2.8 Analytical Techniques: 1-hour Pack

AQA 7405 · Calculator allowed · about 60 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 Three isomers with molecular formula $C_4H_{10}O$ are butan-1-ol, $CH_3CH_2CH_2CH_2OH$, 2-methylpropan-2-ol (tert-butanol), $(CH_3)_3COH$, and ethoxyethane (diethyl ether), $CH_3CH_2OCH_2CH_3$. 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)**

(Total for Question 1 is 9 marks)

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2 Required practical: A student separates a mixture of three amino acids, alanine, glycine and leucine, using thin-layer chromatography (TLC), following the required practical procedure for separating species by TLC and interpreting Rf values.

(a) State two precautions that should be taken when spotting the amino acid mixture onto the TLC plate, to obtain reliable results. **(2)**

(b) The solvent front travelled 8.4 cm from the baseline. The spot corresponding to glycine travelled 3.2 cm. Calculate the Rf value for glycine. **(2)**

(c) Amino acids are colourless, so the plate must be treated with a locating agent to make the spots visible. Name a suitable locating agent for amino acids and state the colour change it produces. **(2)**

(d) Reference standards run under the same conditions give Rf values: alanine 0.51, glycine 0.38, leucine 0.74. Using the table and your answer to part (b), identify which amino acid the unknown spot in part (b) is, and explain why comparing Rf values under identical conditions is essential for reliable identification. **(3)**

(e) Suggest one reason why paper chromatography might give poorer separation than TLC for amino acids with very similar Rf values, and suggest one modification that could improve the separation of such closely running compounds. **(2)**

(f) A repeat run gives an Rf value of 0.35 for the same amino acid (glycine), compared with 0.38 previously. Suggest two reasons for this small variation between repeats. **(2)**

(g) State why the TLC plate should not be handled with bare fingers before or during the experiment. **(1)**

(h) A student suggests using UV light instead of ninhydrin to visualise the amino acid spots. Evaluate whether this is likely to work, giving a reason. **(2)**

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(i) State why it is important to use the same TLC plate (or plates from the same batch) when comparing the Rf value of an unknown with reference standards, rather than plates from a different manufacturer or batch. **(2)**

(Total for Question 2 is 18 marks)

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3 Two isomers with molecular formula C_3H_6O are propanal, CH_3CH_2CHO, and propanone, CH_3COCH_3.

(a) Show that the relative molecular mass of C_3H_6O is 58. Use Ar: C = 12.0, H = 1.0, O = 16.0. **(2)**

(b) The mass spectrum of propanone shows a major fragment peak at m/z = 43, formed by loss of a neutral fragment of mass 15 from the molecular ion (58). Identify the fragment lost and the ion formed, including its formula. **(2)**

(c) The mass spectrum of propanal shows a major fragment peak at m/z = 29, formed by loss of a fragment of mass 29 from the molecular ion (58). Suggest the identity of the ion at m/z = 29 and explain how this fragment could help distinguish propanal from propanone. **(3)**

(d) State one other analytical technique, other than mass spectrometry, that could distinguish propanal from propanone, and identify the key spectral difference that would be observed. **(2)**

(Total for Question 3 is 9 marks)

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4 Methyl propanoate, $CH_3CH_2COOCH_3$, is a structural isomer of ethyl ethanoate (see Q8), both with molecular formula $C_4H_8O_2$.

(a) Predict the number of proton environments in methyl propanoate and give the expected splitting pattern for each. **(4)**

(b) Explain how the 1H NMR spectrum of methyl propanoate could be distinguished from that of its isomer, ethyl ethanoate (Q8), even though both show a singlet, a quartet and a triplet. **(3)**

(c) A chemist obtains a 13C NMR spectrum of an unknown $C_4H_8O_2$ ester and finds four distinct peaks. Explain why this result alone cannot be used to distinguish between methyl propanoate and ethyl ethanoate, and state what further data would allow the isomers to be distinguished. **(2)**

(Total for Question 4 is 9 marks)

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Mark scheme · 2.8 Analytical Techniques: 1-hour Pack

