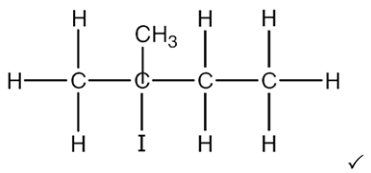
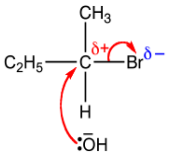
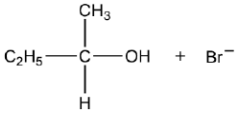
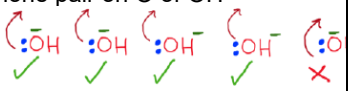
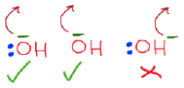
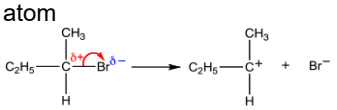
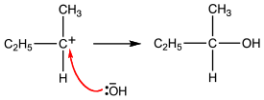
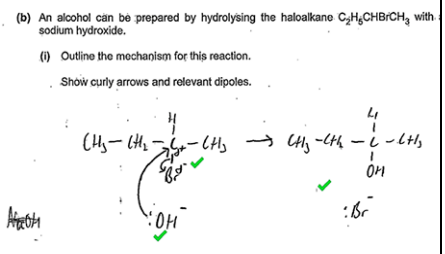
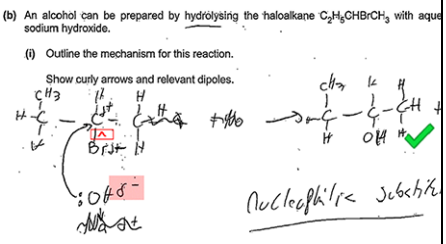
Mark scheme – Analytical Techniques

Question	Answer/Indicative content	Marks	Guidance
1	C=C/alkene peak in region 1620-1680 cm^{-1} ✓ O–H/alcohol peak in region 3200-3600 cm^{-1} ✓	2 (AO3.2×2)	**LOOK ON THE SPECTRUM** for labelled peaks which can be given credit **IGNORE** references to C-O at 1000cm^{-1}
	Total	**2**	
2	*Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question*. **Level 3 (5–6 marks)** The candidate gives thorough explanations of both spectra, and correctly identifies **X** and **Y** with a correct equation. *There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated*. **Level 2 (3–4 marks)** The candidate attempts all three scientific points but explanations are incomplete. **OR** Explains two scientific points thoroughly with few omissions. **AND** Attempts a feasible structure based on deduction from correct M_r. *There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence* **Level 1 (1–2 marks)** The candidate gives a simple description based on at least two of the main scientific points. **OR** Gives a thorough description and explanation of one of the scientific points. *There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant*. **0 marks** *No response or no response worthy of credit*.	6 (AO2.5×1) (AO3.1×2) (AO3.2×3)	**Indicative scientific points** **LOOK AT THE SPECTRA** for labelled peaks <u>Mass Spectrum</u> • M^+ or molecular ion of 86 • *m/z* = 43 shows CH_3CO^+ **OR** $C_3H_7^+$ <u>IR Spectrum</u> • IR shows no broad absorption at 2500–3300 cm^{-1} so no O–H bond **AND** not a carboxylic acid • IR shows absorption at 1700 cm^{-1} for C=O bond **OR** indicates a ketone/aldehyde present <u>Identification and Equation</u> • **X** must be a secondary alcohol, since refluxing a secondary alcohol with acidified potassium dichromate (VI) forms a ketone **OR** primary alcohol → carboxylic acid **AND** tertiary alcohol would not be oxidised. • **X** is $(CH_3)_2CHCHOHCH_3$ **OR** compound **E** **OR** 3-methylbutan-2-ol • **Y** is $(CH_3)_2CHCOCH_3$ **OR** 3-methylbutan-2-one *Equation* $(CH_3)_2CHCHOHCH_3 + [O] \rightarrow (CH_3)_2CHCOCH_3 + H_2O$ **<u>Examiner's Comments</u>**

					* This was a challenging problem-solving question, relying on candidates to make use of all of the information provided to determine the structure. Very few candidates made no attempt at all at this question. The most common error was incorrectly identifying the peak at 3000 cm^{-1} as O-H from a carboxylic acid, despite it being indicated on the data sheet that this would be a broad peak. It suggested that candidates were not familiar with looking at spectra and understanding what data it gave. Candidates should also be reminded when answering these types of question that they should give the structures, not just molecular formulae, where possible.
			Total	**6**	
3	a	i	Molecular mass ✓	1(AO1.1)	**IGNORE** 'relative' **IGNORE** 'molecular ion' alone, answer must relate to **mass** **ALLOW** M_r / molar mass **Examiner's Comments** This was generally well answered. The most common incorrect answer was atomic mass.
		ii	**Y**: $CH_3CH_2CH_2CH_2CH_2^+$✓ **Z**: $CH_3CH_2CH_2^+$✓ ***If positive charge is missing*** *but the structures of* ***Y AND Z*** *are correct, award one mark*	2(AO3.2 ×2)	**FOR ONE MARK** **ALLOW** $C_5H_{11}^+$ **AND** $C_3H_7^+$ **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **Examiner's Comments** Most students gained one mark on this question as they omitted the + sign or wrote the molecular formula instead of the structural formula.
	b	i	 ✓	1(AO1.1)	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **Examiner's Comments** This was well answered by most candidates

