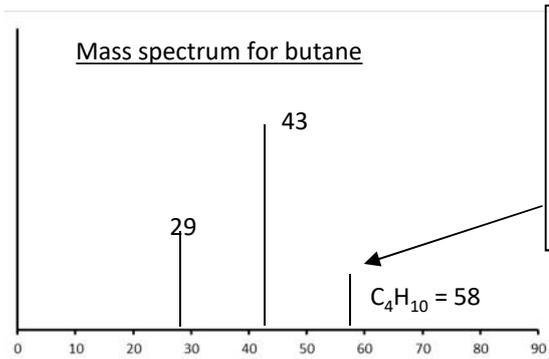# 3.6 Organic Analysis

Mass Spectrometry

When organic molecules are passed through a mass spectrometer, it detects both the whole molecule and fragments of the molecule

Mass spectrum for butane

43

29

C_4H_{10} = 58

The peak with the highest mass/charge ratio will be normally due to the original molecule that hasn't fragmented (called the molecular ion) . As the charge of the ion is +1 the mass/ charge ratio is equal to Mr.

Molecular ion formed: $M \rightarrow [M]^{+\cdot} + e^-$

Definition: **molecular ion** is the molecule with one electron knocked off (It is both an ion and a free radical)

High resolution mass spectrometry can be used to determine the molecular formula of a compound from the accurate mass of the molecular ion

High resolution mass spectroscopy can measure the mass to 5 d.p. This can help differentiate between compounds that appear to have similar Mr (to the nearest whole number)

For example, the following molecular formulas all have a rough M_r of 60, but a more precise M_r can give the molecular formula.

e.g. M_r = 60.02112   molecular formula = $C_2H_4O_2$

            M_r = 60.05751   molecular formula = C_3H_8O

            M_r = 60.03235   molecular formula = CH_4N_2O

Accurate masses of atoms:
H = 1.0078
C = 12.0000
O = 15.9949
N = 14.0031

Carbon has a value of 12.0000 as it is by definintion the standard reference

Example 1

A compound is found to have an accurate relative formula mass of 46.0417. It is thought to be either CH_3CH_2OH or $H_2NCH_2NH_2$. Calculate the M_r of each compound to 4 decimal places to work out which one it is.

    CH_3CH_2OH = (12.0000 x 2) + (15.9949 x 1) + (1.0078 x6) = 46.0417

    $H_2NCH_2NH_2$. = (12.0000 x 1) + (14.0031 x 2) + (1.0078 x6) = 46.0530

M+2 peak

If a compound contains a chlorine or a bromine atom then two molecular ion peaks will occur : a **M** and a **M+2** peak will occur due to the two naturally occurring isotopes of chlorine or bromine.

Chlorine exists as Cl^{35} (75%) and Cl^{37} (25%)
Bromine exists as Br^{79} (50%) and Br^{81} (50%)

CH_3Cl will have a m/z value of **M** of 50 CH_3Cl ^{35} and **M+2** of 52 CH_3Cl ^{37}
The ratio of heights **M:M+2** will be 3:1

CH_3Br will have m/z value of **M** of 94 CH_3Br^{79} and **M+2** of 96CH_3Br^{81}
The ratio of heights **M:M+2** will be 1:1

If a compound contains two chlorine or bromine atoms then a **M+2** and a **M+4** peak will occur
Relative abundances
$Cl^{35}Cl^{35}$ = 0.75 x0.75 = 0.5625 =>**9**
$Cl^{35}Cl^{37}$
$Cl^{37}Cl^{35}$ $= 0.75 x0.25$**x2**$= 0.375$ =>**6**
$Cl^{37}Cl^{37}$ = 0.25 x0.25 =0.0625 =>**1**

÷ smallest to get whole number ratio

$C_2H_4Cl_2$ will have a m/z value of **M** of 98 C_2H_4Cl ^{35}Cl ^{35} , a **M+2** of 100 C_2H_4Cl ^{35}Cl ^{37} and a **M+4** of 102 C_2H_4Cl ^{35}Cl ^{37}
The ratio of heights **M:M+2: M+4** will be 9:6:1

$C_2H_4Br_2$ will have a m/z value of **M** of 186 $C_2H_4Br^{79}Br^{79}$, a **M+2** of 188 $C_2H_4Br^{79}Br^{81}$ and a **M+4** of 190 $C_2H_4Br^{81}Br^{81}$
The ratio of heights **M:M+2: M+4** will be 1:2:1

$C_2H_3Cl_3$ will have a m/z value of **M** of 132 $C_2H_4Cl^{35}Cl^{35}Cl^{35}$, a **M+2** of 134 $C_2H_4Cl^{35}Cl^{35}Cl^{37}$, a **M+4** of 136 $C_2H_4Cl^{35}Cl^{37}Cl^{37}$ and a **M+6** of 138 $C_2H_4Cl^{37}Cl^{37}Cl^{37}$
The ratio of heights **M:M+2:M+4:M+6** will be 27:27:9:1

Relative abundances
$Cl^{35}Cl^{35}Cl^{35}$ = 0.75 x0.75x0.75 = 0.4219 =>**27**
$Cl^{35}Cl^{35}Cl^{37}$ = 0.75 x0.75x0.25**x3**= 0.4219 =>**27**
$Cl^{35}Cl^{37}Cl^{37}$ = 0.75 x0.25x0.25**x3**= 0.1406 =>**9**
$Cl^{37}Cl^{37}Cl^{37}$ = 0.25 x0.25x0.25 =0.0156 =>**1**
÷ smallest to get whole number ratio

Infrared spectroscopy

Certain groups in a molecule absorb infra-red radiation at characteristic frequencies

Complicated spectra can be obtained than provide information about the types of bonds present in a molecule

Above 1500 cm^{-1} – "Functional group identification"
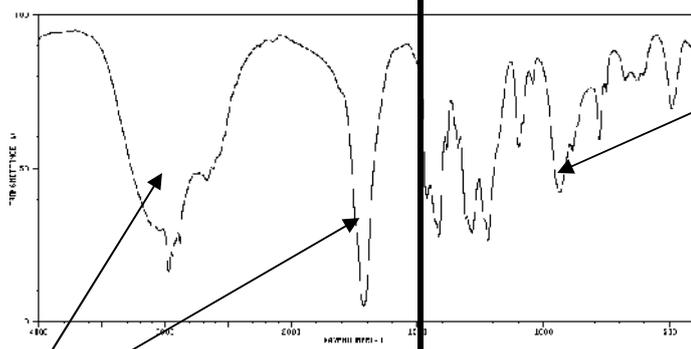
Below 1500 cm^{-1} – "Fingerprinting"

Complicated and contains many signals – picking out functional group signals difficult.

This part of the spectrum is unique for every compound, and so can be used as a "fingerprint".

Use an IR absorption table provided in exam to deduce presence <u>or</u> absence of particular bonds or functional groups

A computer will compare the IR spectra against a database of known pure compounds to identify the compound

e.g.   C=O 1680 – 1750 cm^{-1}

O-H (acid) 2500- 3000 cm^{-1}

Infrared absorption data

Bond	Wavenumber /cm^{-1}
N − H (amines)	3300 − 3500
O − H (alcohols)	3230 − 3550
C − H	2850 − 3300
O − H (acids)	2500 − 3000
C ≡ N	2220 − 2260
C = O	1680 − 1750
C = C	1620 − 1680
C − O	1000 − 1300
C − C	750 − 1100

