Analytical Chemistry

Chemical tests for different chemical species

Metal cations in ionic compounds – Flame test

A flame test can be conducted on ionic compounds to test for the metal cations.

Procedures:

- 1. Dip a platinum wire in **concentrated** HCl.
- 2. Dip the platinum wire into the sample
- 3. Heat the platinum wire with a non-luminous(blue) Bunsen flame

Metal cation	Expected observation
Na^+	Golden yellow flame
\mathbf{K}^{+}	Lilac flame
Ca^{2+}	Brick red flame
Cu^{2+}	Bluish green

These are the 4 most important metals to remember the flame colour of.

Metal cations in ionic compounds – Test with alkalis

Metal	Expected observation (OH·)	Expected observation (NH ₃)
cation		
Ca^{2+}	White precipitate is formed	White precipitate is formed
Mg^{2+}	White precipitate is formed	White precipitate is formed
\mathbf{Al}^{3+}	White precipitate is formed.	White precipitate is formed
	The precipitate redissolves to form a	
	clear solution in excess $OH_{(aq)}$	
${f Z}{f n}^{2+}$	White precipitate is formed.	White precipitate is formed.
	The precipitate redissolves to form a	The precipitate redissolves to form a
	clear solution in excess $OH_{(aq)}$	clear solution in excess $NH_{3(aq)}$
$\mathbf{Fe^{2+}}$	Dirty green precipitate is formed	Dirty green precipitate is formed
${ m Fe}^{3+}$	Brown precipitate is formed	Brown precipitate is formed
Pb^{2+}	White precipitate is formed.	White precipitate is formed
	The precipitate redissolves to form a	
	clear solution in excess OH-(aq)	
Cu^{2+}	Blue precipitate is formed	Blue precipitate is formed.
		The precipitate redissolves to form a
		deep blue solution in excess $\mathrm{NH}_{3(\mathrm{aq})}$
$\mathbf{A}\mathbf{g}^{+}$	Brown precipitate is formed	Brown precipitate is formed.
		The precipitate redissolves to form a
		clear solution in excess $NH_{3(aq)}$

Test for different gases

Gas	Test and expected observation	
\mathbf{H}_2	Place a burning splint into a test tube with the gas.	
	If the gas is H ₂ , the burning splint stops burning with a 'pop' sound is produced.	
O_2	Place a glowing splint into a test tube with the gas.	
	If the gas is O_2 , the glowing splint relights	
CO_2	Pass the gas to limewater, CO ₂ turns limewater milky	
$\mathbf{NH_4}^+$	First heat with NaOH _(aq) inside a test tube	
	Pass the gas to a piece of moist red litmus paper, the moist red litmus	
	paper turns from red to blue	
\mathbf{NH}_3	Pass the gas to a piece of moist red litmus paper, the moist red litmus	
	paper turns from red to blue //	
	Pass $NH_{3(g)}$ near $HCl_{(g)}$ which produces a dense white fume.	
H_2O	Place the sample in dry cobalt(II) chloride paper.	
	If water is present, the dry cobalt(II) chloride paper will turn from blue to	
	pink.	
Cl_2	Pass the gas to a piece of moist blue litmus paper.	
	The piece of moist blue litmus paper changes from blue to red to white.	
HCl	Pass the gas to a piece of moist blue litmus paper ,	
	If HCl is present, the piece of moist blue litmus paper changes from blue	
	to red //	
	Pass $HCl_{(g)}$ near $NH_{3(g)}$ which produces a dense white fume.	
SO_2	Pass the gas to acidified potassium dichromate.	
	If SO ₂ is present, the solution will change colour from orange to green.	