		ii	**Similarity** Both have a peak at (*m/z* =) 198 (X) **OR** 71 (Y) **OR** 29 ✓ **Difference** 2-iodo-2-methylbutane has **no** peak at (*m/z* =) 43 (Z) ✓	2(AO3.2 ×2)	**ALLOW** same molecular ion peak / M_r **IGNORE** statements where no specific ion peak is suggested e.g. "different ion peaks" **Examiner's Comments** Most candidates answered the similarity part correctly, many wrote vague answers to the difference and were not specific. A common error focused on the peak at m/z = 71, very few recognised that the Z peak at 43 would not be present for 2-iodo-2-methylbutane
			Total	**6**	
4		i	**ANNOTATE ANSWER WITH TICKS AND CROSSES** --- **Curly arrows 2 marks** curly arrow from OH− to C atom of C–Br bond ✓ dipole shown on C−Br bond, $C^{\delta+}$ and $Br^{\delta-}$, **AND** curly arrow from C–Br bond to Br atom  **IGNORE** incorrect R groups for curly arrow marks **IGNORE** presence of Na^+/Na but OH^- needed i.e. Na^+OH^-; $NaOH^-$ can be allowed with correct use of curly arrow --- **Products 1 mark** correct organic product **AND** Br^- ✓  **IGNORE** presence of Na^+ but Br^- needed i.e. Na^+Br^-/$NaBr^-$ can be allowed **BUT** NaBr does **NOT** show Br^- **NOTE**: curly arrows can be straight, snake-like, etc. but **NOT** double headed or half headed arrows	**3**	**1st curly arrow must** • go to the C of C–Br **AND** • start from, **OR** be traced back to **any point across width** of lone pair on O of OH^-  • **OR** start from – charge **on O** of ^-OH ion  *(Lone pair **NOT** needed if curly arrow shown from O^-)* **2nd curly arrow** must start from, **OR** be traced back to, **any part of** C–Br bond and go to Br  --- **ALLOW** S_N1 mechanism for 2 curly arrow marks **First mark** Dipole shown on C–Br bond, $C^{\delta+}$ and $Br^{\delta-}$, **AND** curly arrow from C–Br bond to Br atom  **Second mark** Curly arrow from OH^- **AND** to correct carbocation 

					Use curly arrow criteria in guidance above **<u>Examiner's Comments</u>** As with 25(a)(i), this question rewarded the well-prepared candidate. The large number of proposed mechanisms showed little resemblance to the accepted mechanism for nucleophilic substitution. Mechanisms were often seen showing curly arrows going in the wrong direction and between the wrong bonds and atoms, charges and dipoles were often incorrect, and partial changes used where full charges were required. Two exemplars are shown. The first exemplar shows clear curly arrows, the role of the lone pair and all charges correct. The second exemplar shows a typical muddled response. Although the curly arrow from the hydroxide ion has been accurately drawn, the hydroxide ion has a partial charge rather than a - charge. There is also no curly arrow showing breaking of the C–Br bond. The only mark available is for the correct organic product and a Br^- ion. Some mechanisms were so poor that it was impossible to credit many candidates with any marks. Writing mechanisms is an important skill in organic chemistry and it is recommended that candidates learn and practice their writing. **Exemplar 7**  (b) An alcohol can be prepared by hydrolysing the haloalkane $C_2H_5CHBrCH_3$ with sodium hydroxide. (i) Outline the mechanism for this reaction. Show curly arrows and relevant dipoles. **Exemplar 8**

					
		ii	**Disappearance** of peak at 500-800 cm^{-1} **OR** C–Br peak ✓ Appearance of peak at 3200-3600 cm^{-1} **OR alcohol** O–H peak	**2**	**ALLOW** value within range 500–800 $cmcm^{-1}$ **ALLOW** value within range 3200–3600 $cmcm^{-1}$ **DO NOT ALLOW** responses that only describe the spectrum shown **Examiner's Comments** This part discriminated very well with able candidates identifying that the absorption for the C–Br bond would disappear, with a new peak appearing for the alcohol O–H bond. A significant number of candidates did not seem to understand what was required, with many interpreting the spectrum as that of the alcohol, rather than predicting how the spectrum would change during the reaction. A common error was to interpret the absorption for a C–H bond at ~3000 cm^{-1} as that of an O–H bond.
			Total	**5**	
5			*Please refer to the marking instructions on page 5 of the mark scheme for guidance on how to mark this question.* **Level 3 (5-6 marks)** A comprehensive description including most of the evidence to justify the correct structure of **F** (accept *cis* or *trans*). *There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.* **Level 2 (3–4 marks)** The candidate attempts all three scientific points, but explanations are incomplete. **OR** Explains two scientific points thoroughly with few omissions. **AND** an attempt at a feasible structure based on deduction from	6	**LOOK AT THE SPECTRA** for labelled peaks **Indicative scientific points may include:** **Empirical formula** • empirical formula = C_4H_6O element | % mass | Ar | moles | ratio C | 68.6 | 12 | 5.72 | 4 H | 8.6 | 1 | 8.60 | 6 O | 22.8 | 16 | 1.43 | 1 **IR and spectra and molecular formula** • infrared absorption; 1630–1820 cm^{-1}, due to C=O

correct molecular formula
There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.

