Measurement and data processing SL (answers)

IB CHEMISTRY SL

25	16		6	2	25
Mn	**S**	**J**	**C**	**He**	**Mn**
Manganese	Sulfur		Carbon	Helium	Manganese
54.938045	32.065		12.0107	4.002602	54.938045

11.1 Uncertainties and errors in measurement and results

Understandings:

- Qualitative data includes all non-numerical information obtained from observations not from measurement.
- Quantitative data are obtained from measurements, and are always associated with random errors/uncertainties, determined by the apparatus, and by human limitations such as reaction times.
- Propagation of random errors in data processing shows the impact of the uncertainties on the final result.
- Experimental design and procedure usually lead to systematic errors in measurement, which cause a deviation in a particular direction.
- Repeat trials and measurements will reduce random errors but not systematic errors.

Applications and skills:

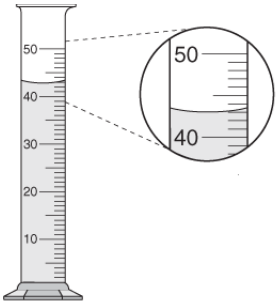
- Distinction between random errors and systematic errors.
- Record uncertainties in all measurements as a range ($\pm$) to an appropriate precision.
- Discussion of ways to reduce uncertainties in an experiment.
- Propagation of uncertainties in processed data, including the use of percentage uncertainties.
- Discussion of systematic errors in all experimental work, their impact on the results and how they can be reduced.
- Estimation of whether a particular source of error is likely to have a major or minor effect on the final result.
- Calculation of percentage error when the experimental result can be compared with a theoretical or accepted result.
- Distinction between accuracy and precision in evaluating results.

Guidance:

- The number of significant figures in a result is based on the figures given in the data. When adding or subtracting, the final answer should be given to the least number of decimal places. When multiplying or dividing the final answer is given to the least number of significant figures.
- Note that the data value must be recorded to the same precision as the random error.
- SI units should be used throughout the programme.

Quantitative and qualitative data

- Quantitative data is data taken from measurements made in the laboratory and is associated with random errors.
- Examples include mass and volume.



- Qualitative data includes non-numerical data obtained from observations, not from measurements.
- Examples include colour changes or the production of a gas.

Absolute and percentage uncertainty

- The absolute uncertainty of digital apparatus is ± the smallest scale division.

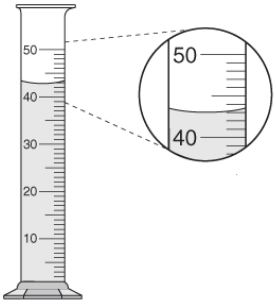
Absolute uncertainty of mass balance is ± 0.01 g

Mass of $CaCO_3$ = 16.43 ± 0.01 g

Percentage uncertainty:

$$\frac{0.01}{16.43} \times 100 = 0.06\ \%$$

- The absolute uncertainty of analog apparatus is ± half the smallest scale division.



Absolute uncertainty of measuring cylinder is ± 0.5 cm^3

Volume of H_2O = 43.0 ± 0.5 cm^3

Percentage uncertainty:

$$\frac{0.5}{43.0} \times 100 = 1\%$$

Recording data

- A results table should include quantitative data with units and uncertainties.
- Quantitative data should be recorded to the appropriate precision.
- Qualitative data should also be recorded.

Example data table for a titration

	Trial 1	Trial 2	Trial 3	Trial 4
Initial volume of $NaOH_{(aq)}$ (± 0.05 cm^3)	0.00	0.00	0.00	0.00
Final volume of $NaOH_{(aq)}$ (± 0.05 cm^3)	11.10	11.00	10.85	10.90
Total volume of $NaOH_{(aq)}$ (± 0.10 cm^3)	11.10	11.00	10.85	10.90
Colour change with phenolphthalein	dark pink	pink	light pink	light pink

Random errors

- Random errors are caused by unpredictable changes in the experiment (in the conditions or apparatus).
- With random errors, there is an equal probability of the measured value being too high or too low.

Examples of random errors:

- Changes in the environment during the experiment (such as a change in the room temperature).
- Observer misinterpreting the reading.
- Insufficient data (not conducting repeat trials).
- Random errors cannot be eliminated but can be reduced by conducting repeat trials.
- They can also be reduced by using precise apparatus (such as using a volumetric pipette rather than a beaker to measure volume).

Systematic errors

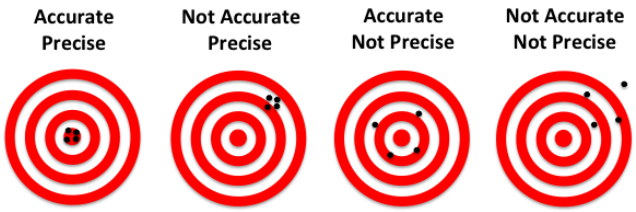
- Systematic errors occur as a result of a flaw in the experimental design or apparatus.
- Systematic errors cause the measured values to be consistently higher or lower than the actual value.
- They cannot be reduced by conducting repeat trials.

Examples of systematic errors:

- Heat loss in an experiment to measure enthalpy change.
- Losing a product (such as a gas) in a reaction.
- Overshooting the endpoint in a titration.
- Reading from the top of the meniscus when measuring volume.
- Forgetting to zero a mass balance.