Test for various anions

Anion	Test and expected observation	
OCl ⁻	Turns blue or red litmus paper white //	
	Gives yellowish green gas (Cl ₂) with pungent smell of bleaching solution	
	upon addition of HCl	
$\mathrm{CO_3}^{2 ext{-}}$	Pass the solution to limewater, white precipitate is formed in CO ₃ ² is present	
	$//$ Add dilute $\mathrm{HCl}_{(aq)}$ to the sample, colourless gas bubbles are formed.	
$\mathbf{SO_3}^{2\text{-}}$	Pass the solution to limewater, white precipitate is formed in SO ₃ ² is present	
	// Add dilute HCl _(aq) to the sample, colourless gas bubbles are formed.	
Halides	Mix with $AgNO_3$ acidified with $HNO_{3(aq)}$	
$(\mathrm{Cl}^{ au}/\mathrm{Br}^{ au}/\mathrm{I}^{ au})$	For Cl ⁻ , white precipitate is formed; pale yellow precipitate is formed for	
	Br ⁻ ; and yellow precipitate is formed for I ⁻ .	

Test for various functional groups in organic compounds

Functional	Test and expected observation
group	
C=C	Pass the sample to $Br_{2(aq)}$, an alkene should turn the $Br_{2(aq)}$ solution from brown to colourless
-ОН	Heat the solution up with $K_2Cr_2O_{7(aq)}/H^+_{(aq)}$, the colour of the solution should turn from orange to green
-СНО	Mix the sample with Tollens' reagent and put it in a warm water bath , a shiny silvery mirror should appear in the test tube // Mix the sample with 2,4-dinitrophenylhydrazine (2,4-DNP) and an orange precipitate should appear.
-CO	Mix the sample with 2,4-dinitrophenylhydrazine (2,4-DNP) and an orange precipitate should appear.
-СООН	React the sample with $Na_2CO_{3(aq)}$ and colourless gas bubbles should be given out.

Checkpoint

1. Describe how to carry out a flame test to test for the presence of potassium ion in a sample of nitrate salt. State the expected observation.

Dip a (clean) Pt wire in concentrated HCl and then dip into the salt sample, put the Pt wire over a non-luminous Bunsen flame, lilac flame should be observed.

- 2. A compound has a molecular formula C3H4O3. It has the following results in chemical tests:
 - Test (I): It has positive results with 2,4-dinitrophenylhydrazine.
 - Test (II): It gives pleasant fruit smell when being warmed with concentrated sulphuric acid and an alcohol.
 - a. What is observed as the positive result in the test with 2,4-DNP?

Orange precipitate is formed.

b. According to the result of the test (II), which functional group does the compound contain?

Carboxyl group (-COOH)

c. Hence, deduce TWO possible structures of the compound C3H4O3.

d. Suggest a chemical test to confirm the structure of the compound C3H4O3.

Mix the compound with Tollens' reagent and put it in a warm water bath. If the compound is an aldehyde (right one), a shiny silvery mirror will be formed inside the test tube. If the compound is the ketone (left one), there are no observable changes.

- 3. Suggest chemical tests to differentiate the following substances
 - a. $CuSO_{4(s)}$ and $CuSO_4$ $\bullet\,5H_2O_{(s)}$

b. $NaOCl_{(s)}$ and $NaCl_{(s)}$

c. $CO_{2(g)}$ and $SO_{2(g)}$

d. $ZnCl_{2(aq)}$ and $Zn(NO_3)_{2(aq)}$

Mix the solutions with $AgNO_{3(aq)}$ acidified with $HNO_{3(aq)}$ separately. For $ZnCl_{2(aq)}$, white precipitate is formed. For $Zn(NO_3)_{2(aq)}$, there are no observable change.

Separation and purification methods

Crystallisation

We do crystallisation to obtain a solute from a solution

Procedures:

- 1. Heat until the solution becomes saturated
- 2. Let the solution slowly cool down at room temperature
- 3. Filter the solution and obtain the residue
- 4. Wash the crystals with a small amount of cold distilled water, dry with filter paper

Recrystallisation

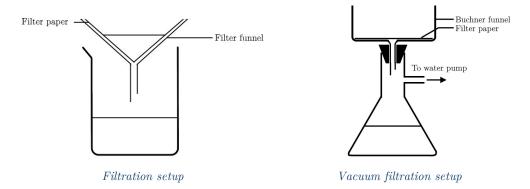
To purify a solid, we can do recrystallisation. When we are choosing the solvent for recrystallisation, we should choose a solvent that is easily to remove (or volatile like ethanol), and not react with any of the chemical species present. Most importantly, it should only be able to dissolve the main product (or at least be much more soluble for) we are looking for instead of the impurities.

