Analytical techniques

A-Level Chemistry

Thin-layer chromatography

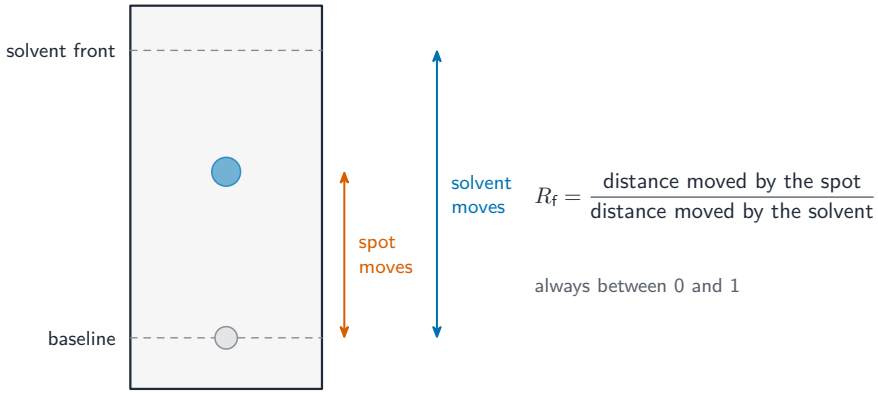
Chromatography 色谱 separates a mixture using two "phases" — one that stays still and one that moves. In **thin-layer chromatography** 薄层色谱 (TLC):

- the **stationary phase** 固定相 stays still (for example aluminium oxide on a plate).
- the **mobile phase** 流动相 moves (a polar or non-polar solvent that travels up the plate).
- the **baseline** 基线 is the starting line where the spots are placed; the **solvent front** 溶剂前沿 is the highest level the solvent reaches.

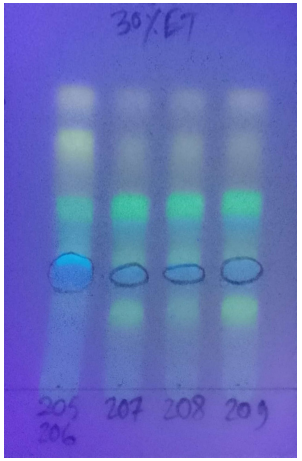
The R_f value compares how far a spot moves with how far the solvent moves:

$$R_f = \frac{\text{distance moved by the spot}}{\text{distance moved by the solvent front}}$$

It is always between 0 and 1. A substance that sticks more strongly to the stationary phase, or is less soluble in the mobile phase, moves less and has a **smaller** R_f.



Thin-layer chromatography: the R_f value is how far the spot moved divided by how far the solvent front moved



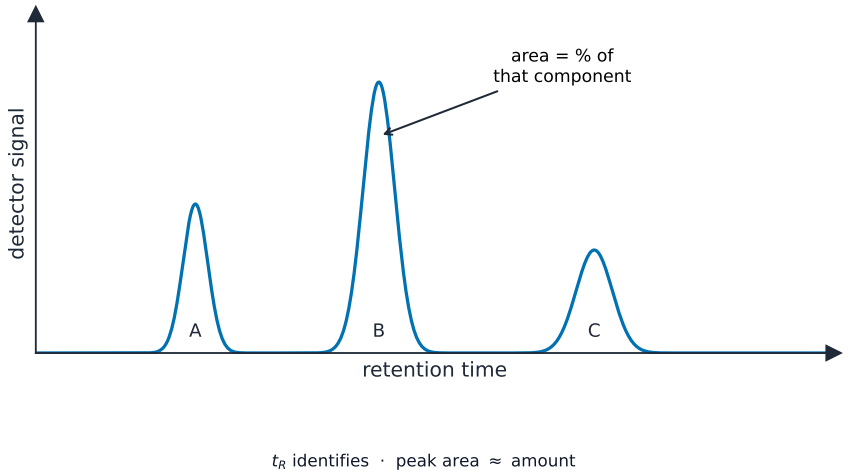
A real TLC plate under UV light: each glowing spot is a separated component of the mixture

Gas/liquid chromatography

In **gas/liquid chromatography** 气液色谱 (GLC):

- the stationary phase is a high-boiling-point non-polar liquid on a solid support.
- the mobile phase is an unreactive carrier gas.
- the **retention time** 保留时间 is how long a component takes to pass through.

The area of each peak gives the percentage of that component in the mixture. A component that interacts more with the stationary phase has a longer retention time.



A gas–liquid chromatogram: each component gives a peak at its own retention time, and the peak area is its percentage in the mixture

Carbon-13 NMR spectroscopy

NMR 核磁共振 (nuclear magnetic resonance) studies how certain nuclei behave in a strong magnetic field.

