AC8D Analytical Techniques: Depth and Exam Drill

AQA 7405 · Calculator allowed · about 150 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 Analytical techniques used in A-level chemistry include mass spectrometry, infrared spectroscopy and NMR spectroscopy.

(a) State what is meant by the term 'base peak' in a mass spectrum. **(1)**

(b) State what is meant by the 'fingerprint region' of an infrared spectrum, including its typical wavenumber range. **(1)**

(c) State what is meant by 'chemical shift' in NMR spectroscopy, including its units. **(1)**

(Total for Question 1 is 3 marks)

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2 1,2-dibromoethane, BrCH2CH2Br, is analysed by mass spectrometry. Bromine has two naturally occurring isotopes, 79Br (abundance approximately 50.7%) and 81Br (abundance approximately 49.3%). Use Ar values C = 12.0, H = 1.0, Br = 79.9 unless told otherwise, and use 79Br = 79 and 81Br = 81 exactly for nominal mass (m/z) calculations.

(a) Calculate the Mr of 1,2-dibromoethane using the Ar values given, to 1 decimal place. **(2)**

(b) The molecular ion region of the mass spectrum shows three peaks. Using the two bromine isotopes and their abundances, deduce the three nominal m/z values in this region and calculate the ratio of their peak heights, giving the ratio to 2 significant figures. **(4)**

(c) A fragment ion peak appears at m/z = 107. This fragment forms by loss of a bromine atom (as a radical, Br dot) from the lowest-mass molecular ion peak at m/z = 186. Deduce the molecular formula of this fragment ion and suggest a plausible structure for it. **(3)**

(Total for Question 2 is 9 marks)

3 Trichloromethane (chloroform), CHCl3, is used as a solvent and is analysed by mass spectrometry. Chlorine has two isotopes, 35Cl (approximately 75%) and 37Cl (approximately 25%).

(a) Calculate the Mr of CHCl3 using Ar: C = 12.0, H = 1.0, Cl = 35.5, to 1 decimal place. **(2)**

(b) Deduce the four nominal m/z values expected for the molecular ion region (M, M+2, M+4, M+6), taking 35Cl = 35 and 37Cl = 37 exactly. **(2)**

(c) Using the binomial expansion of $(3/4 + 1/4)^3$ for the three chlorine atoms, calculate the ratio of peak heights for M : M+2 : M+4 : M+6. Give the ratio in whole numbers. **(4)**

(Total for Question 3 is 8 marks)

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4 A laboratory technician needs to distinguish three colourless liquids recovered after a synthesis: propan-1-amine (CH3CH2CH2NH2), propanenitrile (CH3CH2CN) and propan-1-ol (CH3CH2CH2OH), all with similar boiling points. Each is analysed by infrared spectroscopy. Typical absorption ranges: N-H (primary amine) 3300-3500 cm-1 (two bands, medium); C-N triple bond (nitrile) 2200-2260 cm-1 (sharp, medium to weak); O-H (alcohol) 3230-3550 cm-1 (broad, strong); C-H 2850-3100 cm-1.

(a) Identify which functional group gives an absorption in the 2200-2260 cm-1 region, and explain why this absorption is medium to weak in intensity compared with a typical C=O absorption. **(2)**

(b) Explain how infrared spectroscopy alone could distinguish propan-1-amine from propan-1-ol, given both show absorptions in overlapping regions between 3230 and 3550 cm-1. **(3)**

(c) A fourth unknown sample, Q, shows a single sharp absorption at 2245 cm-1 and no absorption anywhere in the 3230-3550 cm-1 region (other than the normal C-H stretches below 3100 cm-1). Identify the functional group present in Q and explain your reasoning, including why no N-H or O-H bands are seen. **(3)**

(Total for Question 4 is 8 marks)

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5 Three isomers with molecular formula C4H10O are butan-1-ol, CH3CH2CH2CH2OH, 2-methylpropan-2-ol (tert-butanol), (CH3)3COH, and ethoxyethane (diethyl ether), CH3CH2OCH2CH3. Approximate 13C shift ranges: C-C (alkyl carbon, no adjacent O) 5-40 ppm; C-O (carbon bonded to oxygen) 50-90 ppm.

