoring point is not available	

Q4.

Question Number	Acceptable Answers	Reject	Mark
(a)(i)	Overall **yield** higher OR Reduces use of solvents (ALLOW chemicals / reactants) OR Less loss of chemicals OR Less waste products IGNORE References to Energy / fuel / CO_2 References to atom economy More efficient conversion Fewer side products		**1**

Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	Lowers (operating) temperature / energy (requirements) OR Less fuel needed IGNORE References to catalyst properties such as 'lowers E_a', 'can be re-used' Atom economy		**1**

Question Number	Acceptable Answers	Reject	Mark
(b)(i)	$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$ Structural formulae not required Positive charge may be anywhere on the electrophile. IGNORE Curly arrows even if incorrect		**1**

Question Number	Acceptable Answers	Reject	Mark
(b)(ii)	 TE on incorrect electrophile in (b)(i) If benzene used instead of substituted benzene OR If final product is not 1,4 only MP 1 and 2 can be scored Curly arrow from on or within the circle to positively charged carbon		**3**
	ALLOW Curly arrow from anywhere within the hexagon Arrow to **any** part of the electrophile including to the + charge (which can be anywhere on the electrophile) **(1)** Intermediate structure including charge with horseshoe covering at least 3 carbon atoms, **and** facing the tetrahedral carbon **and** with some part of the positive charge within the horseshoe ALLOW dotted horseshoe **(1)** Curly arrow from C—H bond to anywhere in the benzene ring reforming delocalized structure of a stable molecule **(1)** Correct Kekulé structures score full marks Ignore any involvement of $AlCl_4^-$ in the final step	Curly arrow on or outside the hexagon Partial bonds to H and CH_3 unless part of a 3D with a wedge bond	

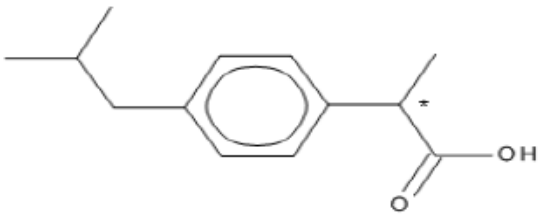
Question Number	Acceptable Answers	Reject	Mark
(b)(iii)	No HCl formed (as a by-product) OR Ethanoic acid easier to recover ALLOW Reverse arguments IGNORE Chlorine containing product References to ozone layer, acid rain, global warming Atom economy	Chlorine	**1**

Question Number	Acceptable Answers	Reject	Mark
(c)(i)	Catalyst (more) easily recovered / separated OR can be filtered OR Facilitates the use of flow (rather than batch) systems IGNORE references to properties of catalysts		**1**

Question Number	Acceptable Answers	Reject	Mark
(c)(ii)	**Reaction 1** (red) phosphorus / P / P_4 and iodine / I_2 ALLOW PI_3 / HI **(1)** **Reaction 3** Hydrochloric acid / HCl(aq) or sulfuric acid / H_2SO_4 (aq) **(1)** **and** reflux / heat **(1)** Award second mark for Acid / H^+ / H_3O^+ **and** reflux OR NaOH(aq) / KOH(aq) **(1)** (reflux) **then** acidify with HCl(aq) or H_2SO_4 (aq) **(1)** IGNORE Omission of states throughout	NaI + H_2SO_4 PI_5 Just H^+ / H_3O^+ reflux / heat without acid or with warm or <50°C	

Question Number	Acceptable Answers	Reject	Mark
(c)(iii)	C=O / carbonyl group (only) in carboxylic acid / ibuprofen **(1)** Absorption / peak at 1725 - 1700 (cm^{-1}) **(1)** If no other mark has been awarded, then ALLOW (for 1 mark) OH in both but in alcohol 3750 - 3200 (cm^{-1}) but in carboxylic acids 3300 to 2500 (cm^{-1})	ketone 1700 - 1680 (cm^{-1}) Single values rather than ranges	**2**

Question Number	Acceptable Answers	Reject	Mark
(d)(i)	(A chiral molecule is) non-superimposable on its mirror image. ALLOW Asymmetric (tetrahedral) carbon atom / has a carbon atom bonded to **four** different groups / atoms IGNORE Has two enantiomers Functional (as in functional groups) Reference to rotation of plane polarized light	molecules / species (for groups)	**1**

Question Number	Acceptable Answers	Reject	Mark
(d)(ii)	 ALLOW any clear indication of chiral carbon		**1**

Question Number	Acceptable Answers	Reject	Mark
(d)(iii)	(A racemic mixture is) an equimolar mixture of the two enantiomers / (optical) isomers ALLOW (for equimolar mixture) equal amounts / concentrations / volumes / proportions OR 50:50 mixture	Just 'no effect on plane polarised light'	**1**

Q5.