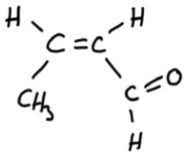
Level 1 (1–2 marks)
The correct empirical formula
AND a simple description based on at least one of the main scientific points.
OR
The candidate explains one scientific point thoroughly with few omissions.
There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.

0 marks No response or no response worthy of credit.

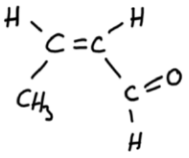
(aldehyde/ketone/carbonyl group)
- molar mass = 70 g mol^{-1} (mass spectrum molecular ion peak *m/z* = 70)
- molecular formula = C_4H_6O

Functional groups, structure and stereochemistry

- alkene / C=C
- aldehyde / −CHO ($C_3H_5^+$ fragment)
- mass spectrum; peak at 41 due to $C_3H_5^+$ (loss of CHO)
- *E/Z or cis-trans* isomer: *E/Z or cis-trans* isomer:



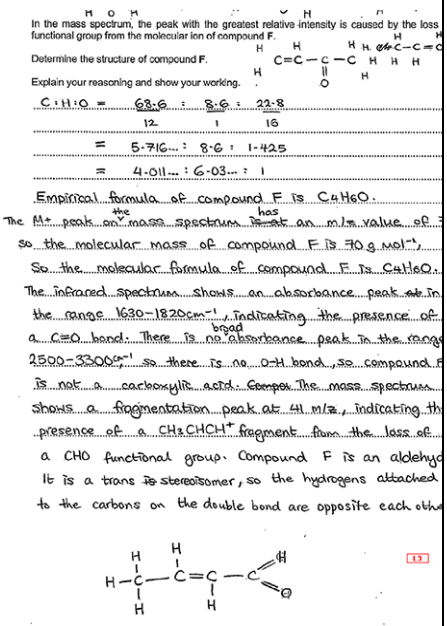
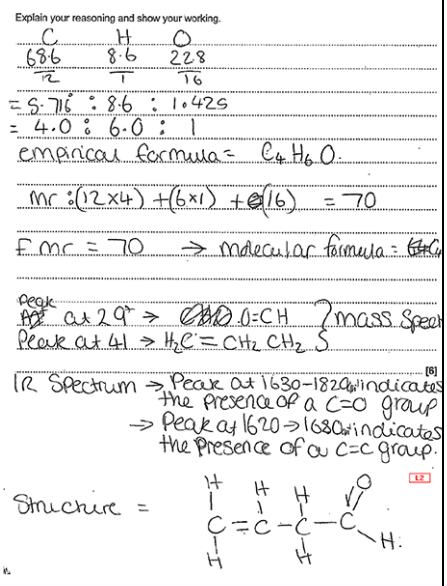
cis

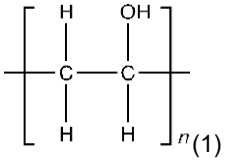


trans (correct structure)

Examiner's Comments

This question was a good discriminator. Most candidates were able to deduce the empirical formula and the C=O peak on the IR spectrum. However, many mistook the C-H peaks around 3000 cm^{-1} for an alcohol O-H peak or assumed from the empirical formula that it was an alcohol so made the spectra 'fit' their hypothesis. At AS, the exposure of candidates to IR and spectra is not as comprehensive as in the second year of A Level and this was evident. There was very little annotation of the spectra and candidates should be encouraged to do this as it is helpful to them in their deductions (and to the examiners for crediting marks). Analysis of the IR spectrum was much more detailed than the mass spectrum. Most candidates just referred to the molecular ion peak and made no attempt, or an incorrect attempt, at discerning the peak at 41. Those that did quickly realised what the structure was and gained 5 or 6 marks. Some candidates, despite ascertaining that a *trans* stereoisomer should be drawn,

					drew the *cis* version instead. **Exemplar 5**  This candidate has very logically worked through all the information provided and has come up with the correct structure from the deductions. **Exemplar 6**  Like most candidates, the crucial information about F being a *trans* isomer was not picked up so they drew the double bond in the wrong place.
			Total	**6**	

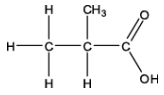
6		i	 (1)	1	
		ii	***Evidence against ethenol:*** No infrared absorption between 3200 and 3600 cm^{-1} from O–H (1) ***Evidence for isomer:*** Infrared absorption between 1640 and 1750 cm^{-1} indicates C=O (1) Mass spectrum: fragmentation peak at *m/z* = 29 suggests CHO^+ **OR** fragmentation peak at *m/z* = 15 suggests CH_3 (1) ***Identification:*** Ethanal / CH_3CHO (1)	4	 **ignore** molecular ion peak at *m*/*z* confirms molecular mass of 44 g mol^{-1}
			Total	**5**	
7			It increases / causes / contributes to global warming **OR** C–H bonds vibrate **OR** absorb IR ✓	**1**	**ALLOW** it is a greenhouse gas / increases temp **IGNORE** ozone, radicals **OR** acid rain **Examiner's Comment:** Most candidates were awarded this straightforward mark for stating that methane is a greenhouse gas. A common error was depletion of the ozone layer.
			Total	**1**	
8	a		***Empirical / molecular formula 3 marks*** Mole ratio C : H : Br is 2.44 : 5.70 : 0.814 ✓ (Empirical formula) = C_3H_7Br ✓ **QWC** (Molecular formula) = C_3H_7Br **AND** relative mass linked to 150 evidence ✓ ***Structural isomers 2 marks*** $CH_3CH_2CH_2Br$ ✓ $CH_3CHBrCH_3$ ✓	5	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** $\frac{29.29}{12.0} : \frac{5.70}{1.0} : \frac{65.01}{79.9}$ Evidence could include a calculation of the relative mass of C_3H_7Br as 122.9 linking to M_r being less than 150 **ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous) **DO NOT ALLOW** missing H atom(s) in a displayed formula for one structure but **ALLOW** missing H atoms in

