| Question |  | Answer | Marks | Guidance |
| :---: | :---: | :---: | :---: | :---: |
| 1 | (a) | M1 EITHER in words: <br> (pyruvic acid forms) hydrogen bonds with water <br> OR correctly labelled diagram showing hydrogen bond between pyruvic acid and water <br> M2 diagram showing dashed/dotted line between $\mathbf{H}^{\boldsymbol{\delta +}}$ in COOH and lone pair of electrons on O in $\mathrm{H}_{2} \mathrm{O}$ <br> OR <br> diagram showing dashed/dotted line between $\mathbf{H}^{\delta+}$ in $\mathrm{H}_{2} \mathrm{O}$ and lone pair of electrons on O of OH in $\mathrm{COOH} \checkmark$ | 2 | FOR M1 only: if use diagram ALLOW a labelled hydrogen bond to O in $\mathrm{C}=\mathrm{O}$ <br> FOR M2 only: IGNORE a hydrogen bond to $\mathrm{C}=\mathrm{O}$, i.e. $\mathrm{C}=\mathrm{O}-\mathrm{-}$ H-O <br> IGNORE bond angles <br> Diagram does not need to show all of pyruvic acid (IGNORE if wrong so allow ethanoic acid) but must have minimum of COOH <br> MIMIMUM requirement is a $\mathrm{H}^{\delta+}$ (on acid or water) and a lone pair on O (in acid or water) involved in a hydrogen bond ie IGNORE ס- |
|  | (b) | $\begin{aligned} & \mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{2} \mathrm{OH}+3[\mathrm{O}] \rightarrow \mathrm{CH}_{3} \mathrm{COCOOH}+2 \mathrm{H}_{2} \mathrm{O} \\ & \text { four correct formulae } \checkmark \\ & \text { balanced } \checkmark \end{aligned}$ | 2 | ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous (IGNORE lack of brackets round $2^{\circ}$ alcohol) <br> DO NOT ALLOW molecular formulae <br> IF propane1,3-diol used score 0 |


|  | uesti | Answer | Marks | Guidance |
| :---: | :---: | :---: | :---: | :---: |
| 1 | (c) |  <br> M1: <br> 1 mark for curly arrow from $\mathrm{H}^{-}$to C of $\mathrm{C}=\mathrm{O} \checkmark$ <br> M2: <br> 1 mark for correct dipoles on $\mathrm{C}=\mathrm{O}$ AND curly arrow from double bond to $\mathrm{O}^{\delta-} \checkmark$ <br> M3: <br> 1 mark for correct intermediate with - charge on O $\checkmark$ <br> M4: <br> 1 mark for curly arrow from $\mathrm{O}^{-}$of intermediate to H in $\mathrm{H}_{2} \mathrm{O}$ <br> AND <br> curly arrow from the $\mathrm{O}-\mathrm{H}$ bond to the O in $\mathrm{H}_{2} \mathrm{O}$ : <br> Do not need to show formation of $\mathrm{OH}^{-}$ | 4 | Curly arrow MUST start from - sign OR lone pair on $\mathrm{H}^{-}$ Lone pair does not need to be shown on $\mathrm{H}^{-}$ <br> Lone pair does not need to be shown on $\mathrm{O}^{-}$ <br> Curly arrow MUST start from - sign OR from lone pair on $\mathrm{O}^{-}$of intermediate <br> Lone pair does not need to be shown on $\mathrm{O}^{-}$ <br> For M4, <br> ALLOW mark for curly arrow from $\mathrm{O}^{-}$of intermediate to $\mathrm{H}^{+}$ |