Question Number	Correct Answer	Reject	Mark
(a)	B		**1**

Question Number	Correct Answer	Reject	Mark
(b)	C		**1**

Question Number	Correct Answer	Reject	Mark
(c)	C		**1**

Question Number	Correct Answer	Reject	Mark
(d)	B		**1**

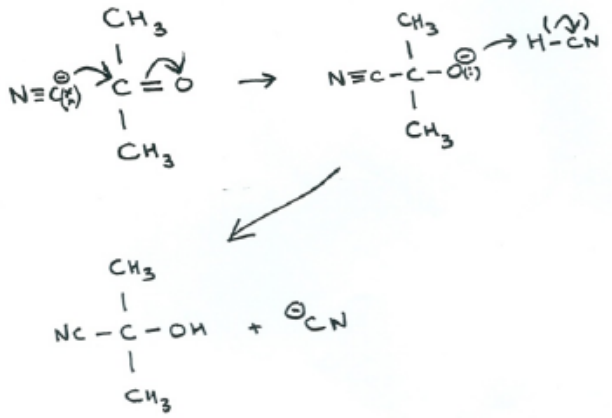
Q6.

Question Number	Correct Answer	Reject	Mark
	B		**1**

Q7.

Question Number	Correct Answer	Reject	Mark
(a)(i)	Sodium/potassium dichromate ((VI)) **and** (Dilute/concentrated) sulfuric acid OR correct formulae / H^+ **and** $Cr_2O_7^{2-}$ ALLOW H^+ **and** $Cr_2O_7^{2-}$/acidified dichromate((VI)) **(1)** Reflux/distil Ignore 'heat', 'warm', and 'boil' alone. ALLOW Just 'under reflux' Just 'under distillation' **(1)** Second mark depends on mention of dichromate/$Cr_2O_7^{2-}$ in first part OR $KMnO_4$ and acid with heat **(1)**	Hydrochloric acid	2

Question Number	Correct Answer	Reject	Mark
(a)(ii)	Carbonyl group – addition of 2,4-dinitrophenylhydrazine / 2,4-DNP(H) / Brady's reagent **(1)** to give yellow/orange/red precipitate/ppt/ppte/solid/crystals ALLOW recognisable spelling e.g., percepitate **(1)** $CH_3C{=}O$ reaction with iodine in alkali/NaOH/KOH/OH^- ALLOW Iodoform/tri-iodomethane/haloform AND reaction/test **(1)** to form (pale) yellow / cloudy precipitate/solid/crystals **(1)** Ignore references to smell Ignore heat in either part	2-DNP/4DNP Just DNP Brick red ppt	4
	Note • In both cases result mark depends on test being recognisably correct even if it did not score a mark Examples: DNP gives yellow ppt Iodine test gives yellow ppt Tests for aldehydes with correct results, no marks		

Question Number	Correct Answer	Reject	Mark
(b)(i)			3
	Arrow (from carbon) of CN^- to carbon of C=O	CN without negative charge	
	AND		
	Arrow from part of C=O double bond to oxygen		
	ALLOW		
	Two steps via a charged canonical form **(1)**		
	Intermediate anion with C-CN bond. **(1)**		
	Arrow from resulting O^- to hydrogen of $HCN/H^+/H_2O$ **(1)**		
	Note	…C-NC bond	
	Arrow directions must be correct to score each mark		
	Penalise half-headed arrows each time in both parts		
	ALLOW skeletal formulae.		

Question Number	Correct Answer	Reject	Mark
(c)(i)	(Acid) hydrolysis OR Alkaline hydrolysis followed by acidification	Hydration	1

Question Number	Correct Answer	Reject	Mark
(b)(ii)	At low pH very few CN^- ions ALLOW No CN^- ions OR No KCN/ only HCN present **(1)** At high pH very few H^+ / HCN ALLOW No H^+ / HCN OR Hydroxide reacts with H^+ / HCN/ acid **(1)**		1

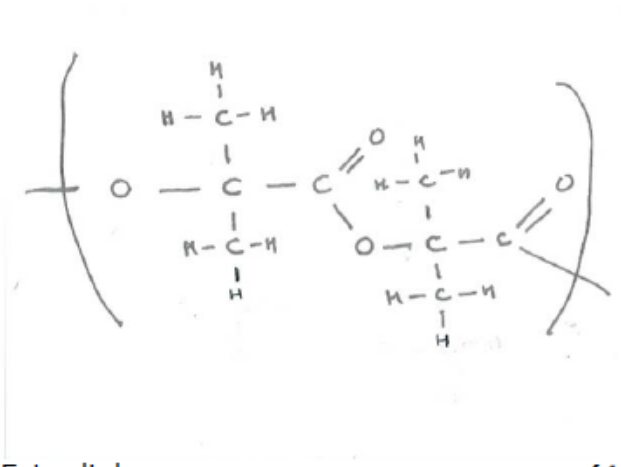
Question Number	Correct Answer	Reject	Mark
(c)(ii)	The O-H absorptions for alcohol and carboxylic acid overlap. OR OH absorption for an acid is very broad OR Quote data booklet values which must show some overlap, to include 3300 to 3200. ALLOW OH absorptions similar/the same.	Just 'both have OH groups' Just 'two OH groups present'	1