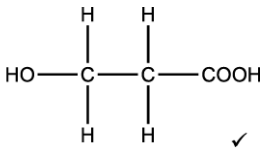
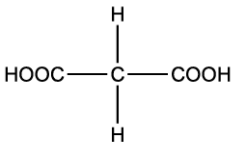
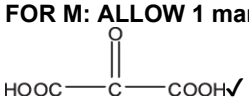
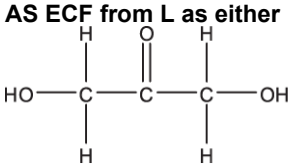
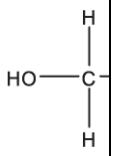
					subsequent structure **Note:** structures from an incorrect molecular formula will be credited on their merits. Please consult TL for advice on how to mark the subsequent parts of this question **Examiner's Comments** Calculation of empirical formula has always been a strength of candidates at this level. Consequently the vast majority were able to deduce the structures of the two isomers correctly. A significant number of candidates failed to secure full marks as they did not link the M_r of the empirical formula with the information about the M_r of the isomers being less than 150. Some candidates tried to use the value of 150 to determine the formula of **C** and **D**, ultimately ending up with an incorrect answer. However, error carried forward marks were allowed through subsequent parts of this question where appropriate.
	b	i	***Infrared for G 2 marks*** 1700 cm^{-1} **AND** C=O/carbonyl group ✓ (broad) 2300–3600 cm^{-1} **AND** O–H in carboxylic acid ✓	6	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **LOOK ON THE SPECTRUM** for labelled peaks which can be given credit **ALLOW** ranges from *Data Sheet*: C=O within range 1640−1750 cm^{-1}; (broad) O−H within range 2500−3300 cm^{-1}
		i	***Structures 3 marks*** $CH_3CH_2CH_2OH$ ✓ $CH_3CHOHCH_3$ ✓ CH_3CH_2COOH ✓		**ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous) **ALLOW** $CH_3CH_2CO_2H$ for carboxylic acid **IGNORE** names **IGNORE** labels **DO NOT ALLOW** missing H atom(s) in a displayed formula for one structure

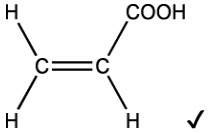
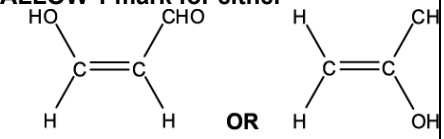
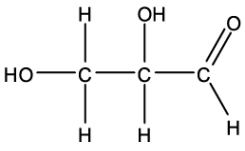
					but **ALLOW** missing H atoms in subsequent structures
		i	***Equation for formation of G 1 mark*** $C_3H_8O + 2[O] \rightarrow C_3H_6O_2 + H_2O$ ✓		**ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above in equation **Examiner's Comments** Candidates were well prepared for a structural determination question and examiners were encouraged by the number of high quality of responses to this question. Most candidates were able interpret the key peaks in the IR spectrum and identified the O-H bond of a carboxylic acid and C=O bond accurately. Most candidates identified all three structures correctly. Only the strongest responses included a correct equation for the formation of **G** by oxidation of **E**. Many responses failed to include this and others often had H_2 as the inorganic product. Candidates are advised to revise oxidation reactions of alcohols thoroughly as it is often the case that incorrect equations are frequently seen in responses to exam questions.
		ii	2 marks for correct ester. $CH_3CH_2COOCH(CH_3)_2$ ✓✓ Award 1 mark for: $CH_3CH_2COOCH_2CH_2CH_3$ **OR** Ambiguous ester: $CH_3CH_2COOC_3H_7$ ✓	2	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous) **ALLOW** $C_2H_5CO_2CH(CH_3)_2$ **IF** there is one bond and its H missing from the correct ester award 1 mark **Examiner's Comments** Most candidates were able to show the structure of the ester formed from propanoic acid (**G** and propan-2-ol **(F)** correctly. Some candidates used the incorrect alcohol, propan-1-ol **(E)** and such responses received only one of the two marks available.
			Total	**13**	