Procedures:

- 1. Dissolve the solid with a minimal amount of hot solvent, filter away any insoluble impurities.
- 2. Allow the solution to cool to room temperature, and allow it to crystallize
- 3. Filter the solution and obtain the residue
- 4. Wash the crystals with a small amount of cold distilled water, dry with filter paper

Filtration

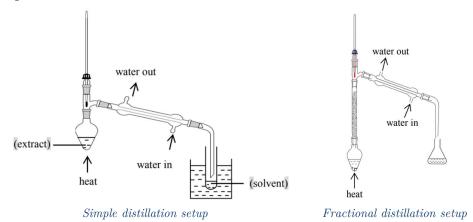
A simple method to extract an insoluble solid from a liquid solution. Filtration can take in two forms, gravitational filtration and vacuum filtration, with the latter being significantly faster than the former.



In vacuum filtration, the water pump lowers the pressure inside the conical flask, the filtrate is then sucked through to the conical flask to due the pressure difference.

Distillation

Distillation allows for substances with different boiling points to be separated. For substances with close boiling points (less than 25°C difference), fractional distillation is required instead so as to obtain a pure distillate.



A way to quickly test the purity of a solid or a liquid is by boiling it. If the solid or liquid has a sharp boiling point at its own theoretical boiling point, then it has a high purity.

Liquid-liquid extraction

Liquid-liquid extraction can separate liquids that are NOT miscible with each other (e.g. alkane and water). Procedures:

- Put the mixture into a separating funnel
- Shake until 2 layers form
- Discard/collect the desired layer

Commonly, your liquids will not be miscible to begin with. Consider the following example: Both benzoic $\operatorname{acid}(C_6H_5COOH)$ and $\operatorname{phenol}(C_6H_5OH)$ are present in a sample, outline a method to extract phenol from the mixture by liquid-liquid extraction, given that both benzoic acid and phenol are not miscible with water.

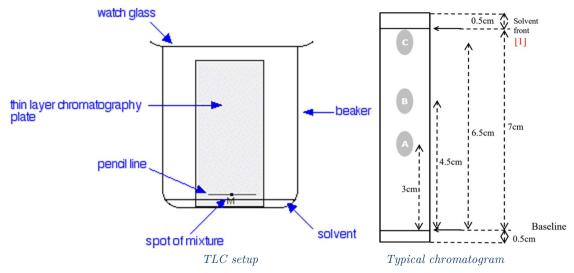
- Pour the mixture into a separating funnel and add excess Na₂CO_{3(aq)}
- This reacts with benzoic acid to turn it into soluble sodium benzoate $(C_6H_5COO^-Na^+)$ that dissolves in water.
- Open the stopcock of the separating funnel from time to time to release the air pressure built up inside.
- Let the separating funnel stand still and (discard the aqueous layer) extract the organic layer, which only contains phenol.

Chromatography

Chromatography is split into 3 types:

- Paper chromatography
- Thin layer chromatography (TLC)
- Column chromatography

The first two chromatography options are used to identify the substances present in the sample, while column chromatography is used to separate those substances. Chromatography works on the principle that different substances have different solubilities in the *mobile phase*; different substances also have different adsorptivity (pay attention to spelling) to the stationary phase. The substances more soluble (have higher affinity for) in the mobile phase move further/faster than those less soluble in the mobile phase.

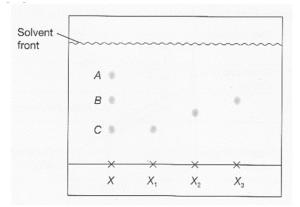


Paper or TLC paper is placed in a beaker with a small amount of solvent (e.g. water) with the baseline ABOVE the solvent level. The solvent then moves into the TLC paper/paper (stationary phase). When the solvent passes the spot of mixture, the substances dissolve in the solvent mobile phase and move along with it. The results of paper/TLC chromatography is called a *chromatogram*, the substances that are more soluble in the mobile phase move further along the mobile phase. The ratio between the distance moved by the substance and the solvent front is called the R_f ