

2.5.4 Preparation, tests and spectral evidence

Name: _____ Class: _____ Date: _____

Total: 42 marks**KEY WORDS** molecular-ion peak • anhydrous

Objective

Combine preparation methods, chemical tests and spectral data without treating one observation as a unique identity. All questions, data and marking guidance are original; practical work requires the approved supervised method.

1 Key knowledge and worked examples

Complete combustion conserves carbon, hydrogen and oxygen. For ethanol, $\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$. Its oxygen atom is already counted on the left. With PCl_5 an alcohol gives a chloroalkane, POCl_3 and HCl . HCl fumes alone are not unique to alcohols: water and other compounds containing suitable OH groups can also react.

■ Worked evidence chain

Two candidates have molecular formula $\text{C}_3\text{H}_6\text{O}$, so both have molecular mass 58. A carbonyl absorption fits an aldehyde or a ketone. A positive warm Fehling's test supports propanal over propanone. Each additional result must eliminate an alternative; repeating the same mass evidence does not create a second independent test.

A fragment's mass can fit several ionic formulae: at m/z 43, CH_3CO^+ has mass $24 + 3 + 16 = 43$, while C_3H_7^+ has mass $36 + 7 = 43$. The spectrum's largest peak is not necessarily the molecular ion. Combine fragmentation, the molecular-ion constraint and other evidence rather than assigning an isomer from one peak.

Extraction separates immiscible bulk phases; drying removes residual water from the organic phase. Remove the drying salt before distillation. Reflux returns condensed vapour; distillation collects a volatile fraction. Compare boiling temperatures at the same pressure, with the thermometer bulb sampling vapour entering the condenser. A narrow boiling range supports purity but does not alone prove identity.

2 Practice

2.1 Write an equation with integer coefficients for complete combustion of propan-1-ol, $\text{C}_3\text{H}_7\text{OH}$. Write its equation with PCl_5 and explain why HCl fumes alone do not uniquely identify an alcohol. [4]

2.2 Butan-1-ol is oxidised with potassium dichromate(VI) in dilute sulfuric acid. Route A distils the product as it forms; route B uses reflux with excess oxidant. The same oxidant reacts with butan-2-ol in route C. Name all three organic products and write [O] equations for A and B. State the dichromate colour change, the positive observation with warm Fehling's or Benedict's solution for A's product, and the observation when B's product meets sodium carbonate. [8]

2.3 A liquid organic product has density 0.87 g cm^{-3} and is extracted with an aqueous phase of density 1.00 g cm^{-3} . Identify its layer. Explain the separate purposes of layer separation, drying with a suitable anhydrous salt and removing that salt. Distinguish reflux from the final distillation. Explain how to measure a meaningful boiling temperature and why a narrow $85\text{--}86^\circ\text{C}$ range alone does not prove identity. [6]

3 Exam-style questions

3.1 An unknown has formula $\text{C}_3\text{H}_6\text{O}$, a singly charged molecular ion at m/z 58, a fragment at m/z 29, a carbonyl IR absorption and a positive warm Fehling's test. Consider propanal and propanone. Check the molecular mass; give two different ionic formulae of mass 29 using $\text{C} = 12$, $\text{H} = 1$, $\text{O} = 16$; then choose the supported isomer and explain why the single fragment cannot establish it alone. [5]

3.2 Use the supplied approximate absorption data to predict the relevant listed regions for each structure: $\text{CH}_2=\text{CHCH}_2\text{NH}_2$; $\text{CH}_3\text{CH}_2\text{Cl}$; HOCH_2CHO ; CH_3COOH . Include C–H regions and distinguish alcohol from acid OH. State functional groups and ranges, rather than claiming that one peak proves a whole structure. [11]

Bond/environment	Supplied region / cm^{-1}
Alkane C–H	2850–3000
Alkene C–H	3000–3100
Aldehyde C–H	2700–2900
C=C	1620–1680
Alcohol O–H	3200–3600, broad
Carboxylic-acid O–H	2500–3300, very broad
C=O	1680–1750
C–Cl	500–800
Amine N–H	3300–3500

3.3 Four unknowns are, in some order, sodium sulfate, ammonium sulfate, propanal and propanone. Each test uses a fresh aliquot. Only A releases a gas on warming with NaOH; the gas turns damp red litmus blue. A and B give a white precipitate with acidified barium chloride. C gives a brick-red precipitate with warm Fehling's solution; D does not. Both C and D have a carbonyl absorption and molecular ion 58. Identify A–D, write ionic equations for the ammonium and sulfate tests, and explain why the separate aliquots matter and why the shared carbonyl/mass results cannot distinguish C from D. [8]

Solutions

Original marking guidance: M1 method, A1 accuracy, B1 reasoning. Additional correct chemical evidence is acceptable when it addresses the stated alternatives.

2.1 $2\text{C}_3\text{H}_7\text{OH} + 9\text{O}_2 \rightarrow 6\text{CO}_2 + 8\text{H}_2\text{O}$. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{POCl}_3 + \text{HCl}$. Water or a carboxylic acid can also produce HCl with PCl_5 , so fumes alone do not uniquely establish an alcohol.

2.2 A butanal, B butanoic acid, C butanone. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{H}_2\text{O}$; $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + 2[\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{H}_2\text{O}$. Dichromate changes orange to green. A gives a brick-red precipitate with warm Fehling's/Benedict's solution; B gives effervescence of CO_2 with sodium carbonate. Ketone C does not give the ordinary positive aldehyde test.

2.3 The stated organic product is the upper layer because $0.87 < 1.00 \text{ g cm}^{-3}$; do not generalise to every organic liquid. Layer separation removes the bulk aqueous phase, whereas an anhydrous salt removes residual water. Decant/filter the salt before distilling to leave the dried liquid product. Reflux returns condensate to the reaction vessel; distillation collects a volatile fraction separately. Place the bulb in the vapour path at the condenser entrance and compare at the same pressure. A narrow range supports purity, but another substance or mixture may have a similar range, so further identity evidence is needed.

3.1 $M_r = 3(12) + 6(1) + 16 = 58$ for both isomers. C_2H_5^+ : $2(12) + 5 = 29$; CHO^+ : $12 + 1 + 16 = 29$. Positive Fehling's evidence supports propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, over propanone. A fragment mass permits different ionic formulae/pathways and does not uniquely locate the carbonyl; use the combined evidence.

3.2 Original marking guidance by structure:

- $\text{CH}_2=\text{CHCH}_2\text{NH}_2$: alkene C–H 3000–3100 and alkane C–H 2850–3000; C=C 1620–1680; N–H 3300–3500.
- $\text{CH}_3\text{CH}_2\text{Cl}$: alkane C–H 2850–3000; C–Cl 500–800.
- HOCH_2CHO : alkane C–H 2850–3000 and aldehyde C–H 2700–2900; broad alcohol O–H 3200–3600; C=O 1680–1750.
- CH_3COOH : alkane C–H 2850–3000; very broad acid O–H 2500–3300; C=O 1680–1750.

The supplied regions overlap; intensities, shapes and other evidence matter. The alcohol and acid answers must distinguish their OH environments rather than merely state “OH present”.

3.3 A ammonium sulfate; B sodium sulfate; C propanal; D propanone. $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$; $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4(\text{s})$. Fresh aliquots prevent reagent carry-over from introducing ions or altering later test conditions. Both isomers contain C=O and have M_r 58, so those shared results cannot distinguish them; the aldehyde's reducing test does. This closed candidate list supports these assignments; it does not make the tests unique among all possible chemicals.