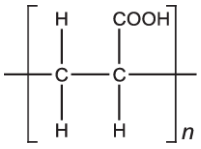
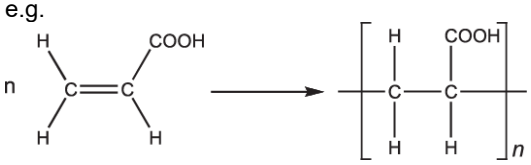
9		i	Evidence that 84 (M^+ peak) = 6 × 14 (mass of CH_2) ✓ e.g. $\frac{84}{14} = 6$	1	**IGNORE** use of molecular formula e.g (6 × 12) + (12 × 1) = 84 *(use of empirical formula required)* **Examiner's Comments** This question required candidates to use the m/z value for the molecular ion peak and the mass of the empirical formula to confirm the molecular formula of the alkene as C_6H_{12}. The most common method employed was to divide 84 by 14 to show that the molecular formula contained 6 empirical formula units. Although many candidates scored this mark, a significant proportion neglected to use the empirical formula and simply showed that the Mr of C_6H_{12} was equal to 84. Candidates should be encouraged to take note of all the supplementary information provided with a question, as it is likely to be required in the response.
		ii	***Structures of species 2 marks*** **peak I** $CH_3CH=CH$ ✓ **peak II** $CH_3CH=CHCH_2CH_2$ **OR** $CH=CHCH_2CH_2CH_3$ ✓ ***+ charge on BOTH CORRECT species 1 mark*** $CH_3CH=CH^+$ **AND** $CH_3CH=CHCH_2CH_2^+$ ✓ **peak I** **peak II**	3	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above **ALLOW** 1 mark if both correct structures are shown but in the incorrect columns **ALLOW** 1 mark for both correct structures if one or both have an 'end bond' **ALLOW** 1 mark for **BOTH** molecular formulae correct C_3H_5 **peak I** **AND** C_5H_9 **peak II** **ALLOW** 'charge mark' for + charge on **BOTH** fragments with **correct** molecular formulae **ALLOW** 'charge mark' for + charge on **BOTH CORRECT** molecular formulae **ALLOW** + change anywhere in structures **OR** outside brackets **Examiner's Comments** In general the attempts at this question

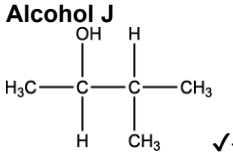
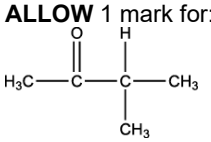
					were good, and the majority of candidates chose to show the fragments as displayed formulae. A common incorrect response for the fragment that gave rise to peak I was CH_3CH_2C. Some candidates failed to show the positive charge on each fragment, although this was less common than in previous sessions.
			Total	**4**	
10			*Please refer to marking instructions on page 4 of mark scheme for guidance on how to mark this question.* **Level 3 (5–6 marks)** A comprehensive description with all three scientific points explained thoroughly. **C** identified as a carboxylic acid containing four carbon atoms linked to the peak in the mass spectrum at 43. *The explanation makes use of all the evidence including the secondary carbocation in justifying the correct structure of C.* **Level 2 (3–4 marks)** Attempts all three scientific points but explanations may be incomplete. **OR** Explains two scientific points thoroughly with few omissions. *The analysis is clear and includes some interpretation o IR and peaks.* **Level 1 (1–2 marks)** A simple explanation based on at least two of the main scientific points. **OR** Explains one scientific point thoroughly with few errors. *The analysis is communicated in an unstructured way and includes interpretation of peaks from IR **OR** spectrum* **0 marks** – No response worthy of credit.	6	**LOOK ON THE SPECTRA** for labelled peaks. **Indicative scientific points may include:** **1. Molecular formula** Element / % mass / Ar / moles / ratio C / 54.5 / 12 / 4.54 / 2 H / 9.1 / 1 / 9.1 / 4 O / 36.4 / 16 / 2.28 / 1 • empirical formula = C_2H_4O • molecular ion peak *m/z* or Mr = 88 • molecular formula = $C_4H_8O_2$ **2. Infrared spectrum** • peak at 2500-3500 (cm^{-1}) is O–H • peak at 1630-1820 (cm^{-1}) is C=O • C is a carboxylic acid **ALLOW** stated values within the ranges above **IGNORE** references to C–O peaks **3. Identifying the carboxylic acid** • ($CH_3CH_2CH_2COOH$ **OR** $(CH_3)_2CHCOOH$) • Mass spectrum peak at *m/z* = 43 = $C_3H_7(^+)$ • secondary carbocation: $CH_3C^+HCH_3$ • compound **C**: $(CH_3)_2CHCOOH$

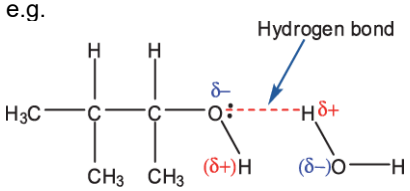
					 **IGNORE** name of carboxylic acid if structure given **Examiner's Comments** The final question on the paper was a six mark level of response question which required candidates to identify a molecule from a range of data. Most candidates were able to process the percentage composition data to arrive at an empirical formula but less able candidates then failed to use the data from the mass spectrum to arrive at the molecular formula. Candidates were generally able to use the infrared spectrum to identify the presence of –OH and C=O and could link this to the carboxyl functional group. The best candidates were able to identify the peak in the mass spectrum at 43 and to link this to a $C_3H_7^+$ fragment which led to the assumption that the carboxylic acid was butanoic acid. Many outstanding candidates were able to discuss the peak at 43 being that of a branched chain secondary carbocation and linked this to the correct branched product. Some answers were unstructured and disorganised and candidates should be encouraged when analysing data to organise their answer sequentially and discuss each piece of data in turn.
			Total	**6**	
11	a		Mole ratio C : H : O is 3.33 : 6.67 : 3.33 ✓ Empirical formula is CH_2O ✓ Molecular formula is $C_3H_6O_3$ **AND** use of 90 **OR** 3 + 30 ✓	3	**ALLOW** $\frac{40.00}{12.0} : \frac{6.67}{1.0} : \frac{53.33}{16.0}$ **ALLOW** mass of C = 0.400 × 90 **or** 36 **AND** mass of H = 0.06677 × 90 **or** 6 **AND** mass of O = 0.5333 × 90 **or** 48 **Examiner's Comments** Almost all candidates were able to correctly calculate the empirical formula of **L**. Although the majority also deduced the correct molecular formula, not all included their working. A small, but significant, proportion of candidates