Accuracy and precision

- Accuracy refers to the closeness of the measured value to the actual value.
- Precision refers to the closeness of the repeat values to each other.



Propagation of uncertainties

- In an experiment to measure the enthalpy change of a reaction the following quantitative data was collected:

Volume of water in calorimeter = 50.0 ± 0.5 cm^3

Trial	Initial temperature of water (± 0.5 °C)	Maximum temperature of water (± 0.5°C)	Change in temperature of water (± 1.0°C)
1	18.5	26.0	6.5
2	18.5	25.5	7.0
3	18.5	26.5	8.0

- Use this data to calculate the enthalpy change for the reaction including the uncertainty.

Volume of water in calorimeter = 50.0 ± 0.5 cm^3

1. Use the half range method to calculate the uncertainty of the average values:
   Calculate average: $\frac{(6.5+7.0+8.0)}{3} = 7.2$ °C
   Half range method: (highest – lowest) ÷ 2
   (8.0 – 6.5) ÷ 2 = 0.8 °C
   Average change in temperature = 7.2 ± 0.8 °C

2. Calculate enthalpy change:
   Density of water = 1 gcm^{-3}
   Specific heat capacity of water = 4.18 J g^{-1} $°C^{-1}$
   $$q=mc\Delta T$$
   $$q = 50.00\ g \times 4.18 \times 7.2 = 1504.8\ J$$
   The temperature change was the **least** precise measurement (two significant figures) so the final value should be quoted to this precision.
   $$\mathbf{q = 1.5 \times 10^3\ J}$$

3. Propagate uncertainties:
   Uncertainty in temperature (already calculated) ± 0.8 °C

Convert to percentage uncertainty:

$$\frac{0.8}{7.2} \times 100 = 11\ \%$$

Uncertainty in volume of water ±0.5cm^3

Convert to percentage uncertainty:

$$\frac{0.5}{50.0} \times 100 = 1\ \%$$

Add together percentage uncertainties: (1+11) = 12 %

q = 1.5 × 10^3 J ± 12 %

Convert back to absolute uncertainty:

$\frac{12}{100}$ × 1500 = 180 J **Final answer: q = 1.5 × 10^3 ± 180 J**

Percentage error

- Percentage error is a measure of how close the experimental value is to the theoretical or accepted value.

$$\%\ \text{error} = \frac{(\text{experimental value}) - (\text{theoretical value})}{\text{theoretical value}} \times 100$$

- If the experimental value is less than the theoretical value, the percentage error will be negative.
- If it is greater than the theoretical value, the percentage error will be positive.

Example:

The experimental value for the enthalpy change of neutralization was found to be -49.6 kJ mol^{-1}. The literature value for the enthalpy change of neutralization is -57.0 kJ mol^{-1}. Calculate the percentage error and suggest possible errors and improvements to the method.

$$\%\ \text{error} = \frac{-49.6 - -57.0}{-57.0} \times 100 = -13\% = 13\%$$

The negative percentage error, although unusual, tells us the experimental value is lower than experimental value. The negative sign is sometimes omitted.

Possible errors: heat loss to the surroundings (systematic error).

Improvements: use an insulated cup.

11.3 Spectroscopic identification of organic compounds

Understandings:

- The degree of unsaturation or index of hydrogen deficiency (IHD) can be used to determine from a molecular formula the number of rings or multiple bonds in a molecule.
- Mass spectrometry (MS), proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and infrared spectroscopy (IR) are techniques that can be used to help identify compounds and to determine their structure.

Applications and skills:

- Determination of the IHD from a molecular formula.
- Deduction of information about the structural features of a compound from percentage composition data, MS, ^{1}H NMR or IR.

Guidance:

- The electromagnetic spectrum (EMS) is given in the data booklet in section 3.
- The regions employed for each technique should be understood.
- The operating principles are not required for any of these methods.
- The data booklet contains characteristic ranges for IR absorptions (section 26),^{1}H NMR data (section 27) and specific MS fragments (section 28). For ^{1}H NMR, only the ability to deduce the number of different hydrogen (proton) environments and the relative numbers of hydrogen atoms in each environment is required. Integration traces should be covered but splitting patterns are not required.

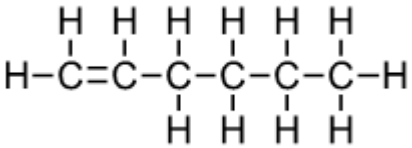
Index of hydrogen deficiency (IHD)

- The index of hydrogen deficiency (IHD) is a count of how many molecules of H_2 need to be added to convert the molecule to the corresponding saturated, non-cyclic molecule.
- By calculating the IHD, we can tell from the molecular formula how many multiple bonds and rings are present in the molecule.
- The IHD for a hydrocarbon with x carbon atoms and y hydrogen atoms is given by the equation:

$$\text{IHD} = \frac{(2x + 2 - y)}{2}$$

Example:

Calculate the IHD of hex-1-ene (C_6H_{12})



$$\text{IHD} = \frac{2\,(6) + 2 - 12}{2} = 1$$

Exercise:

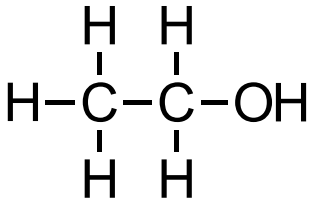
Calculate the IHD for but-1-yne (C_4H_6)

$$\text{IHD} = \frac{2\,(4) + 2 - 6}{2} = 2$$

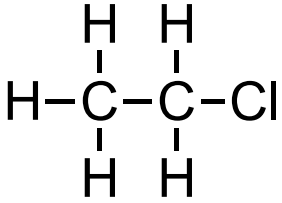
Compounds that contain atoms other than hydrogen (H):

- sulfur (S) and oxygen (O) do not affect the IHD
- halogens (F, Cl, Br and I) are treated like H atoms
- nitrogen (N) – for each N atom, add one to the number of C atoms and H atoms

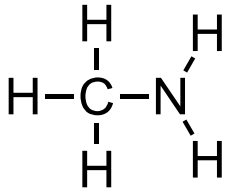
Exercise: calculate the IHD for the following molecules:



$$\text{IHD} = \frac{2\,(2) + 2 - 6}{2} = 0$$



$$\text{IHD} = \frac{2\,(2) + 2 - 6}{2} = 0$$



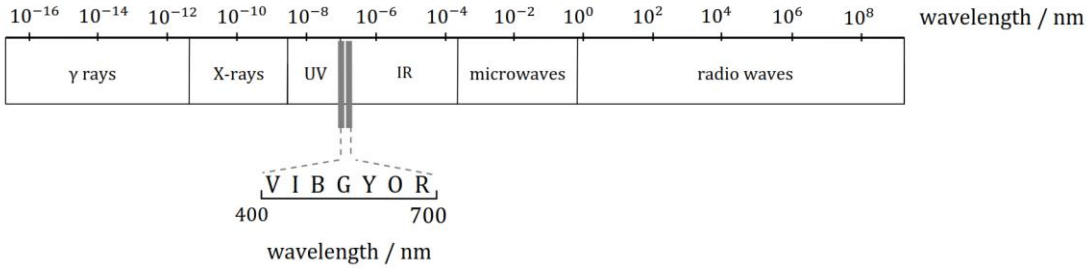
$$\text{IHD} = \frac{2\,(2) + 2 - 6}{2} = 0$$

Summary

IHD	multiple bonds/rings present in molecule	example
0	single bonds (saturated, non-cyclic)	propane C_3H_8
1	double bond / ring structure	but-2-ene C_4H_8 cyclopropane C_5H_{10}
2	triple bond	propyne C_3H_4

Infrared spectroscopy

- When molecules absorb energy in the infrared region of the electromagnetic spectrum, it causes the bonds between the atoms to vibrate (the bonds stretch and bend).



- The frequency of IR radiation that is absorbed is measured as the number of waves per centimeter (wavenumber cm^{-1}).
- Table 26 (from the IB data booklet) gives the wavelength of IR radiation absorbed by different bonds.

26. Infrared data

Characteristic ranges for infrared absorption due to stretching vibrations in organic molecules.

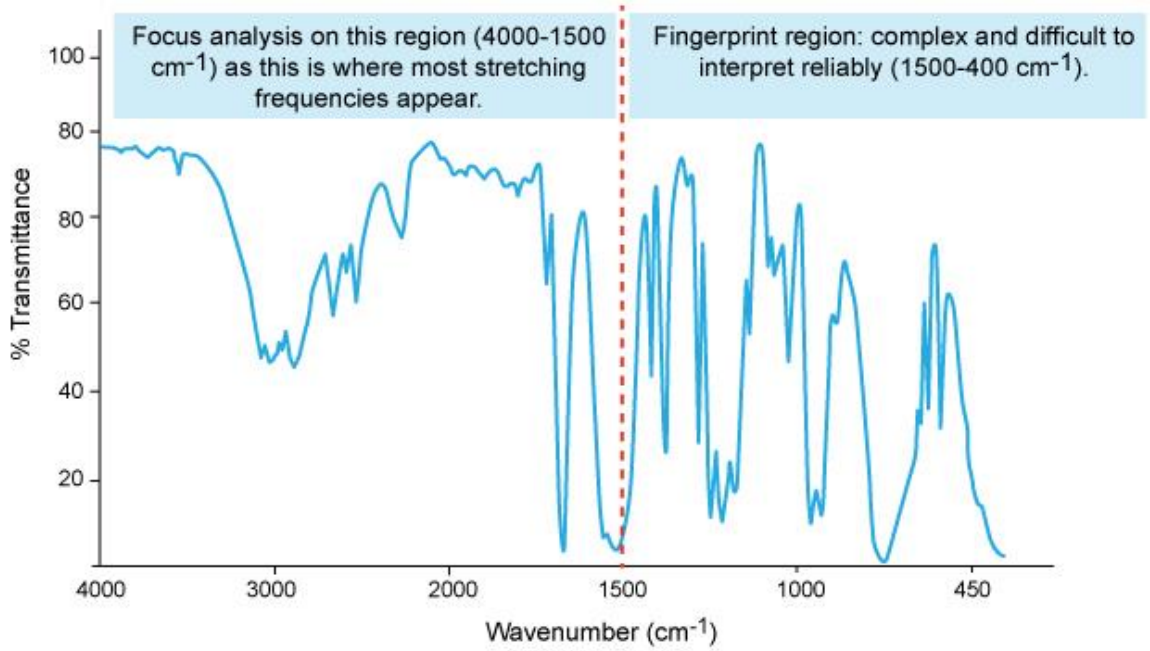
Bond	Organic molecules	Wavenumber (cm^{-1})	Intensity
C–I	iodoalkanes	490–620	strong
C–Br	bromoalkanes	500–600	strong
C–Cl	chloroalkanes	600–800	strong
C–F	fluoroalkanes	1000–1400	strong
C–O	alcohols, esters, ethers	1050–1410	strong
C=C	alkenes	1620–1680	medium-weak; multiple bands
C=O	aldehydes, ketones, carboxylic acids and esters	1700–1750	strong
C≡C	alkynes	2100–2260	variable
O–H	carboxylic acids (with hydrogen bonding)	2500–3000	strong, very broad
C–H	alkanes, alkenes, arenes	2850–3090	strong
O–H	alcohols and phenols (with hydrogen bonding)	3200–3600	strong, broad
N–H	primary amines	3300–3500	medium, two bands