Use spectra to identify particular functional groups and to identify impurities, limited to data presented in wavenumber form
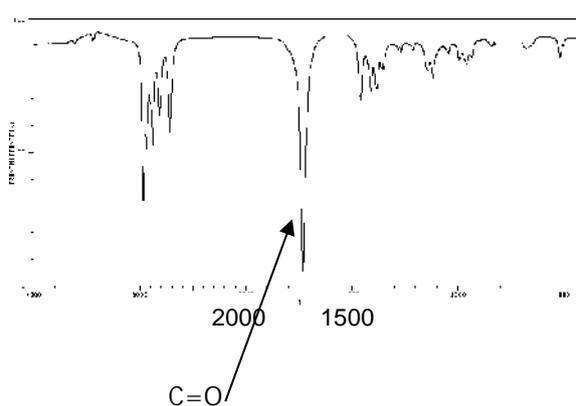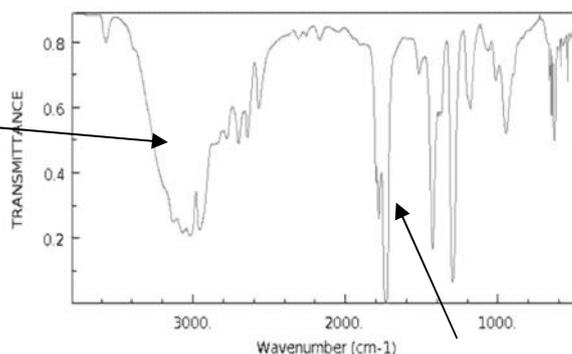

Spectra for butanal

$H_3C-CH_2-CH_2-C\!\!\diagdown^{O}_{H}$

2000   1500

C=O
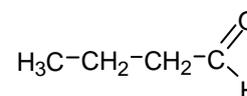
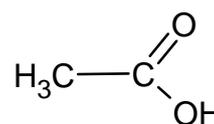Absorption or trough in between 1680-1750 cm^{-1} range indicates presence of C=O bond

Always quote the wave number range from the data sheet

O-H absorptions tend to be broad

Absorption or trough in between 2500-3000 cm^{-1} range indicates presence of O-H bond in an acid

Spectra for ethanoic acid

$$H_3C - C \overset{O}{\underset{OH}{\diagdown}}$$

C=O

Absorption or trough in between 1680-1750 cm^{-1} range indicates presence of C=O bond

"rogue" absorptions can also occur and are indicators of impurities

The absorption of infra-red radiation by bonds in this type of spectroscopy is the same absorption that bonds in CO_2, methane and water vapour in the atmosphere do that maybe causing global global warming.

Identification of Functional Groups by test-tube reactions

Functional group	Reagent	Result
Alkene	Bromine water	Orange colour decolourises
Aldehyde	Fehling's solution	Blue solution to red precipitate
Aldehyde	Tollen's Reagent	Silver mirror formed
Carboxylic acid	Sodium carbonate	Effervescence of CO_2 evolved
1° 2° alcohol and aldehyde	Sodium dichromate and sulfuric acid	Orange to green colour change
chloroalkane	Warm with silver nitrate	Slow formation of white precipitate of AgCl

Tollen's Reagent

Reagent: Tollen's Reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of $[Ag(NH_3)_2]^+$.

Conditions: heat gently

Reaction: aldehydes only are oxidised by Tollen's reagent into a carboxylic acid. The silver(I) ions are reduced to silver atoms

Observation: with aldehydes, a silver mirror forms coating the inside of the test tube. Ketones result in no change.

$CH_3CHO + 2Ag^+ + H_2O \rightarrow CH_3COOH + 2Ag + 2H^+$

Fehling's solution

Reagent: Fehling's Solution containing blue Cu^{2+} ions.

Conditions: heat gently

Reaction: aldehydes only are oxidised by Fehling's Solution into a carboxylic acid. The copper (II) ions are reduced to copper(I) oxide .

Observation: Aldehydes : Blue Cu^{2+} ions in solution change to a red precipitate of Cu$_2$O. **Ketones do not react**

$CH_3CHO + 2Cu^{2+} + 2H_2O \rightarrow CH_3COOH + Cu_2O + 4H^+$
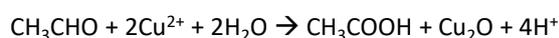
The presence of a carboxylic acid can be tested by addition of **sodium carbonate**. It will fizz and produce carbon dioxide
$2CH_3CO_2H + Na_2CO_3 \rightarrow 2CH_3CO_2^-Na^+ + H_2O + CO_2$