

ANALYSIS II

NMR SPECTROSCOPY

113 - team 4

15

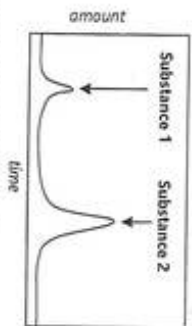
CHROMATOGRAPHY

In chromatography, a stationary phase (e.g. silica in TLC, column or resin in GC) and a moving phase (solvent in TLC, carrier gas in GC) are used to separate substances. Substances are separated because they adsorb to / dissolve in the stationary phase and moving phase to different extents.

GAS CHROMATOGRAPHY

RETENTION TIME

Gas chromatography separates gases by the amount of time they take to go through the chromatography column. This is called the retention time.



CALIBRATION CURVES

The area under each peak is proportional to the concentration of the chemical. A calibration curve can be used to calculate the concentration from the peak area.

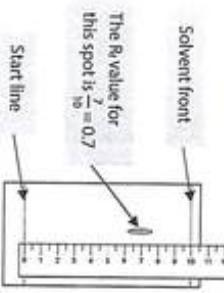
THIN-LAYER CHROMATOGRAPHY

Thin-layer chromatography is a lot like paper chromatography.

Interpreting a chromatograph involves calculating R_f values.

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

R_f VALUES

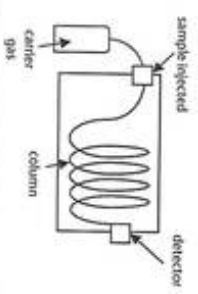


Gas Chromatography

Moving phase = carrier gas

Stationary phase = solid or liquid resin

- Liquid sample is injected into a gas chromatography machine
- Sample is vaporised
- Inert carrier gas draws vapour through a long capillary tube
- Gases are detected at the end of the capillary tube
- The time taken to pass through the capillary tube is recorded on a computer
- A spectrum is produced

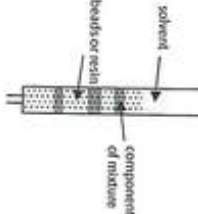


Column Chromatography

Moving phase = solvent

Stationary phase = silica gel or a similar solid

- A column is packed with beads or a gel
- The sample is placed in the top of the column
- A solvent is poured in the top of the column as a mobile phase
- This can be used as a separation technique as different substances pass through at different rates



^1H

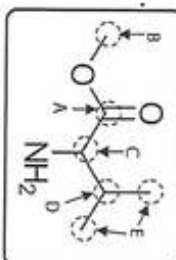
Proton NMR gives the following information:

- number of peaks = number of environments
- shift tells you the environment
- integration = the number of protons in the environment
- splitting = number of adjacent protons

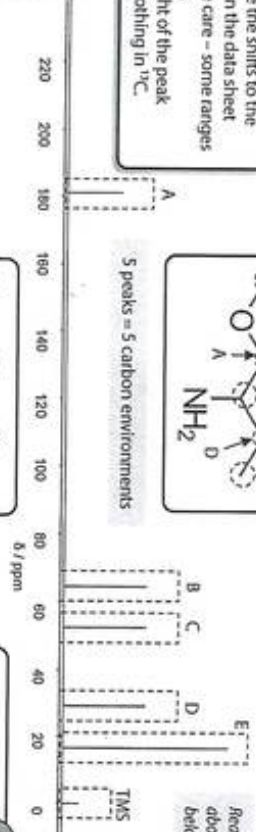
^{13}C

Carbon NMR gives the number and type of carbon 'environments'.

- Strategy:
- Count the number of unique carbon environments.
 - Compare the shifts to the ranges on the data sheet (but take care - some ranges overlap).
 - The height of the peak means nothing in ^{13}C

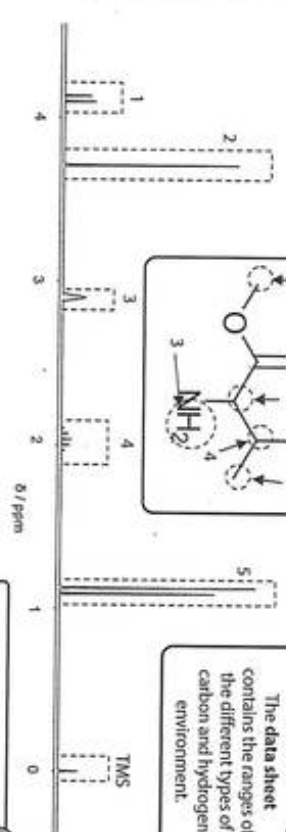
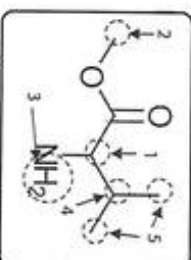


5 peaks = 5 carbon environments



Note that there are two carbons both labelled E. They are equivalent carbon environments.

Read more about TMS below.



EXAM TIP
The data sheet contains the ranges of the different types of carbon and hydrogen environment.

GC-MS

GC-MS is a technique used to analyse components of a sample. The sample is passed through a gas chromatography machine for separation, and then each constituent is analysed using mass spectrometry (MS) for identification.

DEUTERATED SOLVENTS

Deuterated solvents such as CDCl_3 , are used in NMR so that the solvent does not show up in the spectrum because it has no ^1H . CCl_4 may also be used.

ANALYSIS

Peak	Shift	Integration	Group	Splitting	Next to
1	4.1-4.2	1	ROCH	Doublet	1 H
2	3.7-3.8	2	CH ₂ O	Singlet	0 H
3	2.8-2.9	-	RNH ₂	-	?
4	2.9-3.2	1	R ₂ CH	Multiplet	?
5	1.1-1.2	6	RCH ₃	Doublet	1 H

Integration info is given on the spectrum as a ratio of peak areas

EXAM TIP

Structuring information in this way makes it easy for examiners to give you marks!

TMS

TMS is added to NMR samples as a reference to show 0 ppm. All the other peaks are relative to the TMS peak. TMS is suited to this because:

- its protons are all at a lower shift than common organic groups
- it gives a single peak
- it is unreactive

N+1 RULE

The n+1 rule tells you how many peaks you should see in the splitting pattern depending on the number of hydrogen atoms on adjacent carbons.

In the spectrum above:

- 1 is a doublet because there is one hydrogen on an adjacent carbon (environment 4)
- 3 is a singlet because there are no hydrogens on adjacent carbons
- 4 is a multiplet - it is split by different protons
- 5 is a doublet because it is split by one hydrogen in 4

Neighbouring equivalent protons	Pattern
0	Singlet
1	Doublet
2	Triplet
3	Quartet