



GCE

Chemistry A

Advanced GCE

Unit **F324**: Rings, Polymers and Analysis

Mark Scheme for January 2013

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All examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes should be read in conjunction with the published question papers and the report on the examination.

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








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Annotations

Annotation	Meaning
	Benefit of doubt given
	Contradiction
	Incorrect response
	Error carried forward
	Ignore
	Not answered question
	Benefit of doubt not given
	Power of 10 error
	Omission mark
	Rounding error
	Error in number of significant figures
	Correct response

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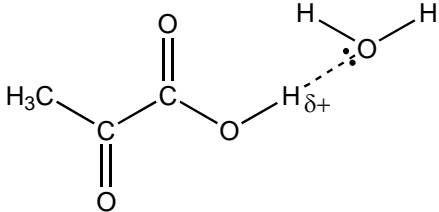
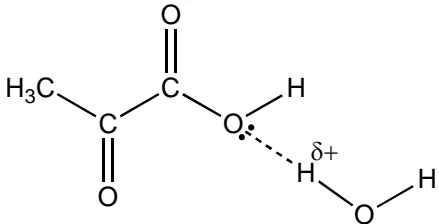
Subject-specific Marking Instructions

Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
()	Words which are not essential to gain credit
—	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

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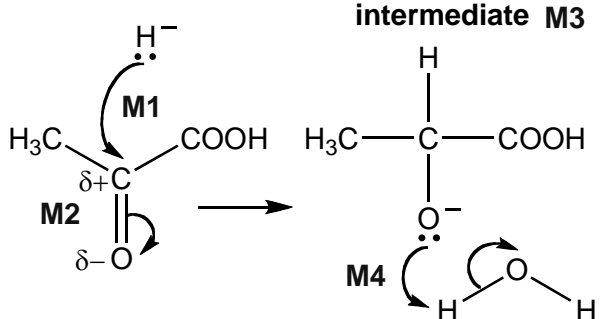
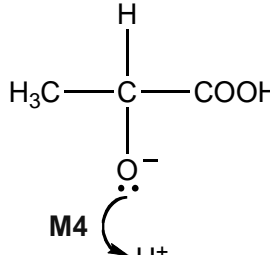
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Question	Answer	Marks	Guidance
1 (a)	<p>M1 EITHER in words: (pyruvic acid forms) hydrogen bonds with water</p> <p>OR correctly labelled diagram showing hydrogen bond between pyruvic acid and water ✓</p> <p>M2 diagram showing dashed/dotted line between H^{δ+} in COOH and lone pair of electrons on O in H₂O</p>  <p>OR</p> <p>diagram showing dashed/dotted line between H^{δ+} in H₂O and lone pair of electrons on O of OH in COOH ✓</p> 	2	<p>FOR M1 only: if use diagram ALLOW a labelled hydrogen bond to O in C=O</p> <p>FOR M2 only: IGNORE a hydrogen bond to C=O, <i>i.e.</i> C=O - - - H-O IGNORE bond angles</p> <p>Diagram does not need to show all of pyruvic acid (IGNORE if wrong so allow ethanoic acid) but must have minimum of COOH</p> <p>MIMIMUM requirement is a H^{δ+} (on acid or water) and a lone pair on O (in acid or water) involved in a hydrogen bond <i>ie</i> IGNORE δ-</p>
(b)	<p>$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH} + 3[\text{O}] \rightarrow \text{CH}_3\text{COCOOH} + 2\text{H}_2\text{O}$</p> <p>four correct formulae ✓</p> <p>balanced ✓</p>	2	<p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous (IGNORE lack of brackets round 2° alcohol)</p> <p>DO NOT ALLOW molecular formulae IF propane-1,3-diol used score 0</p>