Question Number	Correct Answer	Reject	Mark
(c)(iii)	(Chemical shift □) 2.0 - 4.0 (ppm) / any value within this range e.g 3.1/ 3.12/3 ALLOW Correct number followed by□□, eg 3δ		1

Question Number	Correct Answer	Reject	Mark
(c)(iv)	3 (peaks) / three		1

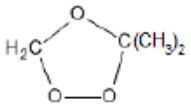
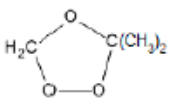
Question Number	Correct Answer	Reject	Mark
(c)(v)	There is no hydrogen atom/proton on the adjacent/neighbouring carbon atom ALLOW No adjacent/neighbouring hydrogens/protons		1

Question Number	Correct Answer	Reject	Mark
(c)(vi)	(No) 2-hydroxy-2-methylpropanoic acid does not have a chiral centre OR It is not chiral OR It does not have a mirror image which is non-superimposable OR Does not have a carbon atom attached to four different groups	Yes...	1

Question Number	Correct Answer	Reject	Mark
(d)(i)	 Ester linkage **(1)** Rest of molecule **(1)** ALLOW Attached chains as structural formulae Ignore n or other numbers outside bracket **COMMENT** Check formulae carefully – different carbon frameworks appear.		1

Question Number	Correct Answer	Reject	Mark
(d)(ii)	Ester		1

Q8.

Question Number	Acceptable Answer	Additional Guidance	Mark
	An answer that makes reference to the following points: • **K** is HCHO/methanal because it is the (only) carbonyl with M_r 30 (1) • the M_r of **L** is 58 so it could be CH_3COCH_3/propanone or CH_3CH_2CHO/propanal **or** • a carbonyl compound with 3 carbon atoms (1) • 2 peaks on the ^{13}C NMR spectrum show 2 different carbon environments so it must be propanone (as propanal would have 3 different carbon environments (1)		**5**
	• **J** is methylpropene/$CH_2=C(CH_3)_2$ /  (1) • $CH_2=C(CH_3)_2 + O_3 \rightarrow$   + $H_2O \rightarrow$ HCHO + $O=C(CH_3)_2$ + H_2O_2 **both** equations correct (1)		

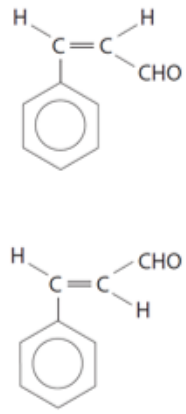
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Q9.

Question Number	Answer	Additional Guidance	Mark
(i)	An answer that makes reference to: • (potassium ions) lilac **and** (strontium ions) crimson / red	Allow scarlet Ignore 'shades' except Do not award 'brick red' / 'orange-red'	(1)

Question Number	Answer	Additional Guidance	Mark
(ii)	An answer that makes reference to: • the crimson/red colour will mask/hide/obscure the (lighter) lilac colour	Allow 'one colour will hide the other' Allow only one colour seen Allow difficult to distinguish the two colours Allow TE from colours in (i) Do not award colour from chloride ions Do not award idea of new colour resulting from both Ignore reference to impurities	(1)

Q10.

Question Number	Answer	Additional guidance	Mark
(b)(i)	• contains C=C/alkene		1
(b)(ii)	• contains carbonyl group/ aldehyde or ketone	C=O alone	1
(b)(iii)	• aldehyde/ -CHO		1
(c)(i)	• 77 $C_6H_5^+$ (1) • 103 $C_8H_7^+$ (1)	Must show a charge but only penalise omission once Allow structural, displayed or skeletal formulae	2
(c)(ii)	 	Allow non-displayed benzene C-Hs	2
(c)(iii)	• The peak is due to the presence of an atom of a (^{13}C) isotope	Allow reference to other named isotope of H or O	1

Q11.

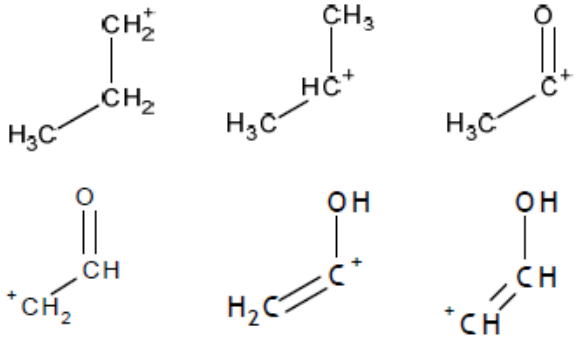
Question Number	Acceptable Answers	Reject	Mark
(a)(i)	So that only the water formed in the combustion is absorbed by X / measured. ALLOW 'reacts with X' for 'absorbed by X' OR Otherwise the mass / amount of the water measured will be too high	Reacts with A References to Y	**1**