| Question |  | Answer | Marks | Guidance |
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| 1 | (d) | Either: | 3 |  |
|  |  | Use Tollens' reagent |  | ALLOW $\mathrm{AgNO}_{3}$ in ammonia OR ammoniacal $\mathrm{AgNO}_{3}$ |
|  |  | AND correct reference to compound A being oxidised or Tollen's reagent acts as oxidising agent $\checkmark$ |  | ALLOW redox reaction |
|  |  | Observation: silver mirror/precipitate/ppt/solid or: |  | ALLOW black ppt OR grey ppt |
|  |  | Use $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ AND $\mathrm{H}_{2} \mathrm{SO}_{4}$ <br> AND correct reference to compound A being oxidised or $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ acts as oxidising agent |  | ALLOW $\mathrm{Na}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ OR $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}$ for $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ If formulae used, formulae must be correct ALLOW acidified dichromate If name given, ALLOW dichromate OR dichromate(VI) IGNORE reference to dilute/conc ALLOW $\mathrm{H}^{+}$ |
|  |  | QWC oxidised/oxidized/oxidation/redox etc. must be spelled correctly at least ONCE (i.e. NOT oxidisation, |  | ALLOW $\mathrm{KMnO}_{4}$ and $\mathrm{H}_{2} \mathrm{SO}_{4}$ / acidified manganate(VII)/ permanganate / alkaline manganate(VII) <br> AND correct reference to compound A being oxidised or $\mathrm{KMnO}_{4}$ acts as oxidising agent <br> Observation: decolourised |
|  |  | oxidated) to score $1^{\text {st }}$ mark <br> UNLESS 2,4-DNP(H)/Brady's reagent is used, when condensation/addition-elimination must be spelled correctly at least ONCE |  | 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 Observation: (brick) red ppt |
|  |  |  |  | ALLOW 2,4-DNP(H)/Brady's reagent AND measure melting point of derivative AND state it is a condensation reaction/additionelimination reaction Observation: orange/yellow/red precipitate <br> ALLOW solid OR crystals OR ppt as alternatives for precipitate |


| Question |  |  | Answer |  |  |  | Marks | Guidance |
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|  |  |  | HOOC | $\mathrm{OH} \checkmark$ |  |  |  | ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous <br> ALLOW COO- if used Tollens' or Fehling's or Benedict's <br> ALLOW correct unambiguous name: <br> propan(e-1,3-)dioic acid <br> IGNORE dipropanoic acid <br> DO NOT ALLOW propan(e-1,3-)dicarboxylic acid <br> if used $2,4-\mathrm{DNP}(\mathrm{H})$ : <br> ALLOW correct hydrazone structure or name ALLOW "(2,4-dinitrophenyl)hydrazone" (derivative) |
| 1 | (e) | (i) |  <br> $\%$ <br> mol <br> ratio <br> empiri <br> molec | C <br> $55.81 \%$ <br> 4.65 <br> 2 <br> ula $=\mathrm{C}_{2} \mathrm{H}_{3}$ $\text { nula }=\mathrm{C}_{4}$ | $\begin{aligned} & \hline \mathrm{H} \\ & \hline 7.02 \% \\ & \hline 7.02 \\ & \hline 3 \end{aligned}$ | O <br> $37.17 \%$ <br> 2.32 <br> 1 | 2 | Alternative method scores 2 marks: $0.0702 / 1 \times 86=6 ; \quad 0.3717 / 16 \times 86=2 ; \quad 0.5581 / 12 \times 86=4$ <br> $\mathrm{C}_{4} \mathrm{H}_{6} \mathrm{O}_{2}$ answer alone worth 2 marks |




