2.8 Analytical Techniques: 2-hour Pack

AQA 7405 · Calculator allowed · about 120 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 Three isomers of molecular formula C_3H_8O are propan-1-ol ($CH_3CH_2CH_2OH$), propan-2-ol ($(CH_3)_2CHOH$) and methoxyethane ($CH_3OCH_2CH_3$).

(a) State what is meant by a 'carbon environment' in 13C NMR spectroscopy. **(1)**

(b) Deduce the number of peaks expected in the 13C NMR spectrum of each of the three isomers. **(3)**

(c) A sample is analysed by 13C NMR and gives exactly two peaks. Identify which isomer this is, and use the approximate shift ranges C-C (alkyl) 0-50 ppm and C-O 50-90 ppm to justify the expected shift of each peak. **(3)**

(d) Explain why 13C NMR spectroscopy alone cannot always distinguish between structural isomers with the same number of carbon environments, and state one other technique that could be used to confirm the identity of an unknown sample. **(2)**

(Total for Question 1 is 9 marks)

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2 The 1H NMR spectrum of propanoic acid, CH_3CH_2COOH, is recorded.

(a) State the 'n+1 rule' used to predict the multiplicity (splitting pattern) of a proton signal in 1H NMR spectroscopy. **(1)**

(b) Predict the splitting pattern and relative integration for each of the three proton environments in propanoic acid. **(4)**

(c) The COOH proton in propanoic acid appears at about 11.8 ppm. When a small amount of D2O is added to the sample and the spectrum re-run, this peak disappears. Explain this observation. **(2)**

(d) Explain why tetramethylsilane (TMS) is used as the standard reference compound in 1H NMR spectroscopy. **(2)**

(Total for Question 2 is 9 marks)

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3 A forensic chemist uses gas chromatography (GC) to determine the concentration of ethanol in a blood sample, using a calibration curve produced from ethanol standards of known concentration.

(a) State one advantage of gas chromatography over thin-layer chromatography for this type of quantitative analysis. **(1)**

(b) The retention time of ethanol under these GC conditions is 2.3 minutes, and a second peak for propan-1-ol (an internal standard) appears at 3.6 minutes. Explain what is meant by 'retention time' and why it can be used to help identify a compound. **(2)**

(c) The calibration line for ethanol is: peak area = 42.5c + 15, where c is the concentration of ethanol in mg per 100 cm^3 of blood. A blood sample gives a peak area of 780. Calculate the concentration of ethanol, in mg per 100 cm^3, in the blood sample. **(3)**

(d) The legal drink-drive limit in England is 80 mg of alcohol per 100 cm^3 of blood. Using your answer to part (c), state whether the sample is above or below the legal limit, and calculate the percentage of the legal limit that this concentration represents. **(2)**

(e) Explain why using an internal standard, such as propan-1-ol, improves the reliability of quantitative GC analysis. **(2)**

(Total for Question 3 is 10 marks)

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4 An anti-doping laboratory tests an athlete's urine sample for a banned substance, X, using GC-MS with an internal standard, IS, added to the sample before extraction. The peak area of X is 5400 and the peak area of IS is 3600. Calibration established the relationship (Area X / Area IS) = k x (mass X / mass IS), with k = 1.20. A 2.00 cm^3 urine sample has 50.0 ng of internal standard added before extraction.

(a) Calculate the peak area ratio (Area X : Area IS) for this sample. **(1)**

(b) Using (Area X / Area IS) = k x (mass X / mass IS), with k = 1.20 and mass IS = 50.0 ng, calculate the mass of X, in ng, present in the 2.00 cm^3 sample. **(3)**

(c) Calculate the concentration of X in the urine sample, in ng per cm3. **(2)**

(d) The World Anti-Doping Agency reporting threshold for X is 30 ng per cm3. State, with a reason, whether this sample would be reported as a positive result, and suggest why laboratories typically require a second, independent confirmatory test (e.g. using a different column or ionisation method) before reporting an adverse finding. **(3)**

(e) Explain why using an internal standard, rather than relying on the absolute peak area of X alone, increases confidence in the accuracy of this quantitative result. **(2)**

(Total for Question 4 is 11 marks)

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5 A brominated organic compound gives a mass spectrum with a molecular ion cluster of two peaks of approximately equal height at m/z = 122 and m/z = 124.

