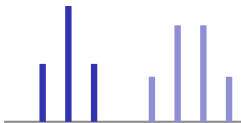


# Analytical Techniques

## A-Level Chemistry ■ Topic 37

A-Level Chemistry



# What we will cover

- 1 Thin-layer chromatography
- 2 Gas/liquid chromatography
- 3 NMR basics
- 4 Splitting & the  $n + 1$  rule
- 5 A proton NMR spectrum



*NMR uses a strong magnet*



# Thin-layer chromatography

The **baseline** is the starting line where the spots are placed; the **solvent front** is the highest level the solvent reaches. The **mobile phase** is the solvent that travels up the plate, the **stationary phase** the coating it travels through. A spot of mixture travels up a plate. Components that adsorb more strongly to the stationary phase move less.

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

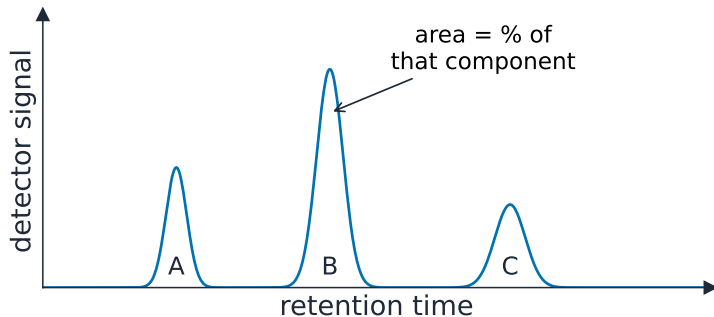
$R_f$  is always between 0 and 1. Identify a component by matching  $R_f$  with a known standard on the same plate.

## Gas/liquid chromatography

In **GLC** a carrier gas sweeps the mixture over a liquid stationary phase.

Each component peaks at its own **retention time** ; the peak **area** gives its percentage in the mixture.

# Gas/liquid chromatography, in detail



$t_R$  identifies · peak area  $\approx$  amount

In **GLC** a carrier gas sweeps the mixture over a liquid stationary phase.



# NMR basics

## carbon-13 NMR

each carbon **environment** gives one peak

## proton NMR

**chemical shift** & peak areas give the proton ratio

**NMR** studies nuclei in a strong magnetic field; the number of peaks = the number of environments.

# Splitting and the $n + 1$ rule

**singlet**

$$n = 0$$

**doublet**

$$n = 1$$

**triplet**

$$n = 2$$

**quartet**

$$n = 3$$

$n$  equivalent neighbours split a peak into  $n + 1$  lines

**Splitting** :  $n$  equivalent neighbouring protons split a peak into  $n + 1$  lines.

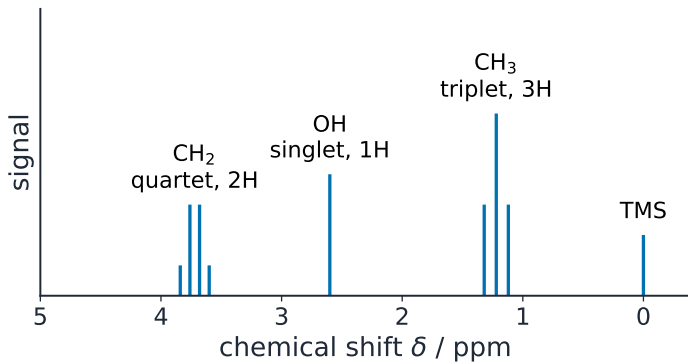
- $0 \rightarrow$  **singlet** ;  $1 \rightarrow$  doublet
- $2 \rightarrow$  triplet;  $3 \rightarrow$  quartet

## A proton NMR spectrum

Ethanol: a  $\text{CH}_3$  triplet, a  $\text{CH}_2$  quartet & an OH singlet (areas 3:2:1).