A bond will only interact with IR radiation if it is a polar covalent bond (non-polar bonds do not absorb IR radiation).
The intensity depends on the dipole moment of the bond:

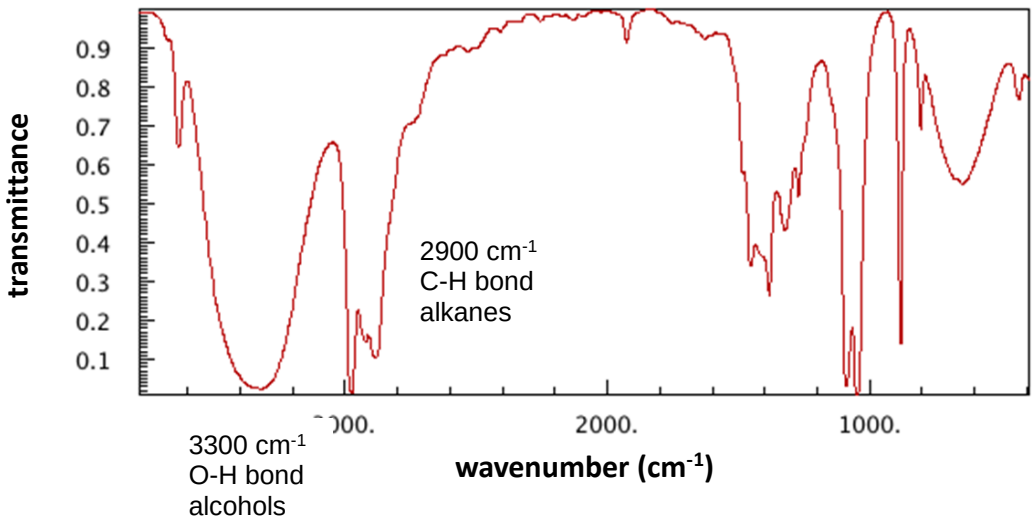
- strongly polar bonds produce strong bands
- bonds with medium polarity produce medium bands
- weakly polar bonds produce weak bands

Example IR spectrum

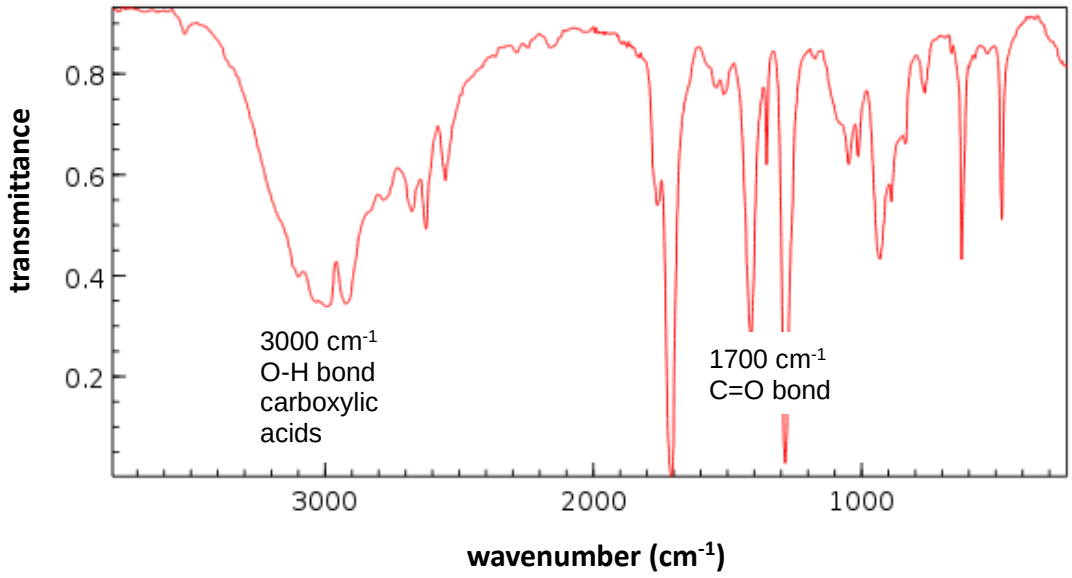
- The region of an infrared spectrum in the range of about 500 to 1500 cm^{-1} is called the fingerprint region.
- This region of the spectrum is almost unique for any given compound and can be used to identify an unknown compound by comparing with the IR spectra of known compounds.
- The functional group region can be used to identify the bonds present in the compound.



Example: use table 26 of the data booklet to identify the functional group present in the compound. **IR spectrum for ethanol C_2H_5OH**



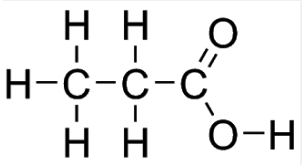
Exercise: use table 26 of the data booklet to identify the functional group present in the compound.



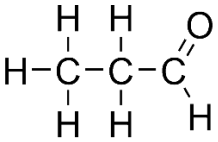
Exercise

The IR spectra below are for propanoic acid, propanal and propan-1-ol, but not in that order.

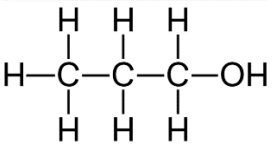
1. Draw the full structural formula of the three compounds and identify the functional group in each molecule



Propanoic acid
(carboxyl group)



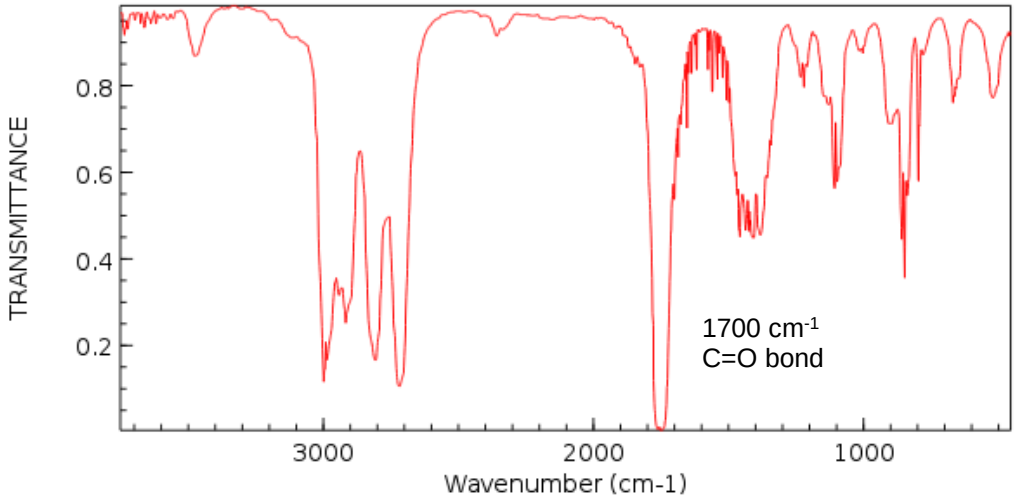
Propanal
(aldehyde group)



Propan-1-ol
(hydroxyl group)

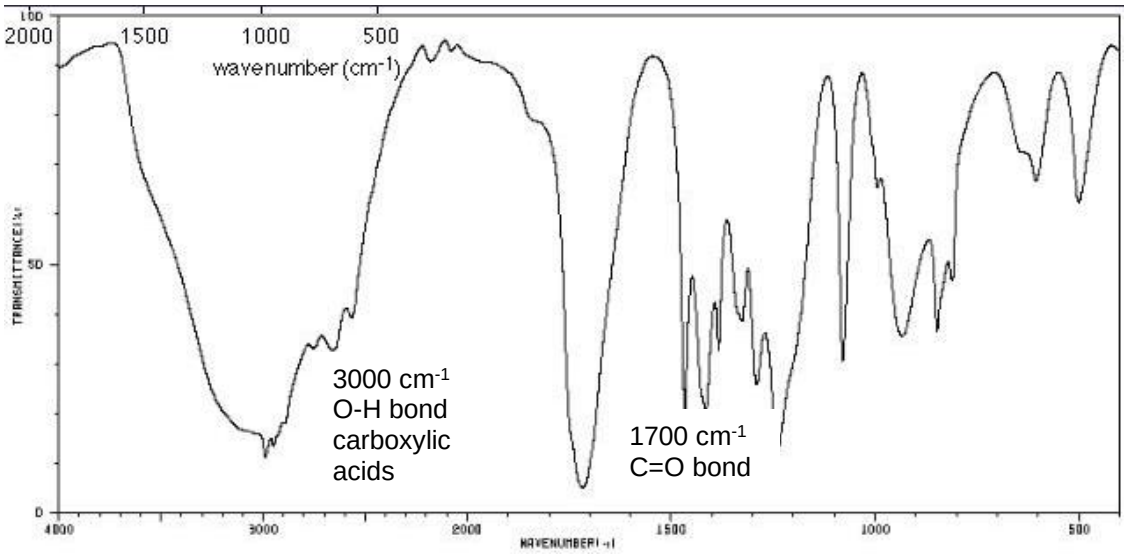
2. Deduce which IR spectrum is for which compound, giving reasons for your choice.