(a) Explain why bromine-containing compounds give two molecular ion peaks of approximately equal (1:1) height, two mass units apart. **(2)**

(b) A different compound contains two chlorine atoms in its structure. State the ratio of peak heights expected for the M : M+2 : M+4 peaks in its mass spectrum, and explain your reasoning. **(3)**

(c) Propan-1-ol (C_3H_8O) and ethanoic acid ($C_2H_4O_2$) both have a nominal (integer) relative molecular mass of 60. Using exact atomic masses C = 12.0000, H = 1.0078, O = 15.9949, calculate the exact mass of each compound to 3 decimal places, and explain how high resolution mass spectrometry could distinguish between them despite their equal nominal Mr. **(5)**

(Total for Question 5 is 10 marks)

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6 An unknown liquid aldehyde, R, has molecular formula $C_5H_{10}O$ (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 6 is 6 marks)

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7 A student oxidises 2-methylpropan-1-ol, $(CH_3)_2CHCH_2OH$ (Mr = 74.0), using excess acidified potassium dichromate(VI) under reflux, to form 2-methylpropanoic acid, $(CH_3)_2CHCOOH$ (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 7 is 11 marks)

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Mark scheme · 2.8 Analytical Techniques: 2-hour Pack

Question 1

(a) carbon atoms that are in identical/equivalent chemical surroundings (bonded to the same groups, or related by symmetry), giving a single peak in the 13C NMR spectrum **B1**

(a) Answer: Carbon atoms in equivalent chemical surroundings, which give a single NMR peak.

(b) propan-1-ol: 3 peaks (three different carbon environments, C1, C2, C3) **B1**

(b) propan-2-ol: 2 peaks (two equivalent CH_3 groups related by symmetry, plus one CH) **B1**

(b) methoxyethane: 3 peaks (OCH_3, CH_2 and CH_3 are all different environments) **B1**

(b) Answer: Propan-1-ol: 3 peaks; propan-2-ol: 2 peaks; methoxyethane: 3 peaks.

(c) propan-2-ol (the only isomer that gives exactly two peaks) **B1**

(c) the two equivalent CH_3 carbons appear at a low shift, in the 0-50 ppm alkyl (C-C) range (approx. 25 ppm) **B1**

(c) the CH carbon (bonded to OH) appears at a higher shift, in the 50-90 ppm (C-O) range (approx. 64 ppm) **B1**

(c) Answer: Propan-2-ol; CH_3 carbons approx. 25 ppm (C-C range), CH carbon approx. 64 ppm (C-O range).

(d) two different structures may coincidentally have the same number of (non-equivalent) carbon environments, giving the same number of peaks, so peak count alone is not conclusive **B1**

(d) 1H NMR (or IR, or mass spectrometry) can provide additional structural information, e.g. splitting patterns and integration, to confirm the structure **B1**

(d) Answer: Peak count alone can be ambiguous between isomers; 1H NMR (or IR/mass spectrometry) provides additional confirming evidence.

Question 2

(a) a proton (or group of equivalent protons) with n equivalent neighbouring (adjacent) protons is split into (n+1) peaks/lines **B1**

(a) Answer: A proton with n equivalent neighbouring protons is split into (n+1) peaks.

(b) CH_3 protons: triplet, relative area 3 (split by 2 neighbouring CH_2 protons, n=2, so n+1=3) **B1**

(b) CH_2 protons: quartet, relative area 2 (split by 3 neighbouring CH_3 protons, n=3, so n+1=4) **B1**

(b) COOH proton: singlet, relative area 1 (no adjacent protons on a neighbouring carbon to split it) **B1**

(b) correct overall integration ratio 3:2:1 for CH_3:CH_2:COOH **B1**

(b) Answer: CH_3: triplet (3H); CH_2: quartet (2H); COOH: singlet (1H); ratio 3:2:1.