(a) Deduce the number of 13C NMR peaks expected for each of the three isomers. **(3)**

(b) Both 2-methylpropan-2-ol and ethoxyethane give exactly two 13C peaks. Using the shift ranges given, describe the expected approximate region of each peak for 2-methylpropan-2-ol, explaining your reasoning. **(3)**

(c) Explain why the number of 13C peaks alone cannot distinguish 2-methylpropan-2-ol from ethoxyethane, and suggest one additional piece of data (from a different technique) that would allow the two to be distinguished. **(3)**

6 1-bromo-3-methylbutane (isoamyl bromide), (CH3)2CHCH2CH2Br, gives a 1H NMR spectrum with four proton environments: a doublet at 0.95 ppm (6H), an overlapping multiplet region at 1.55-1.75 ppm (3H, from two different carbons), and a triplet at 3.40 ppm (2H). Molecular formula C5H11Br.

(a) Using the n+1 rule, predict the splitting pattern of the CH2Br protons (2H) and of the (CH3)2 protons (6H), stating the number of neighbouring protons responsible for each pattern. **(4)**

(b) The CH proton and the middle CH2 protons overlap in the multiplet region between 1.55 and 1.75 ppm, with total integration 3H. Explain, in terms of neighbouring protons, why these two signals are complex multiplets rather than simple doublets or triplets. **(3)**

(c) Calculate the total number of hydrogen atoms shown by the integration values given (6H + 3H + 2H) and confirm this is consistent with the molecular formula C5H11Br. **(2)**

(Total for Question 6 is 9 marks)

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7 A student uses HPLC to determine the concentration of caffeine in an energy drink. A calibration curve is constructed using five caffeine standards of known concentration, giving a line of best fit: peak area = 2350c + 120, where c is the concentration of caffeine in mg per 100 cm3. A 1.00 cm3 sample of the energy drink, diluted by a factor of 10 before injection, gives a peak area of 8720. One can of the energy drink contains 250 cm3.

(a) State one reason why the sample was diluted before injection into the HPLC. **(1)**

(b) Calculate the concentration of caffeine, in mg per 100 cm3, in the diluted sample injected, using the calibration equation. **(3)**

(c) Hence calculate the concentration of caffeine, in mg per 100 cm3, in the original (undiluted) energy drink. **(2)**

(d) Calculate the total mass of caffeine, in mg, in one 250 cm3 can of the energy drink. **(2)**

(Total for Question 7 is 8 marks)

8 In the HPLC analysis in Question 7, each calibration standard was prepared by weighing solid caffeine on a balance reading to ± 0.001 g, then making up to volume in a 100 cm3 volumetric flask (uncertainty ± 0.08 cm3). The 1.00 cm3 aliquot of the diluted energy drink sample was measured using a pipette with an uncertainty of ± 0.02 cm3. The concentration of caffeine in the original drink was calculated as 36.6 mg per 100 cm3, with a combined percentage uncertainty for the full determination of approximately 5%.

(a) A calibration standard is prepared by weighing 0.045 g of caffeine (uncertainty ± 0.001 g) and making up to 100 cm3 (uncertainty ± 0.08 cm3). Calculate the percentage uncertainty in the mass measurement and in the volume measurement, each to 2 significant figures. **(4)**

(b) Calculate the total percentage uncertainty in the concentration of this calibration standard, by summing the individual percentage uncertainties from part (a). **(2)**

(c) Calculate the percentage uncertainty in the 1.00 cm3 pipette measurement (uncertainty ± 0.02 cm3), and explain why this uncertainty has a greater effect on the overall result than the volumetric flask uncertainty calculated in part (a). **(3)**

(d) Using the combined percentage uncertainty of approximately 5% for the full determination, express the caffeine concentration of the original drink (36.6 mg per 100 cm3) with its absolute uncertainty, to an appropriate number of significant figures. **(2)**

(Total for Question 8 is 11 marks)

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9 A food scientist separates a mixture of three synthetic food colourings using thin-layer chromatography (TLC) on a silica plate. The solvent front travels 9.6 cm from the baseline. Reference standards run under the same conditions give Rf values: tartrazine 0.50, sunset yellow 0.65, allura red 0.38.