Spectrum A



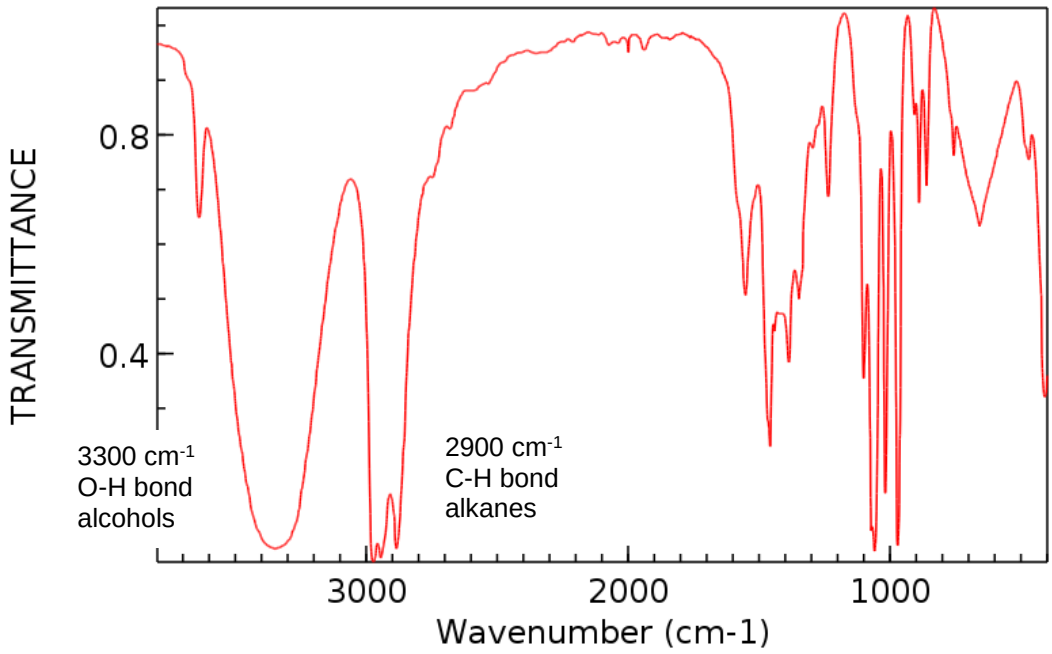
Spectrum A is propanal – note the absorption at 1700 cm^{-1} that corresponds to the C=O bond in the aldehyde group.

Spectrum B



Spectrum B is propanoic acid – note the absorptions at 1700 cm^{-1} and 3000 cm^{-1} that correspond to the C=O and O-H in the carboxyl group, COOH.

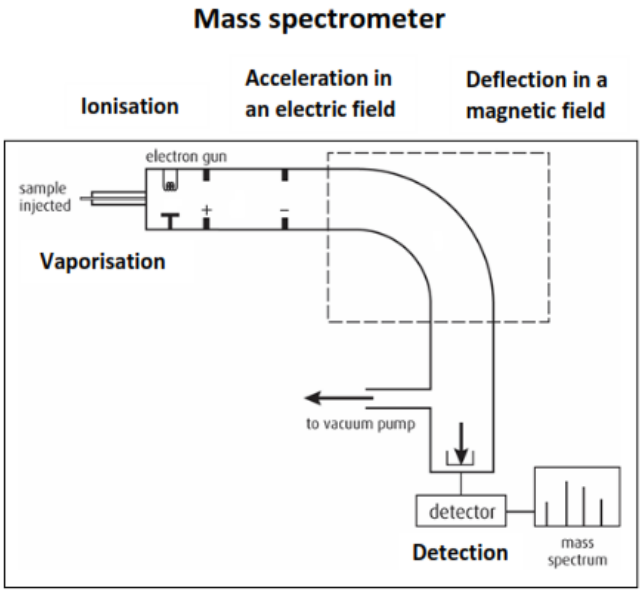
Spectrum C



Spectrum C is propan-1-ol – note the absorptions at 3300 cm^{-1} and 2900 cm^{-1} that correspond to the O-H and C-H bonds respectively.

Mass spectrometry

- Mass spectrometry is used to determine the relative atomic mass (A_r) of an element – it can also be used to determine the structure of a compound.



- When the vaporised organic sample passes into the ionisation chamber of a mass spectrometer, it is bombarded by a stream of electrons.

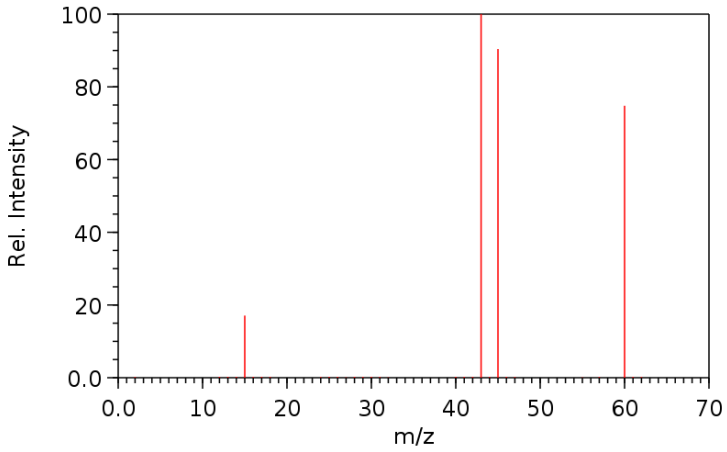
$$M_{(g)} + e^- \longrightarrow M^+_{(g)} + 2e^-$$