| Question |  |  | Answer | Marks | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | (a) | (i) | M1: $\mathrm{HNO}_{3}+\mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{HSO}_{4}^{-}+\mathrm{NO}_{2}^{+} \checkmark$ <br> Note: <br> ALLOW M2 AND M4 for benzene OR ANY substituted benzene compound <br> For M3, credit ONLY the correct intermediate $\text { M5 H } \mathrm{H}^{+}+\mathrm{HSO}_{4}^{-} \rightarrow \mathrm{H}_{2} \mathrm{SO}_{4}$ | 5 | ALLOW $\mathrm{HNO}_{3}+2 \mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}+2 \mathrm{HSO}_{4}^{-}+\mathrm{NO}_{2}{ }^{+}$ <br> ALLOW $\mathrm{HNO}_{3}+\mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow \mathrm{HSO}_{4}^{-}+\mathrm{H}_{2} \mathrm{NO}_{3}{ }^{+}$ <br> then $\mathrm{H}_{2} \mathrm{NO}_{3}{ }^{+} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{NO}_{2}{ }^{+}$ <br> ALLOW ${ }^{+} \mathrm{NO}_{2} \mathrm{OR} \mathrm{NO}_{2}{ }^{+}$ <br> ALLOW first curly arrow from the ring OR from within the ring to any part of the $\mathrm{NO}_{2}{ }^{+}$including the + charge <br> DO NOT ALLOW intermediate with broken ring covering less than half the ring <br> DO NOT ALLOW incorrect orientation of horseshoe <br> ALLOW non-delocalized (Kekulé) structures ALLOW carbocation on either side of $\mathrm{H} / \mathrm{NO}_{2}$ substituents: <br> OR <br> IF $\mathrm{NO}_{2}$ is shown in incorrect position or $\mathrm{COOCH}_{3}$ has been omitted in intermediate DO NOT AWARD M3 but can award other marks (max 4) |
|  |  | (ii) | electrophilic substitution $\checkmark$ | 1 |  |


| Question |  |  | Answer |  |  | Marks | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | (b) | (i) |  |  |  | 1 | ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous |
|  |  | (ii) | Reaction 1 <br> Reaction 2 <br> Reaction 4 | Sn AND concentrated HCl <br> $\mathrm{HNO}_{2}$ OR $\mathrm{NaNO}_{2}$ with (dil) HCl $<10^{\circ} \mathrm{C}$ <br> hot/heated aqueous NaOH | $\checkmark$ | 4 | IGNORE temperature and reaction type/purpose of reagents <br> IGNORE reference to concentration <br> ALLOW (heat under) reflux for 'hot' IGNORE warm/alkaline if temp stated accept $50^{\circ}$ or greater MUST have aq or water or any stated concentration |


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


| Question |  |  | Answer | Marks | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 3 | (a) |  | Both $\mathrm{NH}_{2}$ and COOH are attached to the same carbon $\checkmark$ | 1 | ALLOW amine/amino and carboxyl(ic) <br> ALLOW (it has the structure) <br> ALLOW $\mathrm{RCH}\left(\mathrm{NH}_{2}\right) \mathrm{COOH}$ in any order but C and H must be adjacent (to each other) |
|  | (b) | (i) |  | 1 | ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous <br> ALLOW NH ${ }_{3}{ }^{+}$ <br> ALLOW delocalised carboxylate |
|  |  | (ii) |  | 1 | ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous <br> ALLOW NH ${ }^{+}$ |
|  | (c) |  |  | 1 | Connectivity is being tested: <br> Chiral C must be linked to the C of the COOH , the C of the $\mathrm{C}\left(\mathrm{CH}_{3}\right)_{2} \mathrm{SH}$ and the N of the $\mathrm{NH}_{2}$ <br> eg DO NOT ALLOW an attempted $\mathrm{NH}_{2}$ shown as below: |