(c) the O-H proton is exchangeable and is replaced by deuterium from D2O: -COOH + D2O -> -COOD + HOD oe **B1**

(c) deuterium (D) does not give a signal in a 1H NMR spectrum, so the peak at 11.8 ppm disappears **B1**

(c) Answer: The exchangeable O-H proton is replaced by deuterium (forming O-D), which gives no signal in 1H NMR, so the peak vanishes.

(d) TMS gives a single, strong absorption peak (all 12 H are equivalent) that does not overlap with other proton signals **B1**

(d) TMS is unreactive, volatile and non-toxic and is easily removed from the sample, so it is used to fix the reference point of 0 ppm on the chemical shift scale **B1**

(d) Answer: TMS gives one sharp, non-overlapping peak and is inert/volatile/easy to remove, making it a convenient 0 ppm reference.

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Question 3

(a) GC gives an automated, quantitative measurement (peak area/retention time), allowing concentration to be determined directly and precisely, unlike TLC which is mainly qualitative oe **B1**

(a) Answer: GC gives precise, quantitative peak area/retention time data, allowing concentration to be measured directly (TLC is mainly qualitative).

(b) retention time is the time taken for a component to travel through (elute from) the GC column, from injection to detection **B1**

(b) under fixed/identical conditions (same column, temperature, flow rate), each compound has a characteristic, reproducible retention time, so it can be compared with that of a known standard to help identify it (though this alone is not fully conclusive, e.g. co-elution is possible) **B1**

(b) Answer: Retention time is the elution time of a component; under fixed conditions it is characteristic of a compound, so can be compared with standards to aid identification.

(c) rearrange: c = (780 - 15)/42.5 **M1**

(c) = 765/42.5 **dM1**

(c) 18.0 mg per 100 cm^3 (awrt 18.0) **A1**

(c) Answer: 18.0 mg per 100 cm^3

(d) below the legal limit (18.0 mg per 100 cm^3 < 80 mg per 100 cm^3) **B1**

(d) percentage = (18.0/80) x 100 = 22.5% **M1/A1**

(d) Answer: Below the limit; 22.5% of the legal limit.

(e) a known, fixed amount of internal standard is added to every sample and calibration standard, and the ratio of analyte peak area to internal standard peak area is used, rather than the absolute peak area **B1**

(e) this corrects for/compensates for variations in injection volume or detector response between runs, improving the accuracy/reproducibility of the result **B1**

(e) Answer: Comparing analyte peak area to a fixed internal standard peak area corrects for run-to-run variation (e.g. injection volume), improving reliability.

Question 4

(a) 5400/3600 = 1.50 (cao) **M1/A1**

(a) Answer: 1.50

(b) rearrange: mass X = (area ratio / k) x mass IS **M1**

(b) substitute: (1.50/1.20) x 50.0 **M1**

(b) = 62.5 ng (awrt 62.5) **A1**

(b) Answer: 62.5 ng

(c) 62.5/2.00 **M1**

(c) = 31.25 ng per cm3 (awrt 31.3) **A1**

(c) Answer: 31.25 ng per cm3 (awrt 31.3)

(d) the concentration (31.25/31.3 ng per cm3) exceeds the 30 ng per cm3 threshold, so the sample would be reported/flagged as positive **B1**

(d) a confirmatory test using different chromatographic/MS conditions reduces the chance of a false positive caused by a co-eluting or interfering compound with a similar retention time or fragmentation pattern **B1**

(d) this increases confidence/certainty in the result, given the serious consequences of an adverse finding for the athlete **B1**

(d) Answer: Positive (31.25 ng/cm3 > 30 ng/cm3 threshold); a confirmatory test with different conditions guards against false positives from interfering compounds, which matters given the serious consequences for the athlete.