(a) In the mixture, the spot corresponding to tartrazine travels 4.8 cm from the baseline. Calculate the Rf value for tartrazine. **(2)**

(b) A second, unknown spot in the mixture travels 6.24 cm from the baseline. Using the reference Rf values given, identify this dye, showing your calculation. **(3)**

(c) The student repeats the experiment on a different day and obtains Rf values that are systematically about 0.03 higher for all three dyes, while the differences between the dyes remain consistent. Suggest one likely cause of this systematic shift, and explain how a systematic error like this differs from a random error. **(2)**

(d) Food colourings must be identified accurately for regulatory compliance. Suggest one improvement to the experimental method that would increase confidence in identifying an unknown dye by TLC, other than simply repeating the measurement. **(2)**

(Total for Question 9 is 9 marks)

10 An unknown liquid aldehyde, R, has molecular formula C5H10O (Mr = 86). The following data were obtained. Mass spectrum: molecular ion peak at m/z = 86; major fragment peak at m/z = 57, formed by loss of a fragment of mass 29 from the molecular ion. Infrared spectrum: weak doublet absorptions at 2720 cm-1 and 2820 cm-1; strong absorption at 1725 cm-1; no absorption between 2500 and 3550 cm-1. 1H NMR spectrum: doublet at 0.98 ppm (6H); multiplet at 2.20 ppm (1H); signal at 2.35 ppm (2H); triplet at 9.75 ppm (1H). Using all the data provided, deduce the structure of R. Your answer should use evidence from the mass spectrum, the infrared spectrum and the 1H NMR spectrum to justify the functional group present, the carbon skeleton, and the final structure.

(Total for Question 10 is 6 marks)

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11 A student oxidises 2-methylpropan-1-ol, (CH3)2CHCH2OH (Mr = 74.0), using excess acidified potassium dichromate(VI) under reflux, to form 2-methylpropanoic acid, (CH3)2CHCOOH (Mr = 88.0), as product P. The student uses 7.40 g of 2-methylpropan-1-ol and isolates 6.98 g of P.

(a) Write a balanced equation, using [O] to represent the oxidising agent, for the oxidation of 2-methylpropan-1-ol to 2-methylpropanoic acid. **(1)**

(b) Calculate the amount, in moles, of 2-methylpropan-1-ol in 7.40 g, and hence calculate the maximum theoretical mass of 2-methylpropanoic acid that could be formed. **(3)**

(c) The student isolates 6.98 g of product. Calculate the percentage yield. **(2)**

(d) The student records the infrared and 1H NMR spectra of the isolated product to confirm it is the carboxylic acid rather than the aldehyde (an intermediate in the oxidation). The infrared spectrum shows a broad absorption at 2500-3300 cm-1 and a peak at 1710 cm-1. The 1H NMR spectrum shows a doublet at 1.20 ppm (6H), a multiplet at 2.55 ppm (1H), and a broad singlet at 11.9 ppm (1H). Explain how this data confirms the product is the carboxylic acid and not the aldehyde. **(4)**

(e) Suggest one reason, in terms of reaction conditions, why using excess oxidising agent under reflux (rather than distillation) favours formation of the carboxylic acid rather than stopping at the aldehyde. **(1)**

(Total for Question 11 is 11 marks)

Mark scheme · AC8D Analytical Techniques: Depth and Exam Drill

Question 1

- (a) **B1** the peak in a mass spectrum with the greatest height (relative abundance), corresponding to the most stable/most abundant fragment ion, usually given a relative abundance of 100% oe
- **(a) Answer: The tallest peak in the mass spectrum, corresponding to the most abundant ion (given a relative abundance of 100%).**
- (b) **B1** the region below about 1500 cm-1 (typically 500-1500 cm-1) containing a complex pattern of absorptions unique to a particular compound, used to confirm its identity by comparison with a reference spectrum oe
- **(b) Answer: The region below about 1500 cm-1, whose complex pattern of absorptions is unique to a compound and used to confirm its identity.**
- (c) **B1** the position of an NMR signal relative to the reference compound TMS (set at 0), measured in parts per million (ppm) oe
- **(c) Answer: The position of an NMR signal relative to TMS (set at 0 ppm), measured in parts per million.**