| Question |  |  | Answer | Marks | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 3 | (d) | (i) | $\mathrm{CH}_{2} \mathrm{Cl}_{2} \checkmark$ | 1 | ALLOW CH $\mathrm{Br}_{2}$ OR CH $\mathrm{I}_{2}$ OR CH $\mathrm{F}_{2}$ <br> OR other dihalogenated methane derivatives eg $\mathrm{CH}_{2} \mathrm{BrCl}$ <br> IGNORE names |
|  |  | (ii) |  | 2 | ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous <br> ALLOW - NH - at other end <br> 'End bonds' MUST be shown (solid or dotted) <br> IGNORE brackets and/or $n$ around two repeat units <br> 1st mark does not require amide group fully displayed ie ALLOW-CONH- <br> DO NOT ALLOW 2nd mark if amide/peptide link wrong <br> If more than 2 repeat units only first mark (peptide link) can be awarded |
|  | (e) | (i) | penicillamine $=4 \checkmark$ methionine $=5 \checkmark$ | 2 |  |
|  |  | (ii) | (CO)OH, NH/NH2 AND SH <br> all undergo proton exchange | 2 | ALLOW (CO)OD, ND/ND ${ }_{2}$, SD, <br> ALLOW H (atoms/protons/ions) replaced by D (atoms/ions) |


| Question |  |  | Answer |  |  |  |  | Marks | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3 | $\text { (e) } \mid \text { (iii) }$ |  | ${ }^{1} \mathrm{H}$ NMR spectrum for methionine |  |  |  |  | 5 | ALLOW any value within ranges given for $\delta / \mathrm{ppm}$ on the Data Sheet |
|  |  |  | Type of proton(s) | Chemical shift | Splitting pattern | Relative peak area |  |  | IGNORE reference to $\mathrm{NH}_{2}$ signals (given as example) |
|  |  |  | $\mathrm{NH}_{2}$ | 4.5 | singlet | 2 |  |  | GUIDANCE |
|  |  |  | $\mathrm{H}_{3} \mathrm{C}-\mathrm{S}-$ | 2.1 | singlet | 3 | $\checkmark$ |  | - mark by rows |
|  |  |  | $-\mathrm{S}-\mathrm{CH}_{2}{ }^{-}$ | 2.4 | triplet | 2 | $\checkmark$ |  | - ALL data in row must be correct for each mark |
|  |  |  | $\mathrm{S}-\mathrm{CH}_{2}-\mathrm{CH}_{2}$ | 0.7-2.0 | multiplet OR quartet | 2 | $\checkmark$ |  | - ALLOW "triplet of doublets" or "doublet of triplets" for multiplet/quartet signal from $-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{~S}-$ |
|  |  |  | $\mathrm{CHNH}_{2}$ | 2.0-3.0 | triplet | 1 | $\checkmark$ |  |  |
|  |  |  | OH | 11-12 | singlet | 1 | $\checkmark$ |  | ALLOW quadruplet |
|  |  |  | Rows can be IGNORE extr <br> Do not need | in any order rows show bon | between at |  |  |  | ALLOW a response that implies a single peak OR 'no splitting' <br> ALLOW a response that implies a splitting into three for a triplet/into four for a quartet |
|  |  |  |  |  |  |  |  |  | Clear and unambiguous identification of the protons (when more than one type is present) other than by position number should be credited eg for $\mathrm{CHNH}_{2}$ could be HCCO or CHN or HCN or $\mathrm{CH}_{2} \mathrm{CH}$ eg for $\mathrm{S}-\mathrm{CH}_{2}-\mathrm{CH}_{2}$ could be $\mathrm{CH}_{2} \mathrm{C}(\mathrm{H}) \mathrm{NH}_{2}$ or $\mathrm{CCH}_{2} \mathrm{C}$ or $\mathrm{CH}_{2} \mathrm{CH}_{2}$ or $\mathrm{RCH}_{2} \mathrm{R}$ or RCHR |
|  |  |  |  |  |  |  |  |  | eg ' CH between COOH and $\mathrm{NH}_{2}$ ' OR identification by number labels on chemical structures |
|  |  |  |  |  |  |  | Total | 16 |  |


| Question |  |  | Answer | Marks | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 4 | (a) | (i) | (2-)methylpropan-1-ol $\checkmark$ | 1 | ALLOW without hyphens |
|  |  | (ii) |    <br> $\checkmark$ | 3 | DO NOT MARK top left hand structure: (on paper) <br> ALLOW in any order <br> ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous <br> 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 |



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