(e) the internal standard corrects for variations between runs (e.g. differences in injection volume, extraction efficiency or detector response), because both X and IS are affected equally/proportionally **B1**

(e) using the ratio of peak areas (rather than the absolute area of X alone) cancels out these systematic errors, giving a more reliable/reproducible measurement of concentration **B1**

(e) Answer: The internal standard cancels out run-to-run variation, since it affects both X and IS proportionally, making the peak-area ratio more reliable than an absolute area.

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Question 5

(a) bromine occurs naturally as two isotopes, 79Br and 81Br, in an approximately 1:1 (50:50) natural abundance **B1**

(a) the M peak (containing 79Br) and the M+2 peak (containing 81Br) therefore appear with roughly equal intensity **B1**

(a) Answer: Bromine's two isotopes (79Br, 81Br) occur in roughly equal abundance, giving M and M+2 peaks of similar height.

(b) ratio = 9:6:1 **B1**

(b) with two chlorine atoms and a 3:1 (35Cl:37Cl) natural ratio, the probability of both being 35Cl is $(3/4)^2 = 9/16$, of one 35Cl and one 37Cl is 2 x (3/4)(1/4) = 6/16, and of both being 37Cl is $(1/4)^2 = 1/16$ **M1**

(b) giving the ratio 9:6:1 for M(35,35) : M+2(35,37) : M+4(37,37) **A1**

(b) Answer: M : M+2 : M+4 = 9 : 6 : 1

(c) C_3H_8O: 3(12.0000) + 8(1.0078) + 15.9949 **M1**

(c) = 60.057 (awrt 60.057) **A1**

(c) $C_2H_4O_2$: 2(12.0000) + 4(1.0078) + 2(15.9949) **M1**

(c) = 60.021 (awrt 60.021) **A1**

(c) both compounds have the same nominal mass (60), so low-resolution MS cannot distinguish them; high-resolution MS measures mass to several decimal places, revealing the small difference (60.057 vs 60.021) and so identifies the correct molecular formula/compound **B1**

(c) Answer: C_3H_8O = 60.057; $C_2H_4O_2$ = 60.021; high resolution MS distinguishes them by this small mass difference, which low resolution MS cannot detect.

Question 6

Level 3 A full, logically structured answer that correctly identifies R as 3-methylbutanal, $(CH_3)_2CHCH_2CHO$, 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. **5-6**

Level 2 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. **3-4**

Level 1 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. **1-2**

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 $C_5H_{10}O$.
- 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 CH_3 groups, each split into a doublet by a single adjacent CH proton (n=1), consistent with an isopropyl-type $(CH_3)_2CH$- 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 CH_2 group.
- NMR: the signal at 2.35 ppm (2H) is the CH_2 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 CH_2 group (n=2); this triplet pattern, rather than a doublet, confirms the CHO group is next to a CH_2 and not directly next to the CH, fixing the position of the branching.
- Combining all the evidence gives the structure 3-methylbutanal (isovaleraldehyde), $(CH_3)_2CHCH_2CHO$, consistent with every data point given.

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Question 7

(a) $(CH_3)_2CHCH_2OH + 2[O] \rightarrow (CH_3)_2CHCOOH + H_2O$ **B1**

(a) Answer: $(CH_3)_2CHCH_2OH + 2[O] \rightarrow (CH_3)_2CHCOOH + H_2O$

(b) moles of alcohol = 7.40/74.0 = 0.100 mol **M1**

(b) moles of product = 0.100 mol (1:1 molar ratio from the equation in (a)) **M1**

(b) theoretical mass = 0.100 x 88.0 = 8.80 g (cao) **A1**

(b) Answer: 8.80 g

(c) percentage yield = (6.98/8.80) x 100 **M1**

(c) 79.3% (awrt 79.3) **A1**

(c) Answer: 79.3%

(d) 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 **B1**

(d) 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 **B1**

(d) 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 **B1**

(d) the doublet (6H) and multiplet (1H) confirm the $(CH_3)_2CH$- 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 **B1**

(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) 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 **B1**

(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.

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