Question 2

- (a) **M1** correct substitution: 2(12.0) + 4(1.0) + 2(79.9)
- (a) **A1** 187.8 (cao)
- **(a) Answer: Mr = 187.8**
- (b) **M1** identify the three nominal m/z values as 186 (both 79Br), 188 (one 79Br, one 81Br) and 190 (both 81Br)
- (b) **M1** probability of both 79Br = 0.507^2 = 0.257 and both 81Br = 0.493^2 = 0.243
- (b) **M1** probability of one of each = 2 x 0.507 x 0.493 = 0.500
- (b) **A1** ratio m/z 186 : 188 : 190 = approximately 1.1 : 2.1 : 1.0 (accept any value awrt this, or the simplified ratio 1:2:1) cao
- **(b) Answer: m/z 186 : 188 : 190 is approximately 1.1 : 2.1 : 1.0 (approximately 1:2:1)**
- (c) **M1** fragment formula is C2H4Br+ (i.e. CH2CH2Br+)
- (c) **A1** mass check: 2(12) + 4(1) + 79 = 107, consistent with m/z = 107 (cao)
- (c) **B1** suggests a valid structure, e.g. the bromoethyl cation +CH2CH2Br (any structure with formula C2H4Br+ accepted)
- **(c) Answer: C2H4Br+, e.g. the bromoethyl cation +CH2CH2Br**

Question 3

- (a) **M1** correct substitution: 12.0 + 1.0 + 3(35.5)
- (a) **A1** 119.5 (cao)
- **(a) Answer: Mr = 119.5**
- (b) **M1** M (three 35Cl) = 12 + 1 + 3(35) = 118 and M+6 (three 37Cl) = 12 + 1 + 3(37) = 124
- (b) **A1** M+2 = 120 and M+4 = 122, giving all four values 118, 120, 122, 124 (cao)
- **(b) Answer: 118, 120, 122, 124**
- (c) **M1** expand the four binomial terms: $(3/4)^3$, $3(3/4)^2(1/4)$, $3(3/4)(1/4)^2$, $(1/4)^3$
- (c) **M1** evaluate each term as a fraction of 64: 27/64, 27/64, 9/64, 1/64
- (c) **M1** convert to whole-number ratio by comparing numerators over the common denominator 64
- (c) **A1** M : M+2 : M+4 : M+6 = 27 : 27 : 9 : 1 (cao)
- **(c) Answer: 27 : 27 : 9 : 1**

Question 4

- (a) **B1** the carbon-nitrogen triple bond in a nitrile group (C-N triple bond)
- (a) **B1** the nitrile bond stretch produces a smaller change in dipole moment than a C=O stretch, so it absorbs infrared radiation less strongly, giving a weaker absorption oe
- **(a) Answer: The nitrile C-N triple bond; it gives a weaker absorption because its stretch causes a smaller change in dipole moment than a C=O stretch.**
- (b) **B1** propan-1-amine shows two distinct N-H bands (from symmetric and asymmetric N-H stretching), rather than one broad band
- (b) **B1** propan-1-ol shows a single, broad, strong O-H absorption across its range, generally broader than the sharper amine N-H bands
- (b) **B1** comparing the number and shape (broad versus two sharper bands) of the absorptions in this region allows the two compounds to be distinguished, despite the overlapping wavenumber ranges
- **(b) Answer: Propan-1-amine gives two sharper N-H bands; propan-1-ol gives one broad O-H band. Comparing band number and shape distinguishes them.**
- (c) **B1** a nitrile group (C-N triple bond) is present, shown by the sharp absorption at 2245 cm-1, within the nitrile range
- (c) **B1** the absence of any band in the 3230-3550 cm-1 region confirms there is no N-H or O-H bond present, ruling out an amine or an alcohol
- (c) **B1** this is consistent with Q being a nitrile such as propanenitrile, since a nitrile carbon has no attached N-H or O-H bonds to absorb in that region
- **(c) Answer: A nitrile group (C-N triple bond); the 2245 cm-1 band confirms it and the absence of any 3230-3550 cm-1 absorption rules out N-H or O-H.**