					omitted this part of the question. Candidates are advised to show all working when required.
	b		**Evidence of carboxylic acid (1 mark)** **IR:** 1550–1800 cm^{-1} **AND** C=O / carbonyl **AND** 2300–3700 cm^{-1} **AND** O–H in carboxylic acid ✓ **Evidence of alcohol (1 mark)** (broad) 3200–3700 cm^{-1} linked to O–H in alcohol **OR** (is a primary) alcohol as oxidised (to a COOH) **OR** is an alcohol as it forms a carboxylic acid **OR** is an alcohol as water is eliminated. ✓ **Identifications (2 marks)** **L**:  ✓ **M**:  ✓ **Equation (1 mark)** $C_3H_6O_3 + 2[O] \rightarrow C_3H_4O_4 + H_2O$ ✓	5	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **LOOK ON THE SPECTRUM** for labelled peaks which can be given credit **ALLOW** ranges from *Data Sheet*: C=O within range 1640–1750 cm^{-1}; (broad) O–H within range 2500–3300 cm^{-1} (broad) O–H within range 3200–3550 cm^{-1} **For ALL structures:** **ALLOW** correct structural **OR** skeletal **OR** displayed formula **OR** mixture of the above **IGNORE** names …… ….. **FOR M: ALLOW 1 mark for**  **AS ECF from L as either**  **OR**  **Equation:** $C_3H_6O_3 + 4[O] \rightarrow C_3H_2O_5 + 2H_2O$ ✓ …… ….. **ALLOW** correct structural **OR** displayed

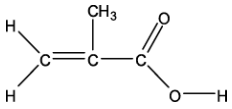
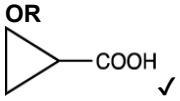
					OR skeletal formula **OR** mixture of the above in equation **Examiner's Comments** This question allowed candidates to demonstrate their knowledge and problem solving skills to tie together all the evidence provided. It was common to see candidates identify the ranges of the characteristic peaks for a carboxylic acid in the IR spectrum but a significant proportion did not identify the relevant bond that each peak referred to. Many candidates interpreted the flowchart given at the start of the question to comment on the presence of an alcohol group in **L**, and using their molecular formula from part (a), deduced structures for both **L** and **M**. The strongest candidates were also able to provide a correctly balanced equation for the formation of **M**. The most common incorrect structure for **L** was 1,3-dihydroxypropanone, however, error carried forward marks were awarded to candidates who provided the corresponding dicarboxylic acid as the oxidation product **M**.
	c		**Monomer N:** **(1 mark)**  ✓ **Polymer P:** **(1 mark)** Section showing at least one repeat unit of a polymer formed from **N** with side links ✓ e.g.	4	**For ALL structures:** **ALLOW** correct structural **OR** skeletal **OR** displayed formula **OR** mixture of the above **IGNORE** names **ALLOW 1 mark for either**  **OR** **AS ECF** from **L:**  …… **For P: ALLOW ECF** from an alkene with molecular formula $C_3H_4O_2$ **ALLOW** one or more repeat units but has to have a whole number of repeat

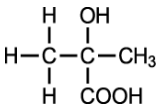
			 **Repeat units** **(1 mark)** n = 10000/72 = 139 ✓ **Equation** **(1 mark)** Balanced equation for formation of P from **N**✓ e.g. 		units **ALLOW** repeat unit with no brackets and absence of n **MUST** be a whole number. **ALLOW** 138 **OR** 140 …… **For equation, ALLOW** molecular **OR** structural **OR** skeletal **OR** displayed formulae **OR** mixture of the above e.g. **ALLOW** $n C_3H_4O_2 \rightarrow (C_3H_4O_2)_n$ n on LHS can be at any height to the left of formula **AND** n on the RHS must be a subscript (essentially below the side link if displayed / skeletal formula is used) **ALLOW** use of calculated value for n in equation e.g. $139C_3H_4O_2 \rightarrow (C_3H_4O_2)_{139}$ **Examiner's Comments** This was a very demanding question and the strongest candidates were able to identify both **N** and **P** in addition to calculating the number of repeat units the polymer. However, not all included the polymerisation equation. Some candidates who were unable to deduce a correct structure for **L** in part (b) approached this part as a 'fresh start'. Using both the molecular formula from (a) and the information in the flowchart worked out the molecular formula of **N** and built a response from there.
			Total	**12**	
12	a		**QWC**: Evidence of the **IR** absorption at 1720 (cm^{-1}) for presence of C=O / carbonyl group ✓	6	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **LOOK ON THE SPECTRUM** for labelled peaks which can be given credit **BOTH IR** at ~ 1720 (cm^{-1}) **AND** C=O required