- The $M^+_{(g)}$ ion is known as the molecular ion.
- Inside the mass spectrometer, some of the molecular ions break down to produce fragments.
- A fragmentation pattern is produced which gives useful information about the structure of the compound.
- Table 28 has the mass and fragments lost

28. Mass spectral fragments lost

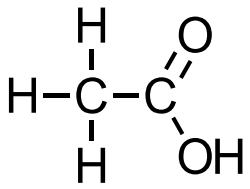
Mass lost	Fragment lost
15	CH_3
17	OH
18	H_2O
28	CH_2=CH_2, C=O
29	CH_3CH_2, CHO
31	CH_3O
45	COOH

Example - mass spectrum of ethanoic acid (CH_3COOH)



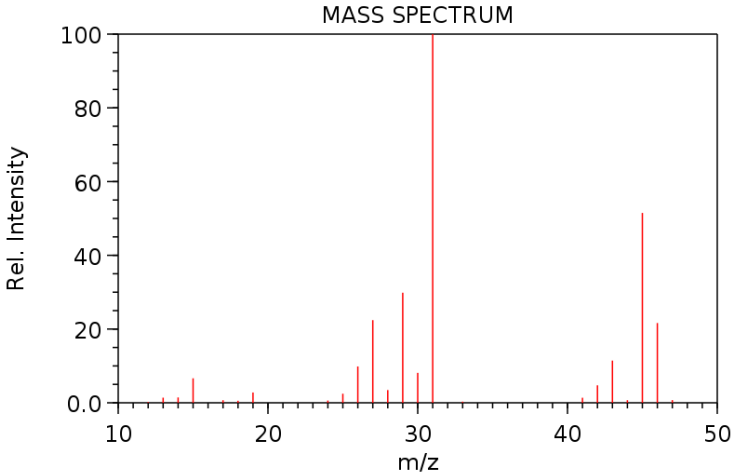
- The peak at m/z = 60 is produced by the molecular ion (M^+)
- The peak at m/z = 45 is produced by the loss of a CH_3 group (60 – 45 = 15)
- The peak at m/z = 43 is produced by the loss of a OH group (60 – 43 = 17)
- The peak at m/z = 15 is produced by the loss of a COOH group (60 – 15 = 45)

Peak	Fragment
45 (60 – 45 = 15)	$COOH^+$ (loss of CH_3)
43 (60 – 43 = 17)	$C_2H_3O^+$ (loss of OH)
15 (60 – 15 = 45)	CH_3^+ (loss of COOH)



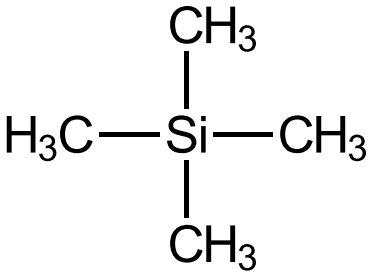
Exercise: The following mass spectrum is for an isomer of C_2H_6O.
Determine the following:

a) the molar mass of the molecular ion 46 g mol^{-1}
b) the fragment that gives rise to the peak at m/z 29 $C_2H_5^+$
c) the fragment that gives rise to the peak at m/z 15 CH_3^+
d) the fragment that gives rise to the peak at m/z 31 CH_3O^+
e) determine the full structural formula of the compound. CH_3CH_2OH

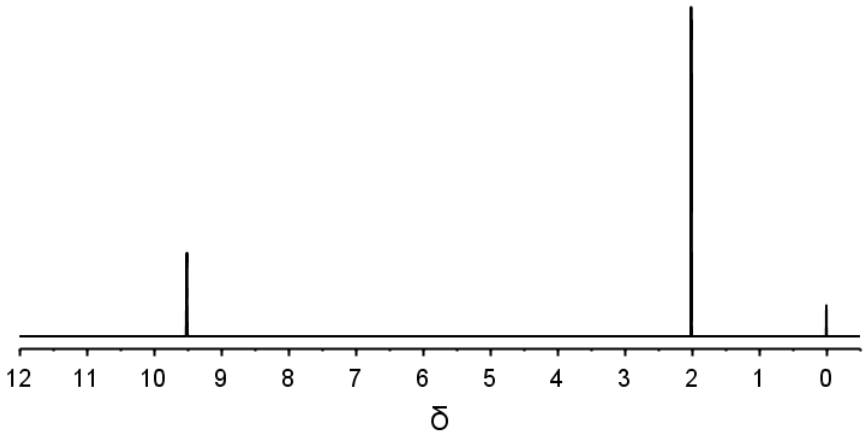


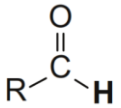
Proton nuclear magnetic resonance spectroscopy