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Question	Answer	Marks	Guidance
1 (c)	<p style="text-align: center;">intermediate M3</p>  <p>M1: 1 mark for curly arrow from H⁻ to C of C=O ✓</p> <p>M2: 1 mark for correct dipoles on C=O AND curly arrow from double bond to O^{δ-} ✓</p> <p>M3: 1 mark for correct intermediate with - charge on O ✓</p> <p>M4: 1 mark for curly arrow from O⁻ of intermediate to H in H₂O AND curly arrow from the O—H bond to the O in H₂O:</p> <p>Do not need to show formation of OH⁻</p>	4	<p>Curly arrow MUST start from - sign OR lone pair on H⁻ Lone pair does not need to be shown on H⁻</p> <p>Lone pair does not need to be shown on O⁻</p> <p>Curly arrow MUST start from - sign OR from lone pair on O⁻ of intermediate Lone pair does not need to be shown on O⁻</p> <p>For M4, ALLOW mark for curly arrow from O⁻ of intermediate to H⁺</p> 

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Question		Answer	Marks	Guidance
1	(d)	<p>Either:</p> <p>Use Tollens' reagent AND correct reference to compound A being oxidised or Tollen's reagent acts as oxidising agent ✓</p> <p><i>Observation:</i> silver mirror/precipitate/ppt/solid ✓</p> <p>or:</p> <p>Use $K_2Cr_2O_7$ AND H_2SO_4 AND correct reference to compound A being oxidised or $K_2Cr_2O_7$ acts as oxidising agent ✓</p> <p><i>Observation:</i> turns (dark) green OR blue ✓</p> <p> QWC oxidised/oxidized/oxidation/redox etc. must be spelled correctly at least ONCE (i.e. NOT oxidisation, oxidated) to score 1st mark UNLESS 2,4-DNP(H)/Brady's reagent is used, when condensation/addition–elimination must be spelled correctly at least ONCE</p>	3	<p>ALLOW $AgNO_3$ in ammonia OR ammoniacal $AgNO_3$</p> <p>ALLOW redox reaction</p> <p>ALLOW black ppt OR grey ppt</p> <p>ALLOW $Na_2Cr_2O_7$ OR $Cr_2O_7^{2-}$ for $K_2Cr_2O_7$ If formulae used, formulae must be correct ALLOW acidified dichromate If name given, ALLOW dichromate OR dichromate(VI) IGNORE reference to dilute/conc ALLOW H^+</p> <p>ALLOW $KMnO_4$ and H_2SO_4 / acidified manganate(VII)/permanganate / alkaline manganate(VII) AND correct reference to compound A being oxidised or $KMnO_4$ acts as oxidising agent <i>Observation:</i> decolourised</p> <p>ALLOW Benedict's or Fehling's reagent/solution AND correct reference to compound A being oxidised or Benedict's or Fehling's acts as oxidising agent <i>Observation:</i> (brick) red ppt</p> <p>ALLOW 2,4-DNP(H)/Brady's reagent AND measure melting point of derivative AND state it is a condensation reaction/addition-elimination reaction <i>Observation:</i> orange/yellow/red precipitate</p> <p>ALLOW solid OR crystals OR ppt as alternatives for precipitate</p>