- **TMS** is the zero reference
- a **deuterated solvent** gives no signal
- $\text{D}_2\text{O}$  removes the O—H/N—H peak

# A proton NMR spectrum, in detail



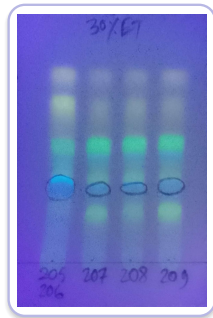
$n+1$  rule · integration 3 : 2 : 1 · TMS = 0 ppm

Ethanol: a  $\text{CH}_3$  triplet, a  $\text{CH}_2$  quartet & an OH singlet (areas 3:2:1).

## Practical points

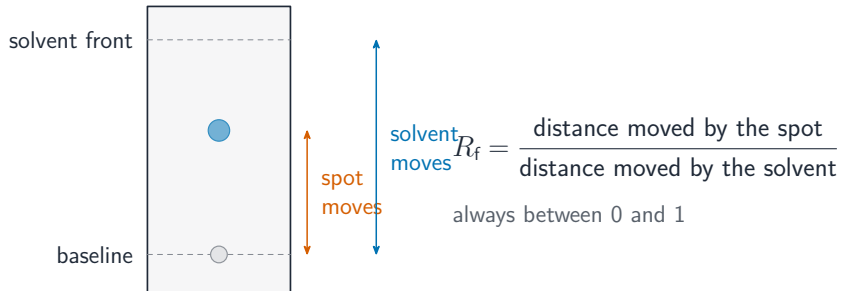
- **tetramethylsilane** (TMS) is the standard, set at a chemical shift of 0.
- a **deuterated solvent** (such as  $\text{CDCl}_3$ ) is used so that the solvent itself gives no proton signal.
- shaking the sample with  $\text{D}_2\text{O}$  makes the O–H and N–H peaks disappear (their hydrogen is swapped for deuterium), which identifies those protons.

## Thin-layer chromatography, continued



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

## Thin-layer chromatography, continued (2)



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

## Exam tips

- In  $^{13}\text{C}$  NMR the number of peaks equals the number of carbon environments – use symmetry to count them.
- In  $^1\text{H}$  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  $\text{D}_2\text{O}$  shake removes O-H and N-H peaks.
- Combine IR, mass spectrum and NMR to deduce a structure, stating which evidence gives which feature.



## Worked example – reading an NMR spectrum

$\text{C}_3\text{H}_8\text{O}$  gives three  $^1\text{H}$  peaks: 6H doublet, 1H septet, 1H singlet that vanishes with  $\text{D}_2\text{O}$ . Identify it.

- Three peaks  $\Rightarrow$  three proton environments; the areas 6 : 1 : 1 give the H in each.
- The singlet that vanishes with  $\text{D}_2\text{O}$  is an O–H (it exchanges, and does not split).
- 6H as a doublet: two equivalent  $\text{CH}_3$  next to one H ( $n + 1 = 2$ ).
- 1H as a septet: that H has six neighbours ( $n + 1 = 7$ ).
- $(\text{CH}_3)_2\text{CH} - \text{OH}$ : propan-2-ol.

Peaks = environments; area = how many H; splitting =  $n + 1$  neighbours. A peak lost with  $\text{D}_2\text{O}$  is O–H or N–H.

## Topic 37 – key takeaways

1

### TLC

$R_f = \text{spot distance} / \text{solvent distance}$

2

### GLC

retention time; peak area = percentage

3

### NMR

peaks = chemical environments

4

### Splitting

$n$  neighbours give  $n + 1$  lines

## Check yourself

- 1 What does the  $R_f$  value compare?
- 2 What does a GLC peak area tell you?
- 3 What does the number of NMR peaks tell you?
- 4 Three neighbouring protons split a peak into how many lines?



**Answers** 1. spot distance vs solvent distance 2. the percentage of that component  
3. the number of carbon environments 4. four (a quartet)