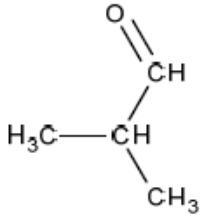
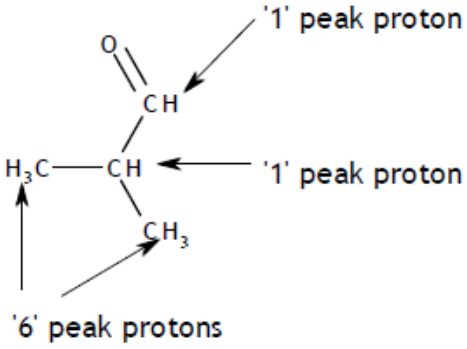
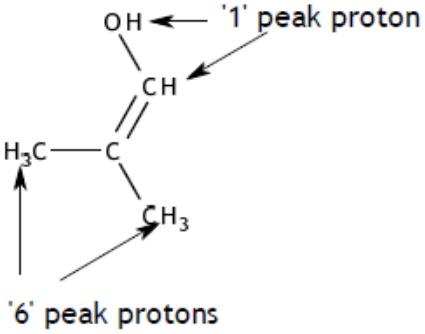
Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	(Anhydrous) Calcium chloride / $CaCl_2$ / Magnesium sulphate / $MgSO_4$ / silica gel / sodium sulphate / Na_2SO_4 ALLOW Phosphorus(V) oxide / phosphorus pentoxide / P_4O_{10} / P_2O_5 / Silica beads	Sulfuric acid Calcium oxide Silica / SiO_2 anhydrous copper(II) sulfate	**1**

Question Number	Acceptable Answers	Reject	Mark
(a)(iii)	Soda lime OR calcium hydroxide / $Ca(OH)_2$ **and** sodium hydroxide / NaOH ALLOW sodium hydroxide / NaOH / potassium hydroxide / KOH / Calcium oxide / CaO	Limewater	**1**

Question Number	Acceptable Answers	Reject	Mark
(a)(iv)	The methods below illustrate the allocation of marks. But the first four marks may be scored by any correct method. **Method 1** mol CO_2 = 8.8/44 = 0.2 (= mol C) **(1)** mol H_2O = 3.6/18 = 0.2 mol H = 2 x mol H_2O = 0.4 **(1)** mass O = 3.6 – (12 x 0.2 + 1 x 0.4) = 0.8 (g) **(1)** mol O = 0.8/16 = 0.05 **(1)** **Method 2** Mass H = 3.60 x 2/18 = 0.40 (g) = 0.40 / 1 = 0.40 (mol) **(1)** Mass C = 8.80 x 12/44 = 2.4 (g) = 2.4 / 12 = 0.20 (mol) **(1)** Mass O = 3.60 – (0.40 + 2.4) = 0.80(g) **(1)** = 0.80 / 16 = 0.05 (mol) **(1)**		**5**
	Empirical formula = C_4H_8O **(1)** TE on incorrect moles but the ratio **must** be whole number IGNORE use of O_2 for O in the 'words' Correct empirical formula with some working at each stage scores full marks **but** Correct empirical formula with **no** working or **unclear and non-scoring** working scores final mark only		

Question Number	Acceptable Answers	Reject	Mark
(b)(i)	(Molecular ion is m/e =) 72 (= M_r of **A**)**(1)** Molecular formula = C_4H_8O **(1)** No TE on incorrect molecular ion	Structural Or Displayed Or Molecular ion	**2**

Question Number	Acceptable Answers	Reject	Mark
(b)(ii)	Any three of (1 mark for each structure)  ALLOW structural formulae (eg CH_3CO^+) IGNORE Position of positive charge Penalise omission of charge or negative charge once $C_3H_7^+$ and /or $C_2H_3O^+$ scores 1 if no scoring structure		**3**

Question Number	Acceptable Answers		Reject	Mark
***(c)**	Structure of **A** (1)  Three (proton/H) environments (1) **Identify** the 6 protons in one environment and 1 each in the other two (1) No TE on incorrect structures except propan-2-ol : scores MP3 only	OR diagram (1)  6 proton label (1) **both** 1 proton labels (1) ALLOW enol structure  6 proton label (1) **both** 1 proton labels (1)		**3**

Q12.

Question Number	Answer	Additional Guidance	Mark
	• absorbance for **A** (1) • absorbance for **B** (1) • absorbance for **C** (1)	Example of table Absorbance: Absorbance expected in infrared spectrum of **A** but **not** in **B** or **C** — Wavenumber range / cm^{-1}: 1720 – 1700; Allow 1725 - 1700 Absorbance: Absorbance expected in infrared spectrum of **B** but not in **A** or **C** — Wavenumber range / cm^{-1}: 1669 – 1645 Absorbance: Absorbance expected in infrared spectrum of **C** but not in **A** or **B** — Wavenumber range / cm^{-1}: 1740 – 1725; Allow 1740 - 1720 Allow values in reverse order e.g. 1700 – 1720 for **A** If single values are given instead of a range award (2) for 3 correct values within the ranges and (1) for 2 correct values Do not award a single value that occurs in two ranges i.e 1720-1725 If no other mark is awarded, allow (1) for: **A** 3300-2500 **and C** 2900-2820 / 2775-2700	(3)

Q13.