An NMR spectrometer: the large cylinder holds a superconducting magnet that makes the very strong magnetic field the technique needs

In carbon-13 NMR, each different **chemical environment** 化学环境 of carbon gives one peak. So:

- the **number of peaks** tells you how many different carbon environments there are (equivalent carbons share a peak).
- the position of each peak (its chemical shift) suggests the type of carbon, which helps you deduce possible structures.

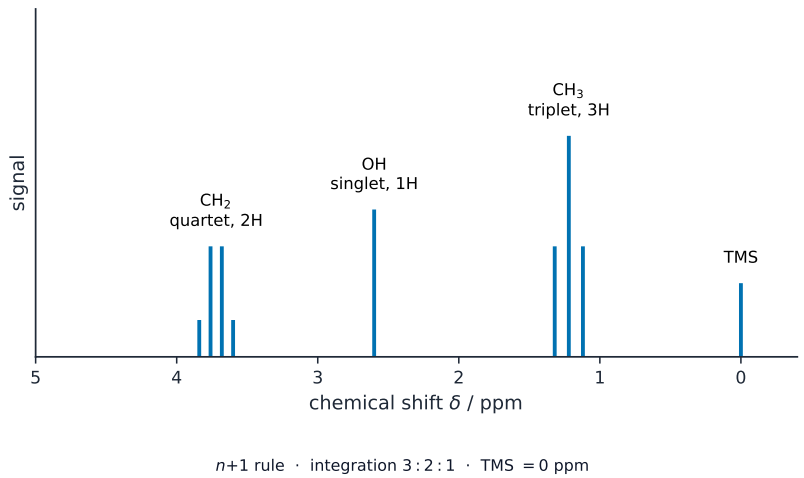
Proton (^{1}H) NMR spectroscopy

Proton NMR looks at the hydrogen atoms (**proton** 质子 nuclei). From the spectrum you read off:

- **chemical environments**: protons in different environments appear at different **chemical shift** 化学位移 values.
- **relative numbers**: the relative peak **areas** give the ratio of each type of proton.
- **splitting** 裂分: a peak is split by the protons on the neighbouring carbon, following the $n+1$ **rule** — n equivalent neighbours split a peak into $n+1$ lines:

Neighbours (n)	Pattern
0	**singlet** 单峰
1	**doublet** 双峰
2	**triplet** 三峰
3	**quartet** 四峰
many	**multiplet** 多重峰

The $n+1$ rule: n equivalent neighbouring protons split a peak into $n+1$ lines (singlet, doublet, triplet, quartet)



Proton NMR of ethanol: three environments give a CH_3 triplet, a CH_2 quartet and an OH singlet, with areas in the ratio 3 : 2 : 1

Practical points

- **tetramethylsilane** 四甲基硅烷 (TMS) is the standard, set at a chemical shift of 0.
- a **deuterated solvent** 氘代溶剂 (such as $CDCl_3$) is used so that the solvent itself gives no proton signal.
- shaking the sample with D_2O makes the O–H and N–H peaks disappear (their hydrogen is swapped for deuterium), which identifies those protons.

Worked example. A compound $C_4H_8O_2$ gives three proton NMR peaks: a **triplet** at δ 1.2 (area 3), a **quartet** at δ 4.1 (area 2), and a **singlet** at δ 2.0 (area 3). Deduce the structure. Read the areas first, then the splitting. Areas 3 : 2 : 3 give three proton environments holding 3, 2 and 3 hydrogens. Apply the $n+1$ rule **in reverse**: a **triplet** (area 3) is a CH_3 with **2** neighbours, and a **quartet** (area 2) is a CH_2 with **3** neighbours - each splitting the other, which is the classic **ethyl group**, CH_3CH_2-. That CH_2 lies far downfield at δ 4.1, so it is attached to an **oxygen**. The remaining **singlet** (area 3) is a CH_3 with **no** neighbours at δ 2.0, so it sits next to the C=O. Together: $CH_3COOCH_2CH_3$, **ethyl ethanoate**. A triplet-and-quartet pair is almost always an ethyl group - spot it first and the rest follows.

Exam tips

- In ^{13}**C NMR** the number of peaks equals the number of **carbon environments** — use symmetry to count them.
- In ^{1}**H NMR** use **chemical shift** (data booklet), **integration** (ratio of H's) and **splitting** (the $n+1$ rule): a triplet + quartet means an ethyl group.
- **TMS** is the reference ($\delta = 0$); a **D_2O shake** removes O-H and N-H peaks.
- Combine IR, mass spectrum and NMR to deduce a structure, stating which evidence gives which feature.