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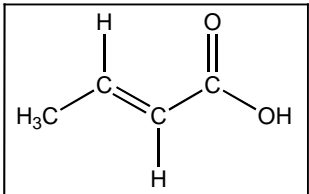
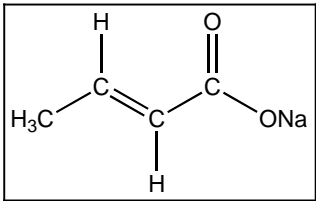
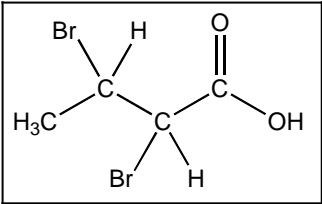
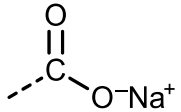
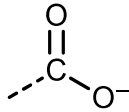
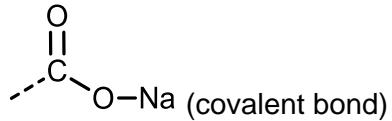
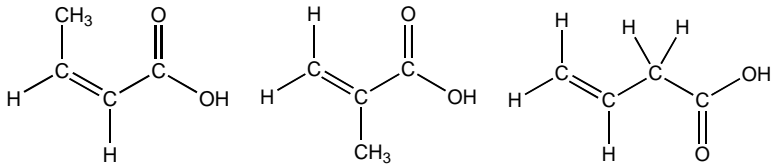
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Question			Answer	Marks	Guidance																
			HOOCCH ₂ COOH ✓		<p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>ALLOW COO⁻ if used Tollens' or Fehling's or Benedict's</p> <p>ALLOW correct unambiguous name: propan(e-1,3-)dioic acid</p> <p>IGNORE dipropanoic acid DO NOT ALLOW propan(e-1,3-)dicarboxylic acid</p> <p>if used 2,4-DNP(H): ALLOW correct hydrazone structure or name ALLOW "(2,4-dinitrophenyl)hydrazone" (derivative)</p>																
1	(e)	(i)	<table border="1"> <thead> <tr> <th></th> <th>C</th> <th>H</th> <th>O</th> </tr> </thead> <tbody> <tr> <td>%</td> <td>55.81%</td> <td>7.02%</td> <td>37.17%</td> </tr> <tr> <td>mol</td> <td>4.65</td> <td>7.02</td> <td>2.32</td> </tr> <tr> <td>ratio</td> <td>2</td> <td>3</td> <td>1</td> </tr> </tbody> </table> <p>empirical formula = C₂H₃O ✓</p> <p>molecular formula = C₄H₆O₂ ✓</p>		C	H	O	%	55.81%	7.02%	37.17%	mol	4.65	7.02	2.32	ratio	2	3	1	2	<p>Alternative method scores 2 marks: 0.0702/1 x 86 = 6; 0.3717/16 x 86 = 2; 0.5581/12 x 86 = 4</p> <p>C₄H₆O₂ answer alone worth 2 marks</p>
	C	H	O																		
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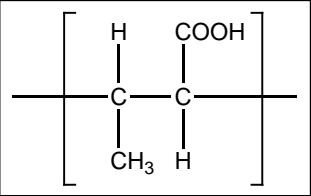
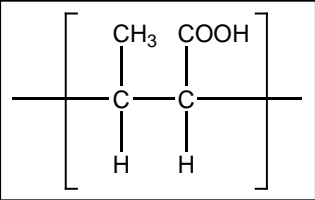
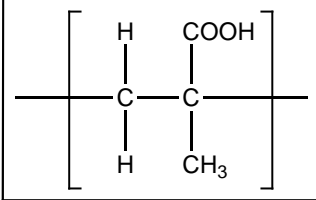
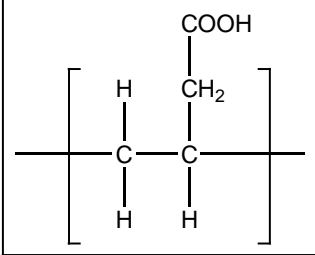
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Question		Answer	Marks	Guidance
1	(e) (ii)	<div style="text-align: center;">  <p>compound B ✓</p> </div> <div style="display: flex; justify-content: space-around; margin-top: 20px;"> <div style="text-align: center;">  <p>compound C ✓</p> </div> <div style="text-align: center;">  <p>compound D ✓</p> </div> </div>	4	<p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous eg COOH does not have to be displayed</p> <p>E/trans stereoisomer is needed</p> <p>For compound C,</p> <p>ALLOW  OR </p> <p>If charges shown on both O and Na then both must be correct</p> <p>DO NOT ALLOW  (covalent bond)</p> <p>ALLOW ECF for C and D if B is identified as one of the following three structures:</p> <div style="text-align: center; margin-top: 20px;">  </div>

