## Mark scheme - Amino Acids, Amides and Chirality

Questi on		ti	Answer/Indicative content	Mark s	Guidance
1		i	Stereoisomers Same structural formula AND Different arrangement (of atoms) in space OR different spatial arrangement (of atoms) AND Type: Optical √	1 (AO1 .2)	ALLOW structure/displayed/skeletal formula DO NOT ALLOW same empirical formula OR same general formula IGNORE same molecular formula IGNORE references to chiral molecules/compounds
		ï	One 3D structure with correct groups attached to the chiral C $\checkmark$ Two 3D structures of (CH3)3CCHBrCH3 that are mirror images <b>AND</b> correct connectivity in both $\checkmark$ $\prod_{(CH_3)_3C} \prod_{H}^{Br} \prod_{H_3C} \prod_{H_3C}^{H_3C} \prod_{H_3$	2 (AO2 .5) (AO1 .2)	ALLOW small slip in one of the groups OR use of C4H9 3D structures must have four central bonds with <b>at least</b> two wedges. For bond into paper accept: $H_{H_{1}}$ ALLOW two 3D structures with 2 groups swapped e.g. Br (CH <sub>3</sub> ) <sub>3</sub> C
			Total	3	
2	a		Correct groups attached to chiral C of cysteine seen <b>once</b> e.g. $\underbrace{-\begin{array}{c} CH_2SH \\ HOOC \\ H \\ $	2	Each structure must have four central bonds with <b>at least</b> <b>two wedges</b> . For bond into paper accept: <b>ALLOW</b> bond to any part of the CH <sub>2</sub> of the CH <sub>2</sub> SH group e.g. <b>ALLOW</b>



				identified the dichloride salt produced by the reaction of lysine with excess acid. Some candidates formed ammonium ions on both nitrogen atoms but omitted the chloride ions. Others only formed a monochloride salt, leaving the R group unchanged. These two approaches scored one mark.
		Total	4	
		Final (reading) 23.15 45.95 32.45 /cm <sup>3</sup> Initial (reading) 0.60 23.15 10.00 √ /cm <sup>3</sup> Burette readings		Table <b>not</b> required <b>ALLOW</b> initial reading before final reading
		<ul> <li>Correct titration results recorded with injitial and final readings, clearly labeled Z2.55 Z2.80 X</li> <li>AND all readings recorded to two decimal places with last figure either 0 or 5</li> <li>Titres</li> </ul>		ALLOW ECF
3	i	<ul> <li>Correct subtractions to obtain final titres to 2 DP</li> </ul>	4	<b>ALLOW</b> units with each value <b>ALLOW</b> brackets for units, i.e. (cm <sup>3</sup> )
		Units		
		• Units of $cm^3$ for initial, final and titres $\checkmark$		ALLOW ECF from incorrect concordant titres
		Mean titre		
		• mean titre = $\frac{22.55 + 22.45}{2}$ = 22.50 <b>OR</b> 22.5 cm <sup>3</sup> $\checkmark$ <i>i.e. using concordant (consistent) titres</i>		<b>Examiner's Comment:</b> This question should have been four straightforward marks, but it was actually found very challenging by candidates. Most read the scales correctly but then did not present their findings clearly, often scattering unlabelled numbers around, omitting units with absence of any heading linking them to the burettes.
				0.60 was very often shown as 0.6 and 22.80 as 22.8. Candidates were expected to take the mean of their closest titres but a significant number took an average of all three titres instead. The mark scheme allowed for a

			mean titre obtained from incorrect titres.
			Candidates need to appreciate the importance of communicating their results in a clear and comprehensive way with headings and units, and showing numerical values to the accuracy of the apparatus used.
			ALLOW ECF from incorrect mean titre in 4a(i)
			e.g. From 22.60 cm <sup>3</sup> (mean of all 3 titres in <b>(i)</b> , <i>n</i> (NaOH) = 1.8984 × 10 <sup>-3</sup> (mol)
			ALLOW ECF from incorrect <i>n</i> (NaOH)
	ALLOW 3SF or more throughout IGNORE trailing zeroes, e.g. ALLOW 0.084 for 0.0840		ALLOW ECF from incorrect <i>n</i> ( <b>A</b> )
			<b>ALLOW ECF</b> from incorrect $M(\mathbf{A}) = 75$
	 $n(\text{NaOH}) = 0.0840 \times \frac{22.50}{4000} = 1.89 \times 10^{-3} \text{ (mol) } \checkmark$		
	$n(\mathbf{A})$ in 250 cm <sup>3</sup> = 10 × 1.89 × 10 <sup>-3</sup> = 1.89 × 10 <sup>-2</sup> (mol) $\checkmark$		ALLOW ECF for alkyl group closest to calculated $M$ (alkyl group), e.g. for $M = 45$ , ALLOW C <sub>3</sub> H <sub>7</sub> (43)
	$M(\mathbf{A}) = \frac{2.495}{1.89 \times 10^{-2}} = 132 \text{ (g mol^{-1}) } \checkmark$		
	<i>M</i> (alkyl group) (= 132 – 75) = 57 √	6	ALLOW correct structural OR skeletal OR displayed
	$R = C_4 H_9 \checkmark$		ambiguous
	<b>ALLOW</b> alkyl group in drawn structure with straight chain or branch (es) in wrong position,		<b>IGNORE</b> poor connectivity to OH groups <i>Given in</i> question
	e.g. for R = C4H9, CH3CH2CH2CH2 <b>OR</b> (CH3)3C		<b>Common error for 4 marks max</b> 25.00 instead of 22.50 and scaling by × 10 2.10 × $10^{-3} \times \rightarrow 2.10 \times 10^{-2} \checkmark$
	Structure with chiral carbon atoms identified (see * below)		→ 118.81 $\checkmark$ → 43.81 $\checkmark$ → C <sub>3</sub> H <sub>7</sub> $\checkmark$ 25.00 instead of 22.50 and scaling by
	HO *		× 22.50
	OH CH		$2.10 \times 10^{-3} \times \rightarrow 2.33 \times 10^{-2} \checkmark$ $\rightarrow 106.93 \checkmark \rightarrow 31.93 \checkmark \rightarrow C_2H_5 \checkmark$
			No structure with 2 chiral centres possible ×
			<b>Examiner's Comment:</b> Most candidates made some headway with this problem. Candidates were expected to process their mean titre from $4(a)(i)$ in a conventional titration calculation to arrive at a molar mass of 132 g mol <sup>-1</sup> . From there, candidates
			could determine a $C_4H_9$ alkyl group and draw the structure