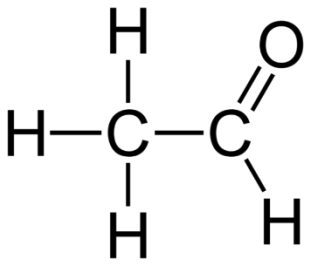
- Hydrogen nuclei behave as little magnets and a hydrogen nucleus can be aligned with an external magnetic field or opposed to it (which has higher energy).
- The energy needed for the hydrogen nuclei to reverse their spin is very small and can be provided by radio waves.
- The number of peaks in a ^1H NMR spectrum gives the number of different chemical environments in which hydrogen atoms are located.
- The position of the NMR signal is measured relative to the signal produced by TMS tetramethylsilane $Si(CH_3)_4$



^1H NMR spectrum for ethanal

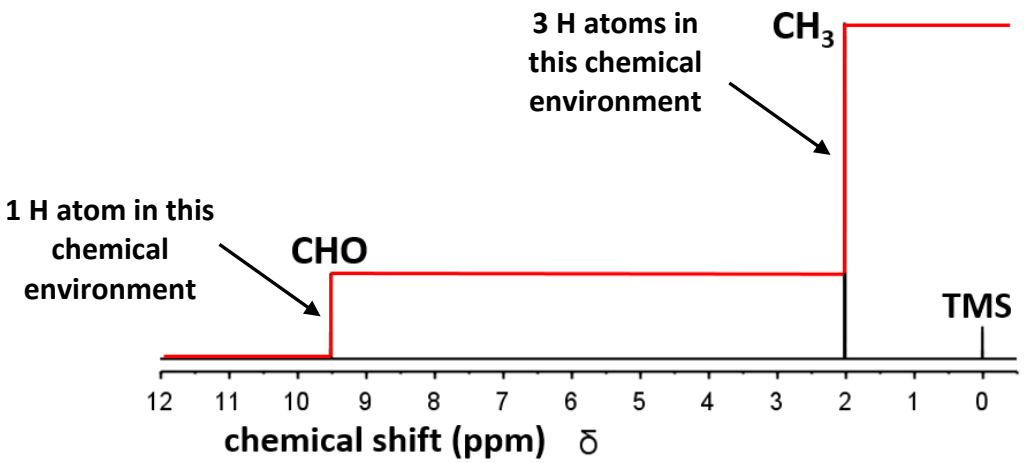


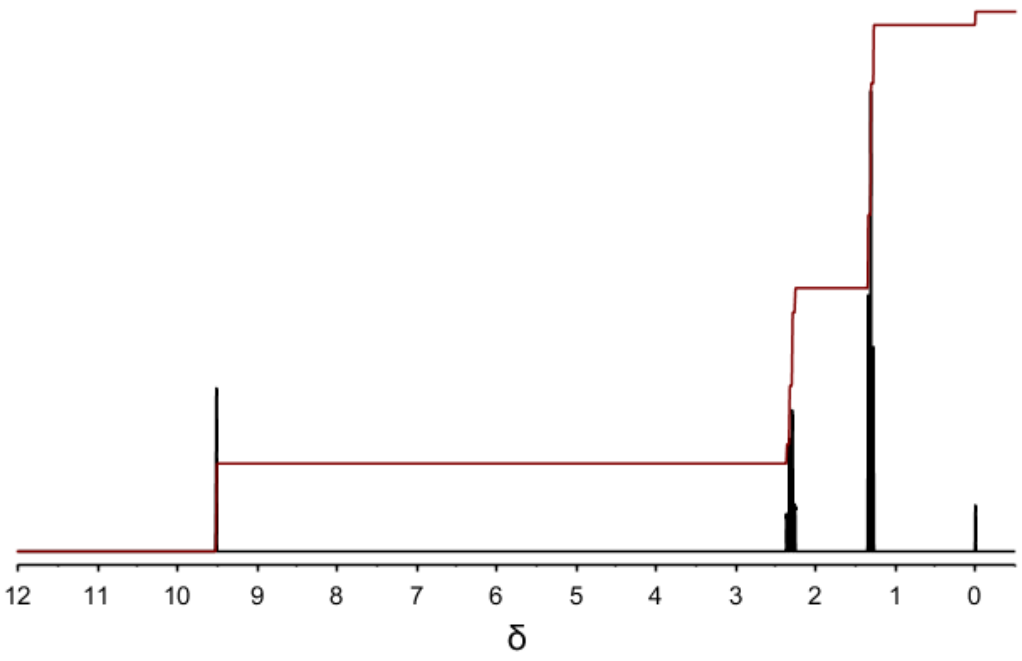
Type of proton	Chemical shift (ppm)
$-C\mathbf{H}_3$	0.9 – 1.0
	9.4 – 10.0



Integrated trace

- The integrated trace goes up in steps which are proportional to the number of hydrogen atoms in the chemical environments.



Exercise: On the following ^{1}H NMR spectrum:

a) Outline the significance of the peak at 0 ppm. TMS peak
b) Deduce the number of different chemical environments in which hydrogen atoms are located. Three
c) Determine the type of proton that produces the peak at 9.5 ppm. R-C**H**O
d) Give the ratio of the hydrogen atoms in each peak. 1:2:3
e) The peaks at 1.3 and 2.2 correspond to a CH_3 and CH_2 group respectively. Determine the structural formula and name of the compound. Propanal CH_3CH_2CHO