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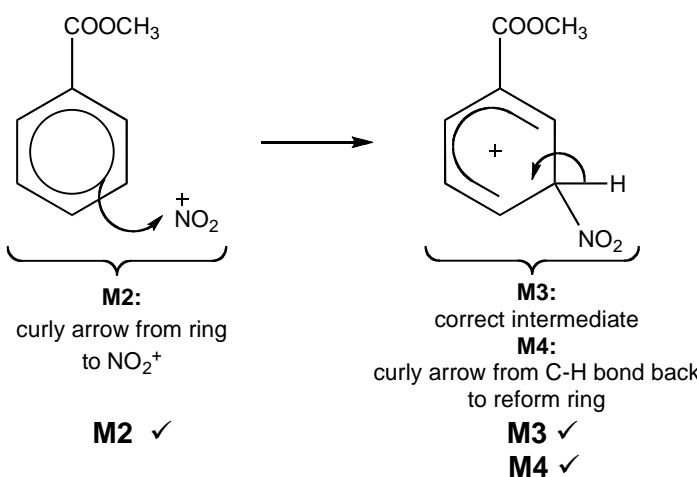
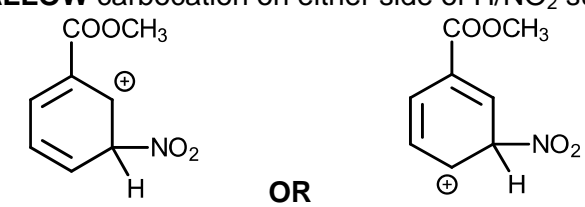
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Question	Answer	Marks	Guidance
	<div style="text-align: center;">  <p>one repeat unit of polymer E ✓</p> </div>		<p>For polymer E, brackets not required IGNORE n Free rotation so CH₃ can be shown at top, next to COOH</p> <p>IF more than one repeat unit has been drawn a single repeat unit MUST be identified by brackets or clear label</p> <p>The only polymers to ALLOW as ECF from incorrect B are:</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  </div> <div style="text-align: center;">  </div> </div> <div style="text-align: center; margin-top: 20px;">  </div>
	Total	17	

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Question		Answer	Marks	Guidance
2	(a) (i)	<p>M1: $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{HSO}_4^- + \text{NO}_2^+$ ✓</p>  <p>M2: curly arrow from ring to NO_2^+ M2 ✓</p> <p>M3: correct intermediate M4: curly arrow from C-H bond back to reform ring M3 ✓ M4 ✓</p> <p>-----</p> <p>Note: ALLOW M2 AND M4 for benzene OR ANY substituted benzene compound For M3, credit ONLY the correct intermediate</p> <p>-----</p> <p>M5 $\text{H}^+ + \text{HSO}_4^- \rightarrow \text{H}_2\text{SO}_4$ ✓</p>	5	<p>ALLOW $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{O}^+ + 2\text{HSO}_4^- + \text{NO}_2^+$</p> <p>ALLOW $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + \text{H}_2\text{NO}_3^+$ then $\text{H}_2\text{NO}_3^+ \rightarrow \text{H}_2\text{O} + \text{NO}_2^+$</p> <p>ALLOW $^+\text{NO}_2$ OR NO_2^+</p> <p>ALLOW first curly arrow from the ring OR from within the ring to any part of the NO_2^+ including the + charge</p> <p>DO NOT ALLOW intermediate with broken ring covering less than half the ring DO NOT ALLOW incorrect orientation of horseshoe</p> <p>ALLOW non-delocalized (Kekulé) structures ALLOW carbocation on either side of H/NO_2 substituents:</p>  <p>OR</p> <p>IF NO_2 is shown in incorrect position or COOCH_3 has been omitted in intermediate DO NOT AWARD M3 but can award other marks (max 4)</p>
	(ii)	electrophilic substitution ✓	1	

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Question			Answer	Marks	Guidance
2	(b)	(i)	<p style="text-align: right;">✓</p>	1	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous
		(ii)	Reaction 1 Sn AND concentrated HCl ✓ Reaction 2 HNO ₂ OR NaNO ₂ with (dil) HCl ✓ < 10°C ✓ Reaction 4 hot/heated aqueous NaOH ✓	4	IGNORE temperature and reaction type/purpose of reagents IGNORE reference to concentration ALLOW (heat under) reflux for 'hot' IGNORE warm/alkaline if temp stated accept 50° or greater MUST have aq or water or any stated concentration