			QWC: No carboxylic acid OH absorption in IR **OR** no peak between 2500–3300 cm^{-1} **AND** so **J** is a secondary alcohol **OR** so **K** is a ketone ✓ **Alcohol J**  ✓✓ **Compound K** Structure of a carbonyl compound that could be obtained from alcohol **J** ✓ **Equation** Balanced equation for conversion of **J** to **K** ✓ e.g. $CH_3CHOHCH(CH_3)_2 + [O] \rightarrow CH_3COCH(CH_3)_2 + H_2O$		**ALLOW** ranges from *Data Sheet*, i.e. C=O within range 1640–1750 cm^{-1}; **IGNORE** any reference to C-O absorption For structures of **J** and **K**, **ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above **IGNORE** any names given for **J** and **K** **ALLOW** 1 mark for the structure of an alcohol with the molecular formula $C_5H_{12}O$ **DO NOT ALLOW** pentan-1-ol (*primary and unbranched*) or 2-methylbutan-2-ol (*branched but tertiary*) **DO NOT ALLOW** any marks for **J** and **K** if more than one structure is given for **J** **Note:** 'sticks' in either **J** and / or **K** will lose only 1 mark **ALLOW** 1 mark for:  **IF** a structure is not given for **J** **NOTE:** structures for **J** and **K** could be awarded from the equation, even if not labelled. **ALLOW** molecular formulae in equation i.e. $C_5H_{12}O + [O] \rightarrow C_5H_{10}O + H_2O$ **DO NOT ALLOW** equations that form a carboxylic acid **Examiner's Comments** This question discriminated well and most candidates were able to score at least one mark, by identifying the C=O peak in the IR spectrum provided. The most able candidates gave succinct responses that included both the correct structures of **J** and **K** as well as a balanced equation. In addition, they included reference to the absence of a carboxylic acid O-H peak in the IR spectrum concluding that **K** must be a ketone. This marking point was missed by a large proportion of the cohort and often a branched primary alcohol for **J** and corresponding aldehyde for **K** were

					suggested. Some candidates incorrectly identified the C—H peak in the spectrum as an O—H and suggested that **K** was a carboxylic acid.
	b		**Labelled** diagram showing at least one H-bond between alcohol molecule and water ✓ e.g.  	1	**IF** diagram is not labelled **ALLOW** Hydrogen bonds / H bonds from text Diagram should include role of an O lone pair and dipole charges on each end of H bond. **IGNORE** alcohol R group, even if wrong **ALLOW** structural **OR** displayed **OR** skeletal formula **OR** mixture of the above **Examiner's Comments** The majority of candidates were able to draw a diagram to show the hydrogen bond between an alcohol and water. However, a significant proportion lacked the accuracy required at this level and failed to show the role of the lone pair. It was also common to see responses that omitted the relevant dipoles. The question asked for the inclusion of relevant dipoles and lone pairs and candidates are advised to double check diagrams to ensure these key features are not neglected.
			Total	**7**	
13		i	**bond** vibrates (more) **OR bond** bends (more) **OR bond** stretches (more) ✓	1	**BOND essential** **IGNORE** molecule vibrates / rotates Assume "It" refers to the molecule and is insufficient **DO NOT ALLOW** any reference to bond breaking **DO NOT ALLOW** a stated bond if **not** present in **C** and **F** e.g. C–O, C–H not present **Examiner's Comments** Most candidates identified that IR radiation would cause the bonds within the molecule to vibrate. However, there were many examples of vague responses such as 'they vibrate'. Candidates are advised identify the

					subject of their statement and avoid the use of words such as 'they' and 'it' in their responses.
		ii	CI_3C^+ ✓ CF_2CI^+ ✓	2	**ALLOW** 1 mark for CI_3C **AND** CF_2CI *i.e. no + charge used* **ALLOW** 1 mark for CI_3C^- **AND** CF_2CI^- *i.e. — charge used on both* **Examiner's Comments** The majorly of candidates identified the formulae of the two ions, although not all candidates specified the correct charge. Candidates should be aware that fragmentation in a mass spectrometer produces positive ions.
			Total	**3**	
14			Carboxylic acids have a broad O−H absorption at 2500−3300 (cm^{-1}) (which ketones do not)	1	
			Total	**1**	
15			**Molecular formula for G: 2 marks** Mole ratio C : H : O = $\frac{55.8}{12.0} : \frac{7.0}{1.0} : \frac{37.2}{16.0}$ **OR** 4.65 : 7.0 : 2.33 / 2.325 **OR** 2 : 3 : 1 **OR** C_2H_3O ✓ Molecular formula of **G** $C_4H_6O_2$ ✓ **Mass spectrum for G: 2 marks** Peak **X or peak 41** indicates $C_3H_5^+$ ✓ Peak **Y or peak 45** indicates $COOH^+$ ✓ **Infrared for G: 1 marks**	7	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **ALLOW** mass of C = 0.558 × 86 **or** 48 AND mass of H = 0.07 × 86 or 6 **AND** mass of O = 0.372 x 86 = 32 + charge required for each response **ALLOW** one mark if both formulae are correct but with no charge/incorrect charge **ALLOW** any possible fragments that contain C, H and / or O that have the correct mass. E.g. Peak X indicates C_2OH^+, Peak **Y** indicates $C_2H_5O^+$ Unfeasible fragments are not allowed e.g. $C_3H_9^+$ (too many H atoms) **LOOK ON THE SPECTRUM** for labelled absorbance which can be given credit Candidates must link absorbance to bond in order to gain the mark