Question Number	Answer	Additional Guidance	Mark
(i)	• (The cation in **X** is) Fe^{2+} / iron(II) / Fe(II) (1) • (The anion in **X** is) SO_4^{2-} / sulfate(VI) (1)	Allow Fe^{+2} Allow sulfate / SO_4^{-2} Do not award sulfite / sulfate(IV)	(2)

Question Number	Answer	Additional Guidance	Mark
(ii)	• species and balancing (1) • state symbols (1)	Examples of equation $Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$ **or** $[Fe(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s) + 6H_2O(l)$ **or** $[Fe(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(H_2O)_4(s) + 2H_2O(l)$ Ignore missing square brackets TE on cation that forms an insoluble hydroxide in **Test 1** State symbols conditional on correct species or 'near miss' / non-ionic equation	(2)

Question Number	Answer	Additional Guidance	Mark
(iii)	An answer that makes reference to the following point: • Fe^{2+} is oxidised (to Fe^{3+}) by oxygen / air	Allow iron(III) hydroxide / iron(III) (ions) are formed by reaction with oxygen / air TE on cation in **Test 1** Allow just 'the precipitate / it is oxidised by oxygen / air'	(1)

Question Number	Answer	Additional Guidance	Mark
(iv)	An answer that makes reference to the following point: • to react with / remove any carbonate / sulfite / sulfate(IV) ions **or** to eliminate the possibility of carbonate / sulfite / sulfate(IV) ions	Allow to prevent any other ions forming a precipitate with barium ions / Ba^{2+}	(1)

Q14.

Question Number	Acceptable Answers	Additional Guidance	Mark
	• molecular ion is at $m/z = 168$ **or** 168 is equal to the M_r of **D** / twice the empirical formula / 2 x 84 / 168 ÷ 2 = 84 / M_r of empirical formula is 84 **(1)** • (so the molecular formula is) $C_6H_4N_2O_4$ **(1)**	Allow 168 shown on spectrum along with the rest of the explanation Do not award M1 for any other value Stand alone mark Ignore structural / displayed / skeletal formula Do not award $C_6H_4N_2O_4^+$	**(2)**

Q15.

Question Number	Acceptable Answers	Additional Guidance	Mark
(i)	**Test 1** • (gas is) ammonia / NH_3 **(1)** • (cation is) ammonium / NH_4^+ **(1)** **Test 2** • (cation is) cobalt(II) / Co^{2+} / $[Co(H_2O)_6]^{2+}$ **(1)** • (complex ion is) $[CoCl_4]^{2-}$ **(1)** **Test 3** • (precipitate is) barium sulfate / $BaSO_4$ **(1)** • (anion is) sulfate((VI)) / SO_4^{2-} **(1)**	If name and formula are given, both must be correct Mark independently Do not award gas is ammonium / NH_4 Do not award cation is ammonia / NH_3^+ Oxidation number of cobalt is needed in the name but allow cobalt **with** Co^{2+} Charge is needed on the ion Allow +2 and −2 for the charges on the ions Allow brackets around Cl Ignore missing square brackets in complex ions Do not award $[CoCl_6]^{4-}$ **Note** If cation in Test 2 is identified as copper(II) / Cu^{2+}, do not award M3 but M4 can be awarded as TE for $[CuCl_4]^{2-}$ Oxidation number of sulfate is not needed but if given must be correct e.g. do not award sulfate(IV)	**(6)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(ii)	• correct formula	Examples of correct formula $(NH_4)_2Co(SO_4)_2$ $(NH_4)_2SO_4.CoSO_4$ Allow NH_4, Co and SO_4 in any order Allow multiples Allow any combination of Co^{2+} / NH_4^+ / SO_4^{2-} that gives a neutral complex TE on the **three** ions identified in (a)(i) Ignore missing dot in second formula Ignore any amount of water of crystallisation	**(1)**

Q16.

(a)	B		**1**

Question Number	Correct Answer	Reject	Mark
(b)	C		**1**

Question Number	Correct Answer	Reject	Mark
(c)	D		**1**

Question Number	Correct Answer	Reject	Mark
(d)	A		**1**

Q17.

Question Number	Answer	Additional Guidance	Mark
	An answer that makes reference to: • addition of (dilute/strong) name/formula of acid **(1)** • effervescence/bubbling/fizzing **(1)**	 Allow weak acids If formula given then must be correct Allow Gas given off which turns limewater cloudy Do not award just 'gas/ CO_2 given off' Do not award incorrect observations such as precipitate forming due to addition of acid M2 dependent on M1 or 'near miss'	**(2)**

Q18.

