

4.5.4 Combined spectra and chromatographic evidence

Name: _____ Class: _____ Date: _____

Total: 17 marks

KEY WORDS retention time

Objective

Use independent spectral constraints and recognise limits of chromatographic matches. Questions and marking guidance are original.

1 Key knowledge and worked examples

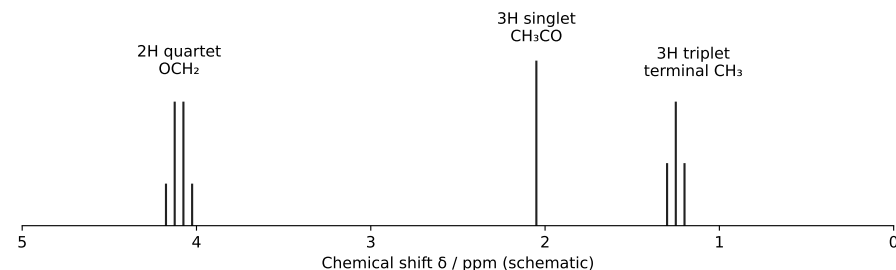
Accurate mass distinguishes formulae with equal nominal masses. Carbon-13 NMR counts carbon environments, not carbon atoms. Proton NMR combines shifts, integrated areas and simple $n + 1$ splitting by equivalent neighbours. OH/NH exchangeable signals may not follow simple splitting.

■ Worked interpretation

Ethyl ethanoate has proton sets $\text{CH}_3\text{CO}-$ (3H singlet), $-\text{OCH}_2-$ (2H quartet) and terminal $-\text{CH}_3$ (3H triplet). The acyl methyl has no adjacent carbon-bound H; each ethyl group end splits according to the other. Integration is 3:2:3. Combine these with ester carbonyl/other supplied shifts rather than identifying by one quartet.

In TLC, $R_f = d_{\text{spot}}/d_{\text{front}}$ from the same baseline. Retention time in GC/HPLC depends on conditions; a reference match supports a candidate but is not unique proof. GC-MS separates components and then supplies mass/fragment evidence. Co-elution can hide multiple compounds in one peak/spot.

Ethyl ethanoate: relative integrated areas 3 : 2 : 3
Stick heights illustrate splitting, not integrated area



2 Practice

2.1 Calculate the accurate mass of $\text{C}_2\text{H}_6\text{O}$ using $\text{C} = 12.0000$, $\text{H} = 1.0078$ and $\text{O} = 15.9949$. [2]

2.2 State the number of carbon-13 environments in propanone and propanal and explain the difference. [3]

2.3 A TLC spot is 4.2 cm above baseline; solvent front is 7.0 cm above it. Calculate R_f and state a condition needed for reference comparison. [3]

3 Exam-style questions

3.1 A $\text{C}_4\text{H}_8\text{O}_2$ sample has an ester carbonyl and proton-NMR sets: 3H singlet, 2H quartet and 3H triplet. Propose a structure and assign each set. Explain one limitation of relying only on integration. [5]

3.2 A forensic sample has one GC peak with the same retention time as a reference drug. Explain why identity and purity are not established, and how GC–MS plus controls strengthen the interpretation. [4]

Solutions

Original marking guidance: M1 method, A1 accuracy, B1 explanation.

2.1 $2(12.0000) + 6(1.0078) + 15.9949 = 46.0417$.

2.2 Two in propanone, three in propanal; propanone has equivalent methyl carbons whereas propanal does not.

2.3 $R_f = 4.2/7.0 = 0.60$, no units. Same solvent/stationary-phase conditions.

3.1 Ethyl ethanoate $\text{CH}_3\text{COOCH}_2\text{CH}_3$. Acyl CH_3 singlet; OCH_2 quartet; terminal CH_3 triplet. Integration gives relative H counts, not unique connectivity; shifts/splitting/formula are also needed.

3.2 Different compounds can share retention time; co-eluting components can form one peak. Mass/fragment evidence supplies an additional structural constraint. Matched standards/blanks and sample provenance/contamination controls test the reliability of attribution.