2.8 Analytical Techniques: Test Pack

AQA 7405 · Calculator allowed · about 70 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 Infrared (IR) spectroscopy can be used to identify functional groups. Typical absorption ranges: O-H (carboxylic acid) 2500-3300 cm-1 (broad); O-H (alcohol) 3230-3550 cm-1 (broad); N-H 3300-3500 cm-1; C=O 1680-1750 cm-1; C-O 1000-1300 cm-1; C-H 2850-3100 cm-1.

(a) The infrared spectra of ethanoic acid, CH_3COOH, and propanone, CH_3COCH_3, both show an absorption at about 1715 cm-1. Identify the bond responsible for this absorption. **(1)**

(b) The infrared spectrum of ethanoic acid shows a broad absorption between 2500 and 3300 cm-1 that is absent from the spectrum of propanone. Explain how this feature allows the two compounds to be distinguished. **(2)**

(c) A sample of car exhaust gas strongly absorbs infrared radiation at 2349 cm-1, characteristic of the C=O bond vibration in carbon dioxide. Explain, in terms of bond behaviour, why CO_2 absorbs infrared radiation but the diatomic gas N_2 does not, and state the environmental significance of this property. **(3)**

(d) An unknown liquid, X, gives an IR spectrum with a strong, sharp absorption at 1735 cm-1 and no absorption between 2500 and 3550 cm-1. Suggest a functional group that is present in X and one that must be absent. **(2)**

(Total for Question 2 is 8 marks)

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3 Trichloromethane (chloroform), $CHCl_3$, 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 $CHCl_3$ 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 1-bromo-3-methylbutane (isoamyl bromide), $(CH_3)_2CHCH_2CH_2Br$, 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 $C_5H_{11}Br$.

(a) Using the n+1 rule, predict the splitting pattern of the CH_2Br protons (2H) and of the $(CH_3)_2$ protons (6H), stating the number of neighbouring protons responsible for each pattern. **(4)**

(b) The CH proton and the middle CH_2 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 $C_5H_{11}Br$. **(2)**

(Total for Question 4 is 9 marks)

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5 An unknown organic compound, Y, has molecular formula $C_4H_8O_2$ (Mr = 88). Mass spectrum: molecular ion peak at m/z = 88; fragment peaks at m/z = 43 and m/z = 45. Infrared spectrum: strong absorption at 1740 cm-1; no absorption between 2500 and 3300 cm-1. 1H NMR spectrum: singlet at 2.0 ppm (3H); quartet at 4.1 ppm (2H); triplet at 1.3 ppm (3H).

(a) Use the infrared data to deduce the type of carbonyl-containing functional group present in Y, giving a reason. **(2)**

(b) Use the 1H NMR data to deduce the number of different proton environments in Y and calculate the total number of hydrogen atoms shown by the integration values. **(2)**

(c) The fragment ion at m/z = 43 is formed by loss of a group of mass 45 from the molecular ion (88). Suggest the identity of the group lost and the fragment ion formed. **(2)**

(d) Using all the data given, deduce the structural formula of Y and explain how the 1H NMR splitting patterns support your answer. **(4)**

(Total for Question 5 is 10 marks)

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6 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 two improvements 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 6 is 9 marks)

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Mark scheme · 2.8 Analytical Techniques: Test Pack

Question 1

(a) 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 **B1**

(a) Answer: The tallest peak in the mass spectrum, corresponding to the most abundant ion (given a relative abundance of 100%).

(b) 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 **B1**

(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) the position of an NMR signal relative to the reference compound TMS (set at 0), measured in parts per million (ppm) oe **B1**

(c) Answer: The position of an NMR signal relative to TMS (set at 0 ppm), measured in parts per million.

Question 2

(a) C=O (carbonyl) bond **B1**

(a) Answer: C=O bond.

(b) the broad absorption at 2500-3300 cm-1 is due to the O-H bond in the carboxylic acid (-COOH) group of ethanoic acid **B1**

(b) propanone has no O-H bond (only a C=O group), so this absorption is absent, allowing the two compounds to be distinguished **B1**

(b) Answer: The broad O-H absorption (2500-3300 cm-1) is present in ethanoic acid but absent in propanone, which has no O-H bond.

(c) bond vibration (stretching/bending) in CO_2 causes a change in the dipole moment of the molecule oe **B1**

(c) N_2 is a symmetrical diatomic molecule with no permanent dipole, and its bond vibration causes no change in dipole moment, so it does not absorb IR radiation oe **B1**

(c) because CO_2 absorbs (and re-emits) infrared radiation, it acts as a greenhouse gas, contributing to the greenhouse effect/global warming **B1**

(c) Answer: CO_2's bond vibrations change its dipole moment so it absorbs IR; symmetrical N_2 has no dipole change on vibration so does not absorb IR. This makes CO_2 a greenhouse gas.

(d) present: a carbonyl-containing group such as an ester (or aldehyde/ketone), shown by the C=O absorption near 1735 cm-1 **B1**

(d) absent: O-H (no alcohol or carboxylic acid group present), as there is no absorption in the 2500-3550 cm-1 region **B1**

(d) Answer: Present: C=O (consistent with an ester); absent: O-H.