Question Number	Answer	Additional Guidance	Mark
	An answer that makes reference to: • addition of barium chloride/nitrate (solution) **(1)** • white precipitate forms **(1)**	 Accept formulae $BaCl_2$/$Ba(NO_3)_2$ Ignore addition of acids such as HCl or HNO_3 but do not award M1 if addition of sulfuric acid Allow white solid If ppt identified then must be correct M2 dependent on M1 or 'near miss'	**(2)**

Q19.

Question Number	Correct Answer	Reject	Mark
(a)	B		1

Question number	Correct Answer	Rejecct	Mark
(b)	D		1

Question Number	Correct Answer	Reject	Mark
(c)	D		1

Question Number	Correct Answer	Reject	Mark
(d)	A		1

Q20.

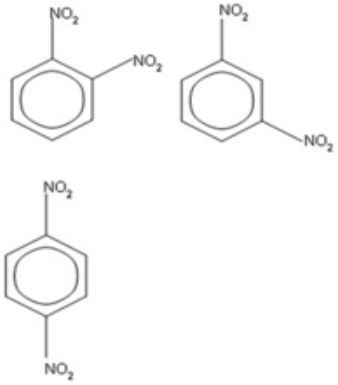
Question Number	Answer	Additional Guidance	Mark
(i)	• (The cation in **Y** is) Cu^{2+} / copper(II) **(1)** • (The anion in **Y** is) Cl^- / chloride **(1)**	Allow Cu^{+2} Ignore water ligands Do not award just copper / Cu Do not award just 'chlorine' / Cl	**(2)**

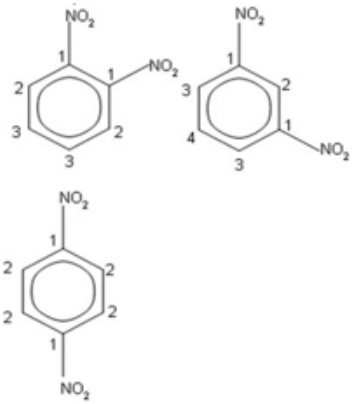
Question Number	Answer	Additional Guidance	Mark
(ii)	• $[Cu(NH_3)_4(H_2O)_2]^{2+}$	Allow $[Cu(NH_3)_4]^{2+}$ Allow $[Co(NH_3)_6]^{2+}$ if Co^{2+} in (i) Ignore missing square brackets	**(1)**

Question Number	Answer	Additional Guidance	Mark
(iii)	A description that makes reference to the following points: • add dilute (aqueous) ammonia (and stir the mixture) (1) • the precipitate dissolves (1)	If Cl^- / chloride / chlorine ion: Allow add aqueous ammonia / $NH_3(aq)$ Do not award concentrated ammonia Conditional on use of ammonia Ignore colourless solution If Br^- / bromide / bromine ion identified in Test 4: precipitate is insoluble in dilute ammonia (1) but soluble in concentrated ammonia (1) If I^- / iodide / iodine ion identified in test 4: precipitate is insoluble (1) in dilute and concentrated ammonia (1) Do not award addition of concentrated sulfuric acid	(2)

Q21.

Question Number	Acceptable Answers	Additional Guidance	Mark
(i)	$C_6H_4^{+}$	Allow $H_4C_6^{+}$ Do not award just C_6H_4	(1)

Question Number	Acceptable Answers	Additional Guidance	Mark
(ii)	• 3 correct formulae **(2)**	Examples of formulae  Allow (1) for any 2 correct formulae Allow (2) for three disubstituted benzenes with incorrect substituents / (1) for any two disubstituted benzenes with incorrect substituents Allow incorrectly displayed formulae of NO_2 groups **In (c)(ii) and (iii):** Allow Kekule structures Allow hydrogen atoms shown on benzene Ignore connectivity of NO_2 groups Penalise missing circle in benzene once only	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(iii)	• **D** identified as 1,3-dinitrobenzene **and** 4 different carbon environments labelled **(1)** • 3 different carbon environments labelled on 1,2-dinitrobenzene **(1)** • 2 different carbon environments labelled on 1,4-dinitrobenzene **(1)**	 <u>Examples of identification</u> These labels may be shown on the structures in (c)(ii) The identification of **D** can be assumed if it is the only structure with 4 carbon environments labelled Allow any form of identification of the carbon environments e.g. numbers, letters, equivalent carbon environments circled TE on disubstituted benzene substituents in (ii) Penalise only half the carbon environments labelled once only	**(3)**

Q22.