					of compound A with two chiral carbon atoms.
					Most candidates scored some marks but processing beyond the molar mass proved to be difficult for weaker candidates. Some candidates showed a structure with a linear $C_4H_9$ group which contains one chiral carbon atom.
					A common error was use of 25.0 cm <sup>3</sup> , instead of the titre, as the volume of NaOH, obtaining an initial value of 2.10 × $10^{-3}$ mol. The mark scheme allowed processing of this value to be credited using error carried forwards. Some candidates omitted to scale their initial value by a factor of ×10, obtaining a molar mass of over 1000 g mol <sup>-1</sup> , e.g. 1320 instead of 132. A large range of marks was seen and the question discriminated extremely well.
			Total	10	
4	а	i	(optical isomers are) non-super imposable mirror images $\checkmark$ Two 3D structures of serine that are mirror images irrespective of connectivity $\checkmark$ HOOC HOOC H H H H H H H H H H	3	
			Correct connectivity in both structures $\checkmark$		
		ii	Dipeptide Ser-Gly $H_{2}N - \begin{pmatrix} H & 0 \\ - & C \\ - & H \\ - & H \\ - & H \\ - & H \\ - & C $	3	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW structures in any order
	b	i	Structure of aspartic acid	4	<b>ALLOW</b> any combination of skeletal <b>OR</b> structural <b>OR</b> displayed formula as long as unambiguous



		√√√		ALLOW sextet/hextet/six (or more than 5) as alternative to multiplet Relative peak area = CH /3H etc. penalise once Examiner's Comments
				same skill three times, the full range of marks was awarded and errors were seen in the chemical shift, relative peak area and splitting pattern. Fully correct responses included either a chemical shift value within the range specified on the data sheet or a range that matched the one given on the data sheet.
		$M^{+}$ peak at 75 (peak 1)		ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous
	ii	$\frac{\text{Im} - \text{peak at 75}}{\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}^*/\text{C}_3\text{H}_9\text{NO}^*}$ $\checkmark$ $\frac{\text{Fragment peak at 44}}{\text{CH}_3\text{CH}(\text{NH}_2)^*/\text{C}_2\text{H}_6\text{N}^*}$ $\checkmark$	2	Positive charge is essential but <b>ALLOW</b> maximum of one mark if both formulae are correct <b>AND</b> neither species has a positive charge <b>Examiner's Comments</b>
				Although peak 2 was often correct, the species responsible for the M+ peak was often missing a positive charge. Possibly students have learned that the particles become charged as part of the fragmentation process and don't realise that only charged particles can be detected by a mass spectrometer.
b	i	Ethanolic ammonia <b>OR</b> ammonia/NH₃ <b>AND</b> ethanol √	1	ALLOW ammonia in a sealed tube ALLOW dilute ethanolic ammonia/NH <sub>3</sub> IGNORE heat ALLOW alcohol for ethanol DO NOT ALLOW any reference to water or hydroxide ions
				<b>Examiner's Comments</b> A well answered question. Some candidates forgot to use a solvent or suggested the use of aqueous ammonia.
	ii	(compound D) $H \xrightarrow{CH_3}_{H \to C} CH_2OH$	1	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous
	$H_3C \longrightarrow CH_2OH$ H		This question discriminated well. Although there were very few blank pages, many incorrect structures were seen.	