Question 1

(a) butan-1-ol: 4 peaks (four different, non-equivalent carbon environments) **B1**

(a) 2-methylpropan-2-ol: 2 peaks (three equivalent CH_3 carbons related by symmetry, plus the quaternary C-OH carbon) **B1**

(a) ethoxyethane: 2 peaks (two equivalent CH_3 carbons and two equivalent OCH_2 carbons, related by the symmetry of the molecule) **B1**

(a) Answer: Butan-1-ol: 4 peaks; 2-methylpropan-2-ol: 2 peaks; ethoxyethane: 2 peaks.

(b) 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 **B1**

(b) the three equivalent CH_3 carbons appear in the lower, C-C (alkyl) range, 5-40 ppm, since they are not directly bonded to oxygen **B1**

(b) the carbon bonded to oxygen is deshielded relative to the plain alkyl carbons, which is why it appears at the higher shift oe **B1**

(b) Answer: The C-OH quaternary carbon falls in the 50-90 ppm C-O range; the three CH_3 carbons fall in the 5-40 ppm C-C range.

(c) both compounds give exactly two 13C peaks (as shown in (a)), so the peak count alone is ambiguous between them **B1**

(c) 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 **B1**

(c) 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 **B1**

(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 2

(a) use a fine capillary tube to apply a small, concentrated spot (allowing it to dry between applications) **B1**

(a) draw the origin line in pencil (not ink) and keep the spot/baseline above the level of the solvent in the developing tank **B1**

(a) Answer: Use a fine capillary tube for a small, concentrated spot; keep the baseline above the solvent level and mark it in pencil.

(b) Rf = distance travelled by spot / distance travelled by solvent = 3.2/8.4 **M1**

(b) 0.38 (awrt 0.38) **A1**

(b) Answer: Rf = 0.38

(c) ninhydrin (spray reagent) **B1**

(c) the plate is sprayed and heated (e.g. in an oven or with a hairdryer), producing purple/pink spots **B1**

(c) Answer: Ninhydrin; sprayed on and heated to give purple/pink spots.

(d) glycine (Rf = 0.38 matches the reference value) **B1**

(d) Rf values depend on conditions such as the solvent used, temperature and the stationary phase, so the reference standards and the unknown must be run under identical conditions **B1**

(d) running standards alongside the unknown on the same plate (rather than comparing with literature values) is more reliable, since exactly matching conditions are guaranteed **B1**

(d) Answer: Glycine; Rf is condition-dependent, so identical conditions (ideally the same plate) are needed for a valid comparison.

(e) paper fibres are less uniform than the fine, even layer of stationary phase on a TLC plate, so paper chromatography generally gives lower resolution/more diffuse spots **B1**

(e) modification: use two-dimensional chromatography (developing in a second solvent at right angles) or a different/more suitable solvent system, to better separate closely running spots **B1**

(e) Answer: TLC's uniform stationary phase gives better resolution than paper; two-dimensional chromatography (or a different solvent) can separate close-running spots further.

(f) a slight difference in laboratory/tank temperature between the two runs (Rf is temperature dependent) **B1**

(f) a slight variation in the exact solvent composition/volume used, or the tank not being fully saturated with solvent vapour (chamber not sealed/equilibrated) before development **B1**

(f) Answer: Small differences in temperature and/or solvent conditions (e.g. tank vapour saturation) between repeats.

(g) oils/grease/sweat from fingers could contaminate the plate, producing extra spots or affecting Rf values and giving inaccurate/misleading results **B1**

(g) Answer: Skin oils can contaminate the plate and affect the spots/Rf values obtained.

(h) UV visualisation only works for compounds that absorb/fluoresce under UV light (or plates containing a fluorescent indicator, showing spots as dark patches) **B1**

(h) most amino acids (other than aromatic ones such as tryptophan, tyrosine or phenylalanine) do not absorb/fluoresce strongly under UV, so ninhydrin (a chemical locating agent) is more suitable/reliable for a general amino acid mixture **B1**

(h) Answer: UV light is unlikely to reveal all the spots reliably, since most amino acids do not absorb/fluoresce under UV; ninhydrin remains the more suitable locating agent.