Question Number	Answer	Additional guidance	Mark
(i)	• brown fumes (1) • a green/blue solution forming (1)		2
(ii)	• $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$	State symbols must be present	1
(iii)	• amount of thiosulfate (1) • uses amount of thiosulfate = amount of iodine to determine amount of thiosulfate = amount of copper(II) ions in 25 cm^3 portion (1) • evaluation of number of moles of Cu in sample (1) • calculates mass of Cu (1) • percentage copper to **3.s.f** (1)	Example of calculation amount of thiosulfate = $\frac{22.7 \times 0.25}{1000}$ = 5.675×10^{-3} (mol) 5.675×10^{-3} (mol) = amount of copper(II) ions in 25 cm^3 portion amount of Cu in sample = $5.675 \times 10^{-3} \times 10$ = 5.675×10^{-2} (mol) mass of Cu = $5.675 \times 10^{-2} \times 63.5$ = 3.603625 percentage copper = 3.603625 x 100 /5.00 = 72.0725 = 72.1% Allow ecf from 2nd mark Correct answer to 3.s.f with no working scores 5 marks	5
(iv)	• calculation of percentage uncertainty from balance = ±0.005x 2 x100/5.00 = 0.2% and percentage uncertainty in mean titre from burette = 2x±0.05 x 100 /22.7 = 0.44% (1) • so burette reading is most significant (1)		2

Q23.

Question Number	Answer	Additional Guidance	Mark
(i)	An answer that makes reference to • **(M1)** (similarity) all have arene C–H absorptions Either 3030 (cm^{-1}) **or** 750 and/or 700 (cm^{-1}) **(1)** • **(M2)** only phenol and phenylmethanol have O–H 3750 - 3200 (cm^{-1}) **(1)** • **(M3)** only benzoic acid has O–H 3300 - 2500 (cm^{-1}) **(1)** • **(M4)** only benzoic acid has C=O 1700 - 1680 (cm^{-1}) **(1)** • **(M5)** only phenylmethanol has alkane C–H absorptions either 2962 - 2853 (cm^{-1}) or 1485 - 1365 (cm^{-1}) **(1)**	Bond and wavenumber ranges necessary for each mark Do not award 880/830/780 (cm^{-1}) Do not award –OH / C–OH by penalising once only in M2 and M3 All 5 correct bonds with no wavenumber ranges scores (3) 4 correct etc scores (2) and 3 correct etc scores (1) All 5 correct wavenumber ranges with no bonds or incorrect bonds scores (3) 4 correct etc scores (2) and 3 correct etc scores (1) Penalise any additional peaks once only Ignore references to different fingerprint regions	**(5)**

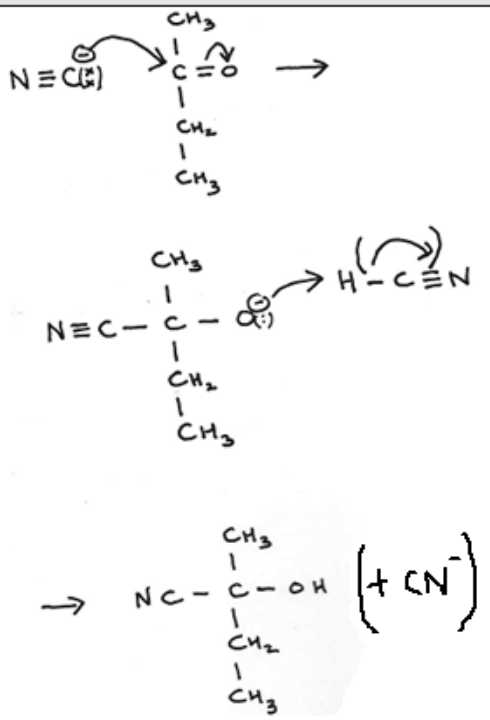
Question Number	Answer	Additional Guidance	Mark
(ii)	An answer that makes reference to • five peaks (in the ^{13}C NMR spectrum) **(1)** • (four) aromatic peaks within the chemical shift range of 165 - 105 (ppm) **(1)** • (one) peak (for the C-OH) within the chemical shift range of 75 - 55 (ppm) **(1)**	Allow any range within the stated ranges Penalise single values as opposed to ranges once only Accept annotations on diagram Penalise additional peaks once only when three or more types of peak are stated	**(3)**

Question Number	Answer	Additional Guidance	Mark
(iii)	An answer that makes reference to • suitable formula of fragment ion **(1)** • matching *m*/*z* value **(1)**	Example of a suitable formula $C_6H_5COO^+$ or $C_6H_5CO^+$ Do not award $C_7H_5O_2^+$ or $C_7H_5O^+$ *m*/*z* = 121 or 105 Allow $COOH^+$ (1) Do not award bond to the fragment, e.g. –$COOH^+$ *m*/*z* = 45 (1) No TE on incorrect fragment ions such as CH_3^+	**(2)**

Q24.