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Question			Answer	Marks	Guidance
2	(b)	(iii)	<p>In amine, (lone) pair of electrons on N is (partially) delocalised into the ring ✓</p> <p> QWC delocalised/delocalized/delocalise, etc. must be spelled correctly in the correct context at least once for 1st mark</p> <p>electron density is high(er) / increases ✓</p> <p>great(er) attraction (from aromatic ring) for electrophile/diazonium ion ✓</p>	3	<p>ALLOW diagram to show movement of (lone) pair into ring but delocalised ring must be mentioned</p> <p>ALLOW (lone) pair of electrons on N is (partially) drawn/attracted/pulled into delocalised ring</p> <p>ALLOW electron density low(er) for benzene</p> <p>IGNORE 'activates the ring'</p> <p>IGNORE charge density alone but ALLOW electron charge density</p> <p>DO NOT ALLOW electronegativity</p> <p>ALLOW less/low attraction from benzene for electrophile/diazonium ion</p> <p>ALLOW amine is a better nucleophile/more susceptible to electrophilic attack</p> <p>DO NOT ALLOW reference to dipole induced in diazonium ion</p> <p>DO NOT ALLOW reference to bromine as electrophile</p>
			Total	14	

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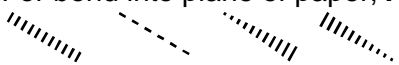

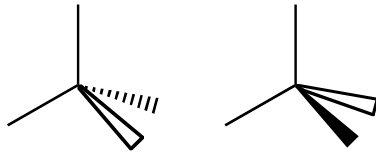
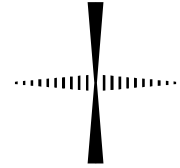
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Question		Answer	Marks	Guidance
3	(a)	Both NH ₂ and COOH are attached to the same carbon ✓	1	<p>ALLOW amine/amino and carboxyl(ic)</p> <p>ALLOW (it has the structure)</p> $\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{COOH} \\ \\ \text{NH}_2 \end{array}$ <p>ALLOW RCH(NH₂)COOH in any order but C and H must be adjacent (to each other)</p>
	(b) (i)	$\begin{array}{ccccccc} & & \text{CH}_3 & \text{H} & & \text{O} & \\ & & & & & // & \\ \text{H}_3\text{C} & - & \text{C} & - & \text{C} & - & \text{C} \\ & & & & & \backslash & \\ & & \text{SH} & \text{NH}_3^+ & & \text{O}^- & \\ & & & \oplus & & & \end{array} \quad \checkmark$	1	<p>ALLOW correct structural OR displayed OR skeletal formulae</p> <p>OR combination of above as long as unambiguous</p> <p>ALLOW NH₃⁺</p> <p>ALLOW delocalised carboxylate</p>
	(b) (ii)	$\begin{array}{ccccccc} & & \text{CH}_3 & \text{H} & & \text{O} & \\ & & & & & // & \\ \text{H}_3\text{C} & - & \text{C} & - & \text{C} & - & \text{C} \\ & & & & & \backslash & \\ & & \text{SH} & \text{NH}_3^+ & & \text{OH} & \\ & & & \oplus & & & \end{array} \quad \checkmark$	1	<p>ALLOW correct structural OR displayed OR skeletal formulae</p> <p>OR combination of above as long as unambiguous</p> <p>ALLOW NH₃⁺</p>
	(c)	$\begin{array}{c} \text{C}(\text{CH}_3)_2\text{SH} \\ \\ \text{H} \cdots \text{C} \\ \swarrow \quad \searrow \\ \text{HOOC} \quad \text{NH}_2 \end{array} \quad \checkmark$	1	<p>Connectivity is being tested:</p> <p>Chiral C must be linked to the C of the COOH, the C of the C(CH₃)₂SH and the N of the NH₂</p> <p>eg DO NOT ALLOW an attempted NH₂ shown as below:</p> $\begin{array}{c} \text{C}(\text{CH}_3)_2\text{SH} \\ \\ \text{H} \cdots \text{C} \\ \swarrow \quad \searrow \\ \text{HOOC} \quad \text{H}_2\text{N} \end{array}$

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Question	Answer	Marks	Guidance
			<p>The structure must have four central bonds, with at least one wedge in AND one wedge out</p> <hr/> <p>For bond into plane of paper, ALLOW:</p>  <p>For bond out of plane of paper, a solid wedge is expected, either way around:</p>  <p>ALLOW a hollow wedge for 'in bond' OR an 'out bond', provided it is different from the other in or out wedge e.g.:</p>  <p>ALLOW examples of other 3D representations provided they are possible: i.e.</p>  <p>CARE: This is a 3D representation so this is possible and the bond are clearly not 90° to one another</p>

