Topic 19: Modern Analytical Techniques II

Edexcel A Level Chemistry • Paper 1 (9CH0/01)

19.1

Be able to use high-resolution mass spec data to: (i) suggest structures from accurate Mr (4 d.p.), (ii) calculate accurate Mr and identify compounds.

High-resolution mass spectrometry measures Mr to 4 decimal places, allowing you to distinguish between compounds that have the same integer Mr but different molecular formulae.

Accurate relative atomic masses to use:

- ^{12}C = 12.0000
- ^{1}H = 1.0078
- ^{16}O = 15.9949
- ^{14}N = 14.0031

Method: calculate the accurate Mr by summing the accurate masses of every atom in the molecular formula. Compare with the measured accurate Mr to identify the compound.

E.g. CO and C_2H_4 both have a nominal mass of 28, but:

- CO: 12.0000 + 15.9949 = 27.9949
- C_2H_4: 2(12.0000) + 4(1.0078) = 28.0313

High-resolution MS can distinguish these; low-resolution MS cannot.

19.2

Understand that ^{13}C NMR provides information about positions of ^{13}C atoms in a molecule.

^{13}C NMR detects the different chemical environments of carbon atoms in a molecule. Each unique carbon environment gives one peak. Equivalent carbons (related by symmetry) give a single shared peak.

The chemical shift (δ, in ppm) indicates the type of environment. A ^{13}C chemical shift table will be provided in the exam.

19.3

Be able to use ^{13}C NMR data to: (i) predict carbon environments from δ values, (ii) justify the number of peaks.

(i) Typical ^{13}C δ values:

- δ 10–40 ppm: C in alkyl groups (C–C, C–H only)
- δ 50–80 ppm: C bonded to O or N (e.g. C–OH, C–O–C, C–NH_2)
- δ 110–150 ppm: aromatic C or C=C (alkene)
- δ 160–220 ppm: C=O (carbonyl: aldehyde, ketone, acid, ester)

(ii) Number of peaks = number of different carbon environments. Use symmetry to identify equivalent carbons.

E.g. propanone (CH_3COCH_3): 2 peaks — the two CH_3 carbons are equivalent (both at ~δ 30); the C=O is different (~δ 206).

E.g. ethanol (CH_3CH_2OH): 2 peaks — CH_3 (~δ 18) and CH_2 (~δ 58).

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19.4 Understand that high-resolution ^1H NMR provides information about positions of ^1H atoms.

^1H (proton) NMR detects the different chemical environments of hydrogen atoms. It provides three key pieces of information:

1. Number of peaks = number of different H environments in the molecule.
2. Peak area / integration = ratio of H atoms in each environment.
3. Splitting pattern = number of adjacent non-equivalent H atoms (n+1 rule).

A chemical shift table and splitting pattern guide will be provided in the exam.

19.5 Be able to use ^1H NMR data to: (i) predict H environments from δ, (ii) use peak areas for ratios, (iii) use the (n+1) rule for splitting, (iv) predict shifts and splitting.

(i) Typical ^1H δ values:

- δ ~0.9 ppm: R–CH_3 (alkyl, terminal methyl)
- δ ~1.3 ppm: R–CH_2–R (alkyl, internal methylene)
- δ ~2.0–2.5 ppm: C–H adjacent to C=O
- δ ~3.3–3.9 ppm: C–H adjacent to O or halogen
- δ ~6.5–8.0 ppm: aromatic H (ArH)
- δ ~9.0–10.0 ppm: CHO (aldehyde)
- δ ~11–12 ppm: COOH (carboxylic acid)

(ii) Peak area ratios: the ratio of the integrated areas under each peak = ratio of H atoms in each environment. E.g. ethanol (CH_3CH_2OH): areas in ratio 3:2:1.

(iii) (n+1) rule: a peak is split into (n+1) lines, where n = number of adjacent non-equivalent H atoms on neighbouring carbons.

- 0 neighbours → singlet (s)
- 1 neighbour → doublet (d)
- 2 neighbours → triplet (t)
- 3 neighbours → quartet (q)

(iv) D_2O shake test: adding D_2O exchanges O–H or N–H protons for deuterium (NMR-inactive). If a peak disappears after adding D_2O, it confirms the presence of an –OH or –NH group.

19.6 Know that chromatography separates components between a mobile phase and a stationary phase.

Chromatography separates mixtures based on the differential distribution of components between:

- Stationary phase: does not move (e.g. silica on a TLC plate, liquid coated on a column packing).
- Mobile phase: moves through or over the stationary phase (e.g. solvent in TLC, gas in GC).

Components with greater affinity for the stationary phase move more slowly and have higher Rf values (TLC) or longer retention times (GC/HPLC). Components with greater affinity for the mobile phase move faster.

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19.7

Be able to calculate Rf values from one-way chromatograms.

Rf = distance moved by substance / distance moved by solvent front

Rf values are always between 0 and 1. They are characteristic of a substance under specific conditions (same solvent, temperature, stationary phase). Comparing Rf values with known standards run on the same plate allows identification of unknown substances.

E.g. substance moves 3.6 cm, solvent front moves 6.0 cm: Rf = 3.6 / 6.0 = 0.60.

19.8

Know that HPLC and GC: (i) are types of column chromatography, (ii) separate by different retention times, (iii) may be used with mass spectrometry (GC-MS) in forensics and drug testing.

HPLC (High Performance Liquid Chromatography): liquid mobile phase is forced through a tightly packed column at high pressure. Separates non-volatile and thermally unstable compounds (e.g. amino acids, drugs, large biomolecules).

GC (Gas Chromatography): gaseous mobile phase (carrier gas, e.g. N_2 or He) carries a vaporised sample through a heated column. Separates volatile compounds (e.g. alcohols, alkanes, flavour compounds).

Both produce chromatograms showing peaks at different retention times. The area under each peak is proportional to the amount of that component.

GC-MS / HPLC-MS: the chromatography column output feeds directly into a mass spectrometer — providing both separation (by retention time) AND identification (by mass spectrum). Used in:

- Forensics (crime scene analysis, toxicology)
- Drug testing in sport (detecting banned substances)
- Pharmaceutical quality control
- Environmental monitoring

ABOUT THESE NOTES

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