Question 3

(a) correct substitution: 12.0 + 1.0 + 3(35.5) **M1**

(a) 119.5 (cao) **A1**

(a) Answer: Mr = 119.5

(b) M (three 35Cl) = 12 + 1 + 3(35) = 118 and M+6 (three 37Cl) = 12 + 1 + 3(37) = 124 **M1**

(b) M+2 = 120 and M+4 = 122, giving all four values 118, 120, 122, 124 (cao) **A1**

(b) Answer: 118, 120, 122, 124

(c) expand the four binomial terms: $(3/4)^3$, $3(3/4)^2(1/4)$, $3(3/4)(1/4)^2$, $(1/4)^3$ **M1**

(c) evaluate each term as a fraction of 64: 27/64, 27/64, 9/64, 1/64 **M1**

(c) convert to whole-number ratio by comparing numerators over the common denominator 64 **M1**

(c) M : M+2 : M+4 : M+6 = 27 : 27 : 9 : 1 (cao) **A1**

(c) Answer: 27 : 27 : 9 : 1

Question 4

(a) CH_2Br protons are adjacent to 2 protons (the middle CH_2 group), so n = 2 gives a triplet **B1**

(a) the $(CH_3)_2$ protons are each adjacent to 1 proton (the CH group), so n = 1 gives a doublet **B1**

(a) the CH_2Br triplet appears at a relatively high shift (approximately 3.40 ppm), deshielded by the adjacent electronegative bromine **B1**

(a) the $(CH_3)_2$ doublet appears at a relatively low shift (approximately 0.95 ppm), typical of alkyl CH_3 groups away from any electronegative atom **B1**

(a) Answer: CH_2Br: triplet (2H, coupled to 2 neighbouring H); $(CH_3)_2$: doublet (6H, coupled to 1 neighbouring H).

(b) the CH proton is adjacent to two different, non-equivalent sets of neighbouring protons: the 6H of the two CH_3 groups and the 2H of the neighbouring CH_2 group, so simple n+1 splitting from a single neighbouring group does not apply, giving a complex multiplet **B1**

(b) the middle CH_2 protons are also adjacent to two different sets of neighbours, the CH proton (1H) and the CH_2Br protons (2H), again producing overlapping splitting rather than a single clean pattern **B1**

(b) because the resulting multiplets from the CH and the middle CH_2 fall in a similar, overlapping shift range, they merge into one broad multiplet region integrating for 3H overall **B1**

(b) Answer: Both the CH and middle CH_2 protons couple to two different neighbouring proton sets, giving complex, overlapping multiplets rather than a simple doublet or triplet.

(c) sum the integrations: 6 + 3 + 2 **M1**

(c) = 11H, consistent with $C_5H_{11}Br$ (cao) **A1**

(c) Answer: 11H, consistent with $C_5H_{11}Br$

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Question 5

(a) ester **B1**

(a) the absorption at 1740 cm-1 corresponds to a C=O stretch, and the absence of a broad O-H absorption (2500-3300 cm-1) rules out a carboxylic acid, consistent with an ester **B1**

(a) Answer: Ester; C=O at 1740 cm-1 with no O-H absorption rules out a carboxylic acid.

(b) three proton environments (singlet, quartet, triplet) **B1**

(b) total H = 3 + 2 + 3 = 8, consistent with molecular formula $C_4H_8O_2$ **B1**

(b) Answer: 3 environments; total 8H, matching $C_4H_8O_2$.

(c) group lost: OCH_2CH_3 (ethoxy, OC_2H_5, mass 45) **B1**

(c) ion formed: CH_3CO+ (acylium ion, mass 43) **B1**

(c) Answer: OC_2H_5 (mass 45) lost; CH_3CO+ (mass 43) formed.

(d) structure: $CH_3COOCH_2CH_3$ (ethyl ethanoate) **B1**

(d) singlet at 2.0 ppm (3H) = CH_3 bonded to C=O, with no adjacent protons, so no splitting **B1**

(d) quartet at 4.1 ppm (2H) = OCH_2, split by the adjacent CH_3 (3H, n+1 = 4) **B1**

(d) triplet at 1.3 ppm (3H) = CH_3 of the ethyl group, split by the adjacent OCH_2 (2H, n+1 = 3) **B1**

(d) Answer: Y is ethyl ethanoate, $CH_3COOCH_2CH_3$.

Question 6

(a) Rf = distance travelled by spot / distance travelled by solvent = 4.8/9.6 **M1**

(a) 0.50 (cao) **A1**

(a) Answer: Rf = 0.50

(b) Rf = 6.24/9.6 **M1**

(b) = 0.65 **M1**

(b) sunset yellow (matches the reference Rf value of 0.65) cao **A1**

(b) Answer: Sunset yellow

(c) 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 **B1**

(c) 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 **B1**

(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) 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 **B1**

(d) 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 **B1**

(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.

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