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3	(d)	(i)	CH_2Cl_2 ✓	1	ALLOW CH_2Br_2 OR CH_2I_2 OR CH_2F_2 OR other dihalogenated methane derivatives eg CH_2BrCl IGNORE names
		(ii)	$ \begin{array}{ccccccc} & & \text{C}(\text{CH}_3)_2\text{SH} & & \text{C}(\text{CH}_3)_2\text{SH} & & \\ & & & & & & \\ \text{---N} & \text{---C} & \text{---} & \text{C} & \text{---N} & \text{---C} & \text{---C} \text{---} \\ & & & & & & \\ & \text{H} & & \text{O} & & \text{H} & \text{O} \end{array} $ <p>peptide link ✓ rest of structure ✓</p>	2	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous ALLOW —NH— at other end 'End bonds' MUST be shown (solid or dotted) IGNORE brackets and/or <i>n</i> around two repeat units 1st mark does not require amide group fully displayed ie ALLOW —CONH— DO NOT ALLOW 2nd mark if amide/peptide link wrong If more than 2 repeat units only first mark (peptide link) can be awarded
	(e)	(i)	penicillamine = 4 ✓ methionine = 5 ✓	2	
		(ii)	(CO)OH, NH/NH ₂ AND SH ✓ all undergo proton exchange ✓	2	ALLOW (CO)OD, ND/ND ₂ , SD, ALLOW H (atoms/protons/ions) replaced by D (atoms/ions)

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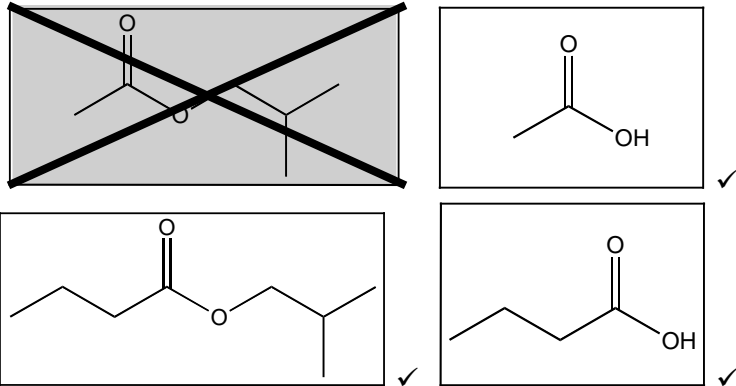
January 2013

Question			Answer				Marks	Guidance																																			
3	(e)	(iii)	<p style="text-align: center;">¹H NMR spectrum for methionine</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th>Type of proton(s)</th> <th>Chemical shift</th> <th>Splitting pattern</th> <th>Relative peak area</th> <th></th> </tr> </thead> <tbody> <tr> <td>NH₂</td> <td>4.5</td> <td>singlet</td> <td>2</td> <td></td> </tr> <tr> <td>H₃C-S-</td> <td>2.1</td> <td>singlet</td> <td>3</td> <td>✓</td> </tr> <tr> <td>-S-CH₂-</td> <td>2.4</td> <td>triplet</td> <td>2</td> <td>✓</td> </tr> <tr> <td>S-CH₂-CH₂</td> <td>0.7–2.0</td> <td>multiplet OR quartet</td> <td>2</td> <td>✓</td> </tr> <tr> <td>CHNH₂</td> <td>2.0–3.0</td> <td>triplet</td> <td>1</td> <td>✓</td> </tr> <tr> <td>OH</td> <td>11–12</td> <td>singlet</td> <td>1</td> <td>✓</td> </tr> </tbody> </table> <p>Rows can be in any order IGNORE extra rows Do not need to show bonds between atoms</p>				Type of proton(s)	Chemical shift	Splitting pattern	Relative peak area		NH ₂	4.5	singlet	2		H ₃ C-S-	2.1	singlet	3	✓	-S-CH ₂ -	2.4	triplet	2	✓	S-CH ₂ -CH ₂	0.7–2.0	multiplet OR quartet	2	✓	CHNH ₂	2.0–3.0	triplet	1	✓	OH	11–12	singlet	1	✓	5	<p>ALLOW any value within ranges given for δ /ppm on the Data Sheet IGNORE reference to NH₂ signals (given as example)</p> <p>GUIDANCE</p> <ul style="list-style-type: none"> mark by rows ALL data in row must be correct for each mark ALLOW “triplet of doublets” or “doublet of triplets” for multiplet/quartet signal from —CH₂CH₂S— <p>ALLOW quadruplet</p> <p>ALLOW a response that implies a single peak OR ‘no splitting’</p> <p>ALLOW a response that implies a splitting into three for a triplet/into four for a quartet</p> <p>Clear and unambiguous identification of the protons (when more than one type is present) other than by position number should be credited eg for CHNH₂ could be HCCO or CHN or HCN or CH₂CH</p> <p>eg for S-CH₂-CH₂ could be CH₂C(H)NH₂ or CCH₂C or CH₂CH₂ or RCH₂R or RCHR</p> <p>eg ‘CH between COOH and NH₂’ OR identification by number labels on chemical structures</p>
Type of proton(s)	Chemical shift	Splitting pattern	Relative peak area																																								
NH ₂	4.5	singlet	2																																								
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OH	11–12	singlet	1	✓																																							
			Total			16																																					

