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.

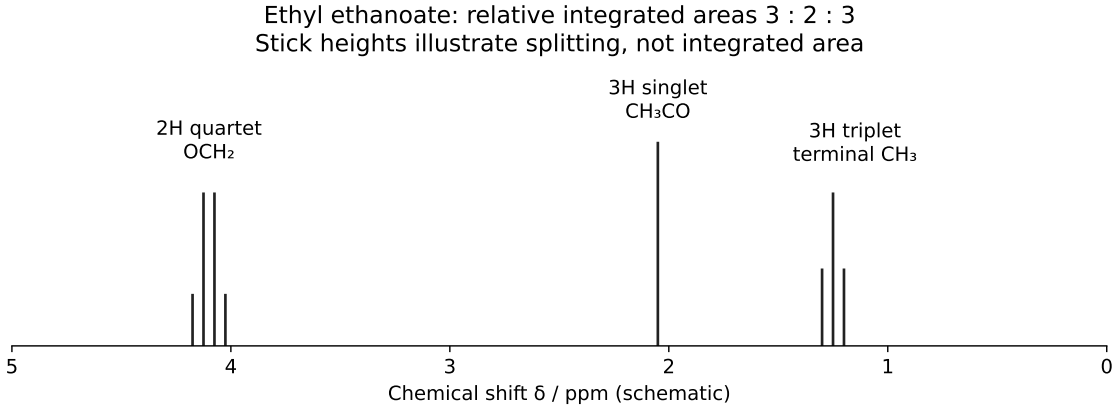
1 Key knowledge and worked examples

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 CH_3CO– (3H singlet), –OCH_2– (2H quartet) and terminal –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, $R_f = d_{spot}/d_{front}$ 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.



2 Practice

2.1 Calculate the accurate mass of C_2H_6O using C = 12.0000, H = 1.0078 and 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 Rf and state a condition needed for reference comparison. [3]

3 Exam-style questions

3.1 A $C_4H_8O_2$ 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]