			Peak at 1640–1750 cm^{-1} indicates presence of C=O **AND** Peak at 2500–3300 cm^{-1} (indicates the presence of) −OH group linked carboxylic acid / COOH **QWC ✓**		**ALLOW** 1700 cm^{-1} For 2500–3300 cm^{-1}, **ALLOW** 2900 cm^{-1} or any stated wavenumber with range 2500–3300 cm^{-1} **ALLOW** wavenumber range up to 2400–3500 cm^{-1}
			Structure of G: 2 marks Correct structure:  **✓✓** 1 mark for one of the following structures of $C_4H_6O_2$: $H_2C=CH—CH_2—COOH$ **OR** $H_3C—CH=CH—COOH$ **OR**  **✓**		**ALLOW** structural, skeletal or displayed formula. **DO NOT ALLOW ECF** from incorrect molecular formula **Examiner's Comments** This question allowed the candidates to demonstrate their understanding of the more complex aspects of the course and use their problem-solving skills to tie together the all of the evidence. The calculation of the empirical formula was completed well and most candidates were able to determine the molecular formula of **G**. Many of the more able candidates were able to identify one, if not both, of the ions responsible for peaks **X** and **Y** in the mass spectrum. A number of candidates were able to show correct fragments but omitted the positive charge. Candidates should be reminded to include the correct charge when suggesting particles responsible for peaks in mass spectra. The majority of candidates were able to recognise the characteristic absorptions in the IR spectrum. The strongest responses attributed these peaks to the appropriate bonds and deduced that **G** was a carboxylic acid. Two marks were available for the structure of **G**. The most able candidates were able to interpret all the information and provide the correct branched carboxylic acid. Some candidates recognised that the number of hydrogen atoms present suggested the presence of a carbon- carbon double bond, but suggested a straight

					chain compound. Other candidates provided a cyclic carboxylic acid. These two approaches were awarded one mark. The most common incorrect structure seen for **G** was butanoic acid.
			Total	**7**	
16			***Use of elemental analysis data*** | | C | H | O | | % | 46.1 | 7.7 | 46.2 | | mol | 3.84 | 7.7 | 2.89 | | ratio | 1.33 | 2.66 | 1 | atom ratio with calculation empirical formula = $C_4H_8O_3$ ***IR spectrum*** (very) broad absorption 2500–3300 cm^{-1} (CO**OH**) **AND** absorption 1640–1750 cm^{-1} (C=O) absorption 3450 cm^{-1} (alcohol **−OH**) ***Identification*** conclusion from data: compound contains −COOH and −OH (empirical formula confirms no other C=O than in COOH) in place of the previous chlorine-containing groups 	5	**ALLOW** any values given within ranges given on Data Sheet **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous
			Total	**5**	
17			** Please refer to the marking instruction point 10 for guidance on how to mark this question.* **(Level 3)** Candidate provides a method for identifying the alcohols **AND** provides all supporting evidence from IR spectrum **AND** gives details of reagents and conditions and correct equations. *The explanation is detailed and well structured. The information is clearly supported by details of reactions and evidence of oxidation product.* (5–6 marks)	6	**Indicative scientific points may include** **Identification of alcohols** Based on recognition of alcohols as primary, secondary and tertiary (stated or implied by method). Basic procedure involves reflux followed by use of IR to identify different oxidation products. **Reactions** • stated reagents ($H^+/Cr_2O_7^{2-}$ and conditions (reflux))

			(Level 2) Candidate provides a basic method **AND** provides some supporting evidence from IR spectrum **AND** gives details of reagents and conditions with some attempt at equations. *The explanation has some structure. The information is supported by some details of reactions and evidence from IR spectrum.* (3–4 marks) **(Level 1)** Candidate attempts to describe a basic method **AND** gives some supporting evidence from IR spectrum **OR** details of reagents and conditions with some attempt at equations. *The explanation is basic and lacks structure. The information is supported by limited evidence from the reactions and oxidation products and would not lead to identification.* (1–2 marks) No response or no response worthy of credit. (0 marks)		• equations using [O] including structural formulae $CH_3CH_2CHOHCH_3 + [o] \rightarrow CH_3CH_2COCH_3 + H_20$ $CH_3CH_2CH_2CH_2OH + 2[o] \rightarrow CH_3CH_2CH_2COOH + H_2o$ **Identification of oxidation product** • IR: carboxylic acid from broad OH absorption and C=O • IR: carbonyl / ketone from C=O and no OH • tertiary alcohol from lack of C=O and OH peak in IR **OR** no colour change in reflux.
			Total	**6**	
18			**I** = $C_4H_{10}^+$ (1) **II** = $C_3H_7^+$ (1) **III** = $C_2H_5^+$ (1) $C_3H_7^+$ could be $CH_3CH_2CH_2^+$ or $CH_3CHCH_3^+$ **OR** $C_3H_7^+$ could be from $CH_3CH_2CH_2CH_3$ or $CH_3CH(CH_3)_2$ (1) $CH_3CH_2^+$ could only be from $CH_3CH_2CH_2CH_3$ (1)	5	**THROUGHOUT:** **if any charge is missing,** **do not allow** 1st formula but allow subsequent formulae by **ecf** **allow** + charge anywhere
			Total	**5**	
19			(broad) peak at 3300–3600 (cm^{-1}) for O–H (therefore A or C) (1) molar ratio: C : H : O $\frac{78.94}{12.0} : \frac{10.53}{1.0} : \frac{10.53}{16.0}$ **OR** 6.58 : 10 (1) 10 : 16 : 1 **OR** $C_{10}H_{16}O$, therefore C (1)	3	**allow** 3200–3600 cm^{-1} **ignore** references to the peak at ~2900 for C−H **allow** annotation of the spectrum to identify the bond responsible for the peak instead of quoting the wavenumber.

					Conclusion may also follow from empirical formula followed by IR data.
			Total	**3**	