Question 5

- (a) **B1** butan-1-ol: 4 peaks (four different, non-equivalent carbon environments)
- (a) **B1** 2-methylpropan-2-ol: 2 peaks (three equivalent CH3 carbons related by symmetry, plus the quaternary C-OH carbon)
- (a) **B1** ethoxyethane: 2 peaks (two equivalent CH3 carbons and two equivalent OCH2 carbons, related by the symmetry of the molecule)
- **(a) Answer: Butan-1-ol: 4 peaks; 2-methylpropan-2-ol: 2 peaks; ethoxyethane: 2 peaks.**
- (b) **B1** the quaternary carbon bonded to the OH group appears in the C-O range, 50-90 ppm, since it is directly bonded to the electronegative oxygen
- (b) **B1** the three equivalent CH3 carbons appear in the lower, C-C (alkyl) range, 5-40 ppm, since they are not directly bonded to oxygen
- (b) **B1** the carbon bonded to oxygen is deshielded relative to the plain alkyl carbons, which is why it appears at the higher shift oe
- **(b) Answer: The C-OH quaternary carbon falls in the 50-90 ppm C-O range; the three CH3 carbons fall in the 5-40 ppm C-C range.**
- (c) **B1** both compounds give exactly two 13C peaks (as shown in (a)), so the peak count alone is ambiguous between them
- (c) **B1** infrared spectroscopy: 2-methylpropan-2-ol shows a broad O-H absorption (in the range 3230-3550 cm-1) that is absent from ethoxyethane, which has no O-H bond
- (c) **B1** alternatively, 1H NMR: 2-methylpropan-2-ol shows a 9H singlet plus an exchangeable 1H O-H signal, whereas ethoxyethane shows a 6H triplet and a 4H quartet with no exchangeable proton, giving a clear distinction
- **(c) Answer: Both give two 13C peaks, so peak count alone is inconclusive; comparing the IR O-H band (present only in the alcohol) or the 1H NMR pattern would distinguish them.**

Question 6

- (a) **B1** CH2Br protons are adjacent to 2 protons (the middle CH2 group), so n = 2 gives a triplet
- (a) **B1** the (CH3)2 protons are each adjacent to 1 proton (the CH group), so n = 1 gives a doublet
- (a) **B1** the CH2Br triplet appears at a relatively high shift (approximately 3.40 ppm), deshielded by the adjacent electronegative bromine
- (a) **B1** the (CH3)2 doublet appears at a relatively low shift (approximately 0.95 ppm), typical of alkyl CH3 groups away from any electronegative atom
- **(a) Answer: CH2Br: triplet (2H, coupled to 2 neighbouring H); (CH3)2: doublet (6H, coupled to 1 neighbouring H).**
- (b) **B1** the CH proton is adjacent to two different, non-equivalent sets of neighbouring protons: the 6H of the two CH3 groups and the 2H of the neighbouring CH2 group, so simple n+1 splitting from a single neighbouring group does not apply, giving a complex multiplet
- (b) **B1** the middle CH2 protons are also adjacent to two different sets of neighbours, the CH proton (1H) and the CH2Br protons (2H), again producing overlapping splitting rather than a single clean pattern
- (b) **B1** because the resulting multiplets from the CH and the middle CH2 fall in a similar, overlapping shift range, they merge into one broad multiplet region integrating for 3H overall
- **(b) Answer: Both the CH and middle CH2 protons couple to two different neighbouring proton sets, giving complex, overlapping multiplets rather than a simple doublet or triplet.**
- (c) **M1** sum the integrations: 6 + 3 + 2
- (c) **A1** = 11H, consistent with C5H11Br (cao)
- **(c) Answer: 11H, consistent with C5H11Br**

