

Analytical techniques (A Level)

A-Level Chemistry 9701 · Topic 37 revision notes

Everything from the 3 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Chromatography.

2. Proton NMR spectroscopy.

3. Carbon-13 NMR spectroscopy.

1 Chromatography

Syllabus 37.1

All chromatography separates a mixture between a **stationary phase**, which stays put, and a **mobile phase**, which moves through it. A component that interacts more strongly with the stationary phase moves more slowly. In **thin-layer chromatography** (TLC) the stationary phase is silica or alumina on a plate and separation is mainly by **adsorption**; each spot has an **R_f value** = distance moved by the spot ÷ distance moved by the solvent front. In **gas-liquid chromatography** (GLC) an inert carrier gas carries the vapourised sample through a column coated with a non-volatile liquid, and separation is by **partition**. Each component has a characteristic **retention time**, and the **area under each peak** is proportional to the amount of that component, so relative peak areas give the percentage composition.

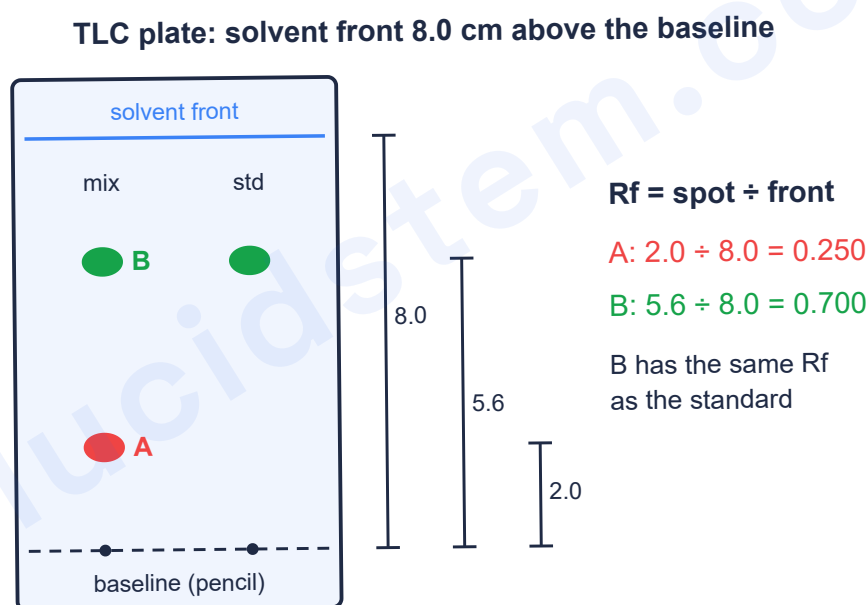


Fig. 1: measuring R_f values on a developed TLC plate

Two phases, two numbers.

- ✓ **Rf** = spot distance $\div$ solvent front distance, both from the baseline.
- ✓ **TLC**: adsorption onto silica or alumina;
GLC: partition into a liquid.
- ✓ **Retention time** identifies a GLC peak, under fixed conditions.
- ✓ **Peak area** $\div$ total area $\times$ 100 gives percentage composition.

Watch out!

Rf is spot distance $\div$ **solvent front** distance, never $\div$ the length of the plate, and both are measured from the **baseline**. In GLC the amount of a component is given by the peak **area**, not its height, and the percentage uses the **total** of all peak areas. A long retention time means strong interaction with the **stationary** phase, not a large amount of substance.

2 Proton NMR spectroscopy

Syllabus 37.2

In a magnetic field, ^1H nuclei absorb radio waves at frequencies that depend on their electron surroundings. The **chemical shift**, δ in ppm, is measured relative to **TMS**, $\text{Si}(\text{CH}_3)_4$, set at 0. The **number of peaks** equals the number of different **proton environments**, and the **relative peak areas** (integration) give the ratio of hydrogens in each. Each peak is split by the hydrogens on neighbouring carbons according to the **$n+1$ rule**: n neighbours give $n+1$ lines, so a singlet, doublet, triplet or quartet. Samples are dissolved in a **deuterated solvent** such as CDCl_3 , which gives no proton signal, and shaking with **D_2O** makes O-H and N-H peaks disappear.