b	Measure distance moved by spot/distance moved by solvent $\checkmark$	2	ALLOW attempt at calculation of R <sub>f</sub> value using distances measured on the chromatogram IGNORE explanation of how chromatography works
	Compare (R <sub>f</sub> ) value with data book values/known values √ Two amino acids have the same/similar R <sub>f</sub> value <b>OR</b> similar adsorption <b>OR</b> move the same/similar distance √	1	ALLOW One spot contains two amino acids ALLOW Two amino acids have not separated IGNORE relative solubility ALLOW two of the amino acids have similar structures Examiner's Comments This question discriminated well with relatively few candidates able to score all three marks. Some candidates attempted to explain how the technique separates components between a mobile phase and a stationary phase which was not required by the question. There was some confusion with gas chromatography and retention times. Vague answers about all amino acids having similar structures did not score the final marking point to explain why only two spots appeared on the chromatogram.
c i	The <b>pH</b> at which the amino acid exists as a <u>zwitterion</u> √ <b>QWC</b> : <b>zwitterion</b> spelled correctly in the correct context	1	DO NOT ALLOW PH/ph ALLOW zwitter ion Examiner's Comments This definition had been learned by the majority of candidates
	$\begin{array}{c} H\\ H_2N & \overbrace{C}{-} COO^-\\ & \downarrow\\ CH_2\\ & \downarrow\\ COO^-\end{array}$	1	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous Two COO <sup>-</sup> groups are required in the structure ALLOW –COO <sup>-</sup> Na <sup>+</sup> OR –COONa ALLOW delocalised carboxylate ALLOW



				conditions. The protonation of hydrolysis products has been well represented in recent papers.
				IGNORE solvent OR food additive
		perfume / fragrance / flavouring  ✓		Examiner's Comments
	i		1	Well answered with most of the correct responses referring to perfumes and flavourings which are the uses listed in the specification. Common responses marked as incorrect were suggestions that this ester could be used for making dyes, polymers or textiles.
				ALLOW NH <sub>3</sub> (dissolved) in ethanol IGNORE other conditions
		Reaction 3: (hot) ethanolic ammonia	3	ALLOW oxidisation / oxidised DO NOT ALLOW redox
	i	Reaction 4: oxidation $\checkmark$		ALLOW nucleophilic addition-elimination DO NOT ALLOW nucleophilic substitution IGNORE acid / base
		Reaction 5: hydrolysis ✓		Examiner's Comments Most candidates were able to score at least one mark here, usually for correctly identifying <b>reaction 4</b> as an oxidation reaction. Although the use of excess reagent was not required for <b>reaction 3</b> , some missed ethanol as an essential solvent and <b>reaction 5</b> was occasionally described as a reduction.
		M1 Compound E H H H <sub>2</sub> C=C-C-CHO $\downarrow$ NH <sub>2</sub> M2 Compound F H H H <sub>2</sub> C=C-COOH	6	ANNOTATE ANSWER WITH TICKS AND CROSSES ETC
				ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous Labels are not required for compound E, F, G or H IGNORE labels for M1, M2, M3 and M4
þ	0			CH <sub>2</sub> =CH must be shown in <b>E</b> ALLOW C <sub>2</sub> H <sub>3</sub> OR CHCH <sub>2</sub> for CH=CH <sub>2</sub> in <b>F</b>
		$\mathbf{M3} \text{ Compound } \mathbf{G}$		ALLOW ECF from error in structure of aldehyde E
				ALLOW multiple repeat units but must be full repeat units
		н снин₂   Соон		ALLOW end bonds shown as DO NOT ALLOW if structures have no end bonds



				the correctly labelled compound and some candidates lost marks here because their description was linked to the wrong polymer.
		Total	13	
8	i		1	<ul> <li>ALL correct for one mark</li> <li>Examiner's Comments</li> <li>This part was answered well by many candidates. Some missed the chiral centre on the proline moiety or added an asterisk to a carbonyl carbon.</li> </ul>
	ii	any <b>two</b> from: no / fewer side effects increases the (pharmacological) activity / effectiveness Reduces / stops the need for / cost / difficulty in separating stereoisomers / optical isomers	2	IGNORE toxic / harmful IGNORE a response that implies a reduced dose IGNORE "it takes (less) time to separate" Examiner's Comments Most candidates gained this mark by stating that the use of a single stereoisomer results in fewer side effects and increased pharmacological activity. Vague answers and comments about a reduced dose did not score marks.
	ii i	$ \begin{array}{c} \checkmark OH \\ H_{2N} \\ \oplus \\ COOH \end{array} \qquad $	4	<ul> <li>ALLOW correct structural OR displayed OR skeletal formulae</li> <li>OR combination of above as long as unambiguous</li> <li>ALLOW + charge on H of NH<sub>2</sub> groups, <i>i.e.</i> NH<sub>2</sub><sup>+</sup></li> <li>IGNORE negative (counter) ions</li> <li>Examiner's Comments</li> <li>This question discriminated well. Most candidates were able to score one mark for the formula of ethanol. Only a small number of able candidates scored full marks for including the correct formulae for the protonated amine groups formed during acid hydrolysis.</li> </ul>
	i V	idea of separating (the components / compounds) AND idea of (identifying compounds by) comparison with a (spectral) database ✓	1	ALLOW (identifies compounds) using fragmentation (patterns) / fragment ions (but IGNORE molecular ions) IGNORE retention times Examiner's Comments