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Question		Answer	Marks	Guidance
4	(a)	(i) (2-)methylpropan-1-ol ✓	1	ALLOW without hyphens
		(ii) 	3	DO NOT MARK top left hand structure: (on paper) ALLOW in any order ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous If use displayed formulae but omit one or more H atoms DO NOT ALLOW each time
	(b)	(i) The time (from the injection of the sample) for the component/compound/substance to leave the column ✓	1	IGNORE (time for) gas to leave column DO NOT ALLOW time in GC/machine/apparatus ALLOW time from injection to detection ALLOW time spent in column ALLOW time taken to reach detector
		(ii) They have similar retention times OR unknown compounds have no reference retention times for comparison ✓	1	ALLOW same retention times ALLOW both are esters therefore relative solubilities/partition/adsorption/retention times will be very similar

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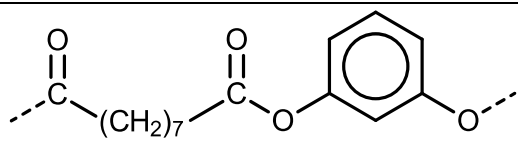
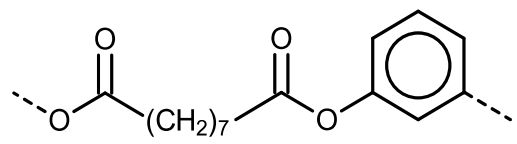
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Question			Answer	Marks	Guidance
4	(c)	(i)		1	<p>IF end repeat unit shown the line of the box must go through the continuation bond</p> <p>ALLOW other possibilities for showing structure with repeat unit displayed, eg repeat unit with O on left and not on right.</p> <p>Other possibilities:</p>
		(ii)	Hydrolysis ✓	1	<p>IGNORE decomposition/biodegradation</p> <p>IGNORE mention of acid/alkali</p>

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Question			Answer	Marks	Guidance
4	(c)	(iii)	<p>broad absorption 2500–3300 (cm^{-1}) ✓ (because) (degradation) forms (di)carboxylic acid / COOH ✓</p>	2	<p>ALLOW carboxyl group IGNORE reference to carbonyl/1640–1750 (cm^{-1}) IGNORE reference to C—O/1000–1300 (cm^{-1})</p>
		(iv)	 <p>M1 ester link ✓</p> <p>M2 the two oxygen atoms from benzene-1,3-diol linked at 1,3 positions ✓</p> <p>M3 one repeat unit fully correct ✓</p>	3	<p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>Ester link does not need to be fully displayed eg accept —COO—</p> <p>ALLOW —O— at other end ie</p>  <p>'End bonds' MUST be shown (solid or dotted) DO NOT ALLOW more repeat units IGNORE brackets and/or <i>n</i> IF more than one repeat unit has been drawn a single repeat unit MUST be identified by brackets or clear label</p>
			Total	13	

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