^1H NMR spectrum of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$

s = singlet, t = triplet, q = quartet
areas 2 : 1 : 3; OH peak vanishes with D_2O

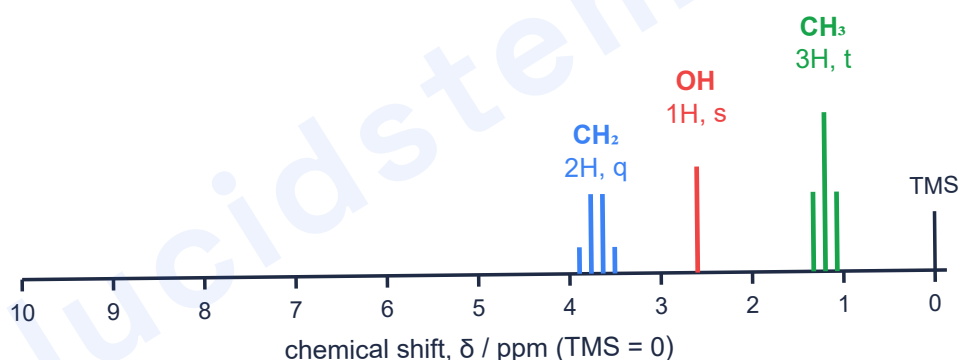


Fig. 1: the high-resolution proton NMR spectrum of ethanol

Peaks, shift, area, splitting.

- ✓ **Number of peaks** = number of H environments.
- ✓ **Shift** (Data Booklet) = type of H; TMS is 0.
- ✓ **Area** ratio = number of H in each environment.
- ✓ **n+1 rule:** n H on adjacent carbons give n+1 lines; O-H vanishes with D₂O.

Watch out!

Splitting comes from H on the **adjacent** carbon, not from the H in the group itself: a CH₃ next to a CH₂ is a **triplet**, not a quartet. Peak **area** gives the number of H; the number of lines does not. The O-H peak is usually a singlet and is the one that **disappears** with D₂O. TMS is at 0 and δ increases to the **left**.

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3 Carbon-13 NMR spectroscopy

Syllabus 37.2

Only about 1.1% of carbon atoms are ^{13}C , but they absorb radio waves in a magnetic field just as protons do. The **number of peaks** equals the number of different **carbon environments**, so symmetry matters: propan-2-ol gives two peaks, propan-1-ol three. The **chemical shift** range is wide, about 0 to 220 ppm, and tells you the type of carbon: **alkyl 5–55**, **C–O 50–90**, **alkene and aromatic 110–160**, **C=O 160–220**. Routine spectra show **no splitting**, so every peak is a single line, and peak heights do not reliably count carbons. Combined with IR (functional groups) and mass spectra (M_r), it pins down a structure.

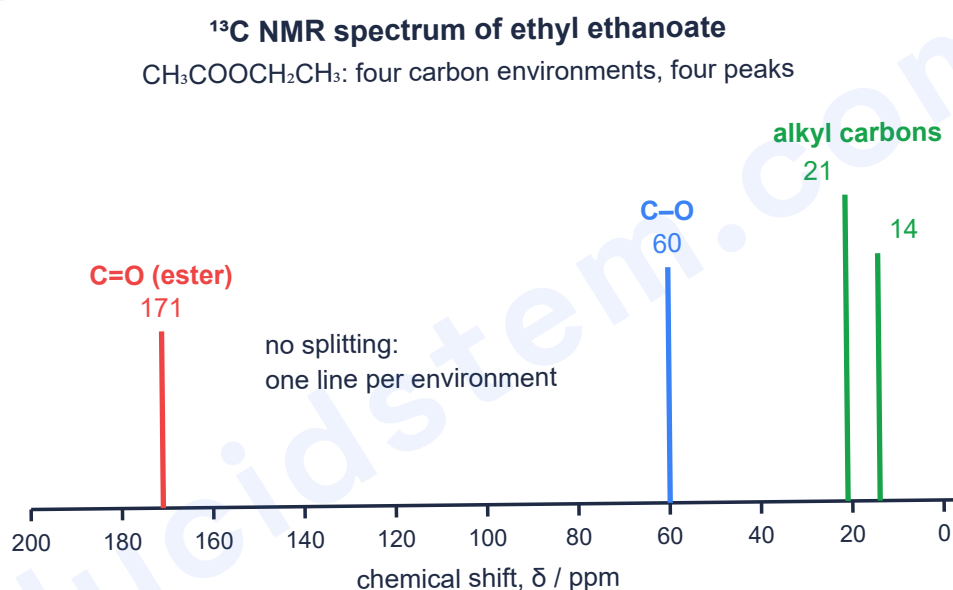


Fig. 1: the carbon-13 NMR spectrum of ethyl ethanoate

Environments, ranges, then combine.

- ✓ **Peaks** = carbon environments; use symmetry.
- ✓ **Ranges:** alkyl 5–55, C–O 50–90, C=C and aromatic 110–160, C=O 160–220.
- ✓ **No splitting**, and heights do not count carbons.
- ✓ **Combine:** MS for M_r , IR for groups, NMR for the skeleton.

Watch out!

Count **environments**, not carbon atoms: the two CH_3 groups of propanone give one peak. ^{13}C peaks are **not split** and their heights do **not** give the number of carbons, unlike proton peak areas. A carbon bonded to O sits at 50–90, while a C=O carbon is far further left at 160–220; do not confuse the two.