Question Number	Correct Answer	Reject	Mark
(a)(i)	Sodium/potassium dichromate ((VI)) **and** (Dilute/concentrated) sulfuric acid OR correct formulae / H^+ **and** $Cr_2O_7^{2-}$ ALLOW H^+ **and** $Cr_2O_7^{2-}$/acidified dichromate((VI)) **(1)** Reflux/distil Ignore 'heat', 'warm', and 'boil' alone. ALLOW Just 'under reflux' Just 'under distillation' **(1)** Second mark depends on mention of dichromate/$Cr_2O_7^{2-}$ in first part OR $KMnO_4$ and acid with heat **(1)**	Hydrochloric acid	**2**

Question Number	Correct Answer	Reject	Mark
(a)(ii)	Carbonyl group – addition of 2,4-dinitrophenylhydrazine / 2,4-DNP(H) / Brady's reagent **(1)** to give yellow/orange/red precipitate/ppt/ppte/solid/crystals ALLOW recognisable spelling e.g., percepitate **(1)** $CH_3C{=}O$ reaction with iodine in alkali/NaOH/KOH/OH^- ALLOW Iodoform/tri-iodomethane/haloform AND reaction/test **(1)** to form (pale) yellow / cloudy precipitate/solid/crystals **(1)**	2-DNP/4DNP Just DNP Brick red ppt	**4**
	Ignore references to smell Ignore heat in either part **Note** • In both cases result mark depends on test being recognisably correct even if it did not score a mark Examples: DNP gives yellow ppt Iodine test gives yellow ppt • Tests for aldehydes with correct results, no marks		

Question Number	Correct Answer	Reject	Mark
(b)(i)	 Arrow (from carbon) of CN^- to carbon of C=O AND Arrow from part of C=O double bond to oxygen ALLOW	CN without negative charge	**3**
	Two steps via a charged canonical form **(1)** Intermediate anion with C-CN bond. **(1)** Arrow from resulting O^- to hydrogen of $HCN/H^+/H_2O$ **(1)** **Note** Arrow directions must be correct to score each mark Penalise half-headed arrows each time in both parts ALLOW skeletal formulae.	...C-NC bond	

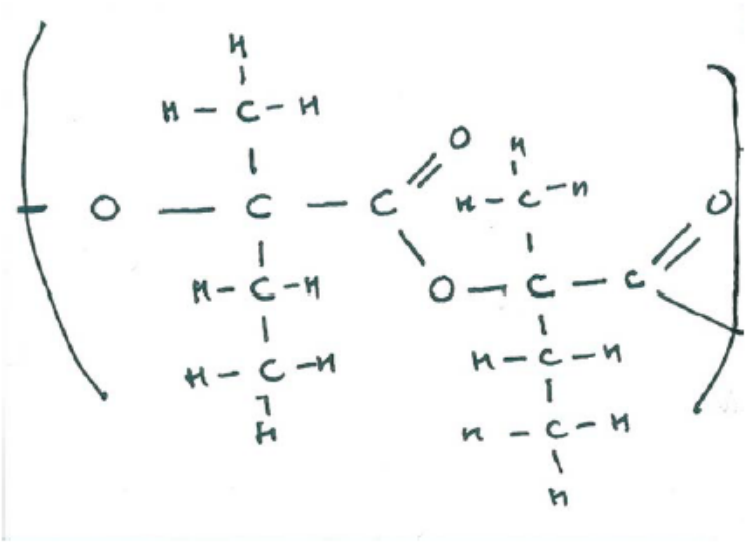
Question Number	Correct Answer	Reject	Mark
(b)(ii)	Forms a racemic mixture **(1)** Because bonds around C=O are planar OR Carbonyl group/reaction site is (trigonal) planar OR Bonds around carbonyl carbon are planar **(1)** Cyanide can attack from either side / above or below **(1)**	Butanone/molecule/it is planar C=O is planar Carbonyl bond is planar Intermediate is planar	**3**

Question Number	Correct Answer	Reject	Mark
(c)(i)	(Acid) hydrolysis OR Alkaline hydrolysis followed by acidification	Hydration	**1**

Question Number	Correct Answer	Reject	Mark
(c)(ii)	The O-H absorptions for alcohol and carboxylic acid overlap. OR OH absorption for an acid is very broad OR Quote data booklet values which must show some overlap, to include 3300 to 3200. ALLOW OH absorptions similar/the same.	Just 'both have OH groups' Just 'two OH groups present'	**1**

Question Number	Correct Answer	Reject	Mark
(c)(iii)	(Chemical shift δ) 2.0 - 4.0 (ppm) / any value within this range ALLOW Correct number followed by δ, eg 3δ		**1**

Question Number	Correct Answer	Reject	Mark
(c)(iv)	There is no hydrogen atom/proton on the adjacent/neighbouring carbon atom ALLOW No adjacent/neighbouring hydrogens/protons		**1**

Question Number	Correct Answer	Reject	Mark
(d)	 Ester linkage **(1)** Rest of molecule **(1)** ALLOW Attached chains as structural formulae Ignore n or other numbers outside bracket		**2**