Question 7

- (a) **B1** to bring the concentration (and resulting peak area) within the linear range of the calibration curve, avoiding detector saturation or overloading the column oe
- **(a) Answer: To bring the concentration within the linear range of the calibration curve and avoid overloading the column or detector.**
- (b) **M1** rearrange: c = (8720 - 120)/2350
- (b) **M1** = 8600/2350
- (b) **A1** 3.66 mg per 100 cm3 (awrt 3.66)
- **(b) Answer: 3.66 mg per 100 cm3**
- (c) **M1** multiply by the dilution factor: 3.66 x 10
- (c) **A1** 36.6 mg per 100 cm3 (awrt 36.6)
- **(c) Answer: 36.6 mg per 100 cm3**
- (d) **M1** scale the concentration to the can volume: 36.6 x (250/100)
- (d) **A1** 91.5 mg (awrt 91.5)
- **(d) Answer: 91.5 mg**

Question 8

- (a) **M1** percentage uncertainty in mass = (0.001/0.045) x 100
- (a) **A1** = 2.2% (awrt 2.2)
- (a) **M1** percentage uncertainty in volume = (0.08/100) x 100
- (a) **A1** = 0.080% (awrt 0.080)
- **(a) Answer: Mass: 2.2%; volume: 0.080%**
- (b) **M1** sum the two percentage uncertainties: 2.2 + 0.080
- (b) **A1** 2.3% (awrt 2.3)
- **(b) Answer: 2.3%**
- (c) **M1** percentage uncertainty = (0.02/1.00) x 100
- (c) **A1** = 2.0%
- (c) **B1** although the absolute uncertainties are of a similar order of magnitude, the volume being measured (1.00 cm3) is much smaller than the flask volume (100 cm3), so the same size of absolute uncertainty represents a much larger fraction of the smaller volume, giving a greater percentage uncertainty and a greater effect on the overall result oe
- **(c) Answer: 2.0%; it has a greater effect because the same absolute uncertainty is a much larger fraction of the smaller 1.00 cm3 volume.**
- (d) **M1** absolute uncertainty = 5% of 36.6 = 1.83
- (d) **A1** 36.6 ± 1.8 mg per 100 cm3 (accept awrt, with the uncertainty quoted to 1 or 2 significant figures consistent with the value, e.g. 37 ± 2)
- **(d) Answer: 36.6 ± 1.8 mg per 100 cm3**

Question 9

- (a) **M1** Rf = distance travelled by spot / distance travelled by solvent = 4.8/9.6
- (a) **A1** 0.50 (cao)
- **(a) Answer: Rf = 0.50**
- (b) **M1** Rf = 6.24/9.6
- (b) **M1** = 0.65
- (b) **A1** sunset yellow (matches the reference Rf value of 0.65) cao
- **(b) Answer: Sunset yellow**
- (c) **B1** a likely cause, e.g. a change in solvent composition or temperature between the two days, or the developing tank not being equilibrated/saturated with solvent vapour in the same way, affecting all spots consistently
- (c) **B1** a systematic error shifts all results consistently in the same direction by a similar amount, whereas a random error causes unpredictable scatter in both directions with no consistent pattern
- **(c) Answer: A likely cause is a change in solvent composition, temperature or tank saturation; unlike random error, a systematic error shifts all results consistently in one direction.**
- (d) **B1** run the reference standards alongside the unknown sample on the same plate under identical conditions (co-spotting), rather than comparing with separately recorded reference Rf values
- (d) **B1** alternatively, use a second, independent technique (e.g. HPLC or mass spectrometry) to confirm identity, since a matching Rf value alone is not fully conclusive
- **(d) Answer: Run the reference standards on the same plate as the unknown (co-spotting), or confirm identity with a second technique such as HPLC.**