(i) different batches/manufacturers of TLC plate may have slightly different stationary phase thickness, particle size or activation, which can affect Rf values **B1**

(i) using the same plate/batch (or running standards and the unknown side by side on the same plate) ensures conditions are identical, making the Rf comparison valid/reliable **B1**

(i) Answer: Different plate batches can give slightly different Rf values, so using the same plate/batch ensures a fair, valid comparison.

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Question 3

(a) correct substitution: 3(12.0) + 6(1.0) + 16.0 **M1**

(a) = 58 (cso, correct answer given, working must be shown) **A1**

(a) Answer: 58

(b) fragment lost: a methyl radical, .CH_3 (mass 15) **B1**

(b) ion formed: CH_3CO+ (acylium ion, formula C_2H_3O+, m/z = 43) **B1**

(b) Answer: .CH_3 lost; CH_3CO+ (C_2H_3O+) formed at m/z = 43.

(c) ion at m/z = 29 is CHO+ (formyl/acylium cation), formed by loss of the ethyl radical, .C_2H_5 **B1**

(c) propanone's spectrum does not show a CHO+ (m/z = 29) fragment (its characteristic fragment is CH_3CO+ at m/z = 43), so the presence or absence of m/z = 29 distinguishes the two isomers **B1**

(c) both compounds show the same molecular ion (m/z = 58, since they are isomers), so it is the fragmentation pattern, not the molecular ion, that is needed to distinguish them **B1**

(c) Answer: CHO+ at m/z = 29; its presence indicates propanal, since propanone does not give this fragment.

(d) infrared spectroscopy or 1H NMR spectroscopy named **B1**

(d) IR: propanal shows an additional C-H (aldehyde) stretch near 2720-2850 cm-1, absent in propanone; OR NMR: propanal shows a characteristic aldehyde CHO proton signal at approx. 9.7-10 ppm, absent in propanone **B1**

(d) Answer: 1H NMR: propanal shows an aldehyde CHO proton at approx. 9.7-10 ppm, which propanone lacks (or IR: additional aldehyde C-H stretch near 2720-2850 cm-1).

Question 4

(a) OCH_3: singlet (3H) **B1**

(a) CH_2: quartet (2H) **B1**

(a) CH_3 (of ethyl group): triplet (3H) **B1**

(a) correct reasoning for at least one pattern using the n+1 rule, e.g. CH_2 is adjacent to the 3H of the ethyl CH_3, so n=3 gives a quartet **B1**

(a) Answer: OCH_3 singlet (3H); CH_2 quartet (2H); CH_3 triplet (3H).

(b) in ethyl ethanoate the singlet (3H) is at a lower shift (approx. 2.0 ppm, CH_3 next to C=O), whereas in methyl propanoate the singlet (3H) is at a higher shift (approx. 3.7 ppm, OCH_3 next to O) **B1**

(b) in ethyl ethanoate the CH_2 quartet is next to oxygen (approx. 4.1 ppm, OCH_2), whereas in methyl propanoate the CH_2 quartet is next to the carbonyl carbon (approx. 2.3 ppm, $COCH_2$), a lower shift **B1**

(b) although the splitting patterns (singlet:quartet:triplet) are the same for both isomers, the precise chemical shift of each peak differs, allowing the two isomers to be distinguished **B1**

(b) Answer: The splitting patterns match, but the chemical shifts of the singlet and quartet differ between the two isomers, distinguishing them.

(c) both methyl propanoate and ethyl ethanoate have four non-equivalent carbon atoms, so both give four peaks in their 13C NMR spectra; the peak count alone cannot distinguish them **B1**

(c) comparing the precise 13C chemical shift values, or using 1H NMR data (e.g. as in part (b)), would allow the isomers to be distinguished **B1**

(c) Answer: Both isomers give four 13C peaks, so peak count is not enough; comparing exact shift values or using 1H NMR data would distinguish them.

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