Question 10

- **Level 3** (5-6): A full, logically structured answer that correctly identifies R as 3-methylbutanal, (CH3)2CHCH2CHO, using evidence from all three techniques (mass spectrum, infrared spectrum and 1H NMR spectrum) to justify both the functional group present and the full carbon skeleton, with clear reasoning linking specific data (m/z values, wavenumbers, chemical shifts, splitting patterns and integrations) to structural features throughout.
- **Level 2** (3-4): Correctly identifies most structural features (for example the aldehyde functional group and/or the branched isopropyl-containing carbon skeleton) using evidence from at least two of the three techniques, with generally sound reasoning, but the final structure may be incomplete, not fully justified, or contain minor errors or omissions in linking the evidence to the structure.
- **Level 1** (1-2): Some relevant points made, for example correctly identifying the functional group present from a single piece of data, or interpreting isolated pieces of data without combining evidence from different techniques; the final structure is incorrect, incomplete or absent.
- **Indicative content:**
  - IR: the weak doublet absorptions at 2720 cm-1 and 2820 cm-1 are the characteristic aldehydic C-H stretch, only seen in aldehydes.
  - IR: the strong absorption at 1725 cm-1 confirms a C=O bond; the absence of any broad absorption between 2500 and 3550 cm-1 rules out a carboxylic acid O-H, supporting an aldehyde or ketone.
  - MS: the molecular ion at m/z = 86 confirms Mr = 86, consistent with molecular formula C5H10O.
  - MS: the fragment at m/z = 57 is formed by loss of a fragment of mass 29 (a CHO radical) from the molecular ion; loss of CHO is characteristic of aldehyde fragmentation, confirming the C=O is terminal (an aldehyde) rather than a ketone.
  - NMR: the doublet at 0.98 ppm, integration 6H, indicates two equivalent CH3 groups, each split into a doublet by a single adjacent CH proton (n=1), consistent with an isopropyl-type (CH3)2CH- unit.
  - NMR: the multiplet at 2.20 ppm (1H) is the CH proton, coupled to both the 6H of the two methyl groups and the 2H of the neighbouring CH2 group.
  - NMR: the signal at 2.35 ppm (2H) is the CH2 group positioned between the CH and the CHO carbon, consistent with its intermediate shift and complex splitting.
  - NMR: the triplet at 9.75 ppm (1H) is the aldehyde CHO proton, split into a triplet by the two protons of the adjacent CH2 group (n=2); this triplet pattern, rather than a doublet, confirms the CHO group is next to a CH2 and not directly next to the CH, fixing the position of the branching.
  - Combining all the evidence gives the structure 3-methylbutanal (isovaleraldehyde), (CH3)2CHCH2CHO, consistent with every data point given.

Question 11

- (a) **B1** (CH3)2CHCH2OH + 2[O] -> (CH3)2CHCOOH + H2O
- **(a) Answer: (CH3)2CHCH2OH + 2[O] -> (CH3)2CHCOOH + H2O**
- (b) **M1** moles of alcohol = 7.40/74.0 = 0.100 mol
- (b) **M1** moles of product = 0.100 mol (1:1 molar ratio from the equation in (a))
- (b) **A1** theoretical mass = 0.100 x 88.0 = 8.80 g (cao)
- **(b) Answer: 8.80 g**
- (c) **M1** percentage yield = (6.98/8.80) x 100
- (c) **A1** 79.3% (awrt 79.3)
- **(c) Answer: 79.3%**
- (d) **B1** the broad absorption at 2500-3300 cm-1 is the O-H stretch of a carboxylic acid; this would be absent for the aldehyde, which has no O-H bond
- (d) **B1** the peak at 1710 cm-1 confirms a C=O bond, but this alone is consistent with either the aldehyde or the acid, so it must be combined with the other evidence
- (d) **B1** the broad singlet at 11.9 ppm (1H) in the NMR corresponds to the carboxylic acid O-H/COOH proton (strongly deshielded); the aldehyde would instead show a CHO proton near 9.7-10 ppm, which is not observed
- (d) **B1** the doublet (6H) and multiplet (1H) confirm the (CH3)2CH- unit is retained in the product, and together with the absence of any CHO signal and the presence of the O-H at 11.9 ppm this confirms the carboxylic acid, not the aldehyde, was isolated
- **(d) Answer: The broad O-H (2500-3300 cm-1) and the 11.9 ppm COOH proton, with no aldehyde CHO signal present, confirm the carboxylic acid was isolated.**
- (e) **B1** under reflux the aldehyde remains in the reaction mixture (rather than being distilled off as it forms) and stays in contact with the excess oxidising agent, so it is further oxidised to the carboxylic acid oe
- **(e) Answer: Under reflux the aldehyde stays in the mixture and is further oxidised by the excess oxidising agent, rather than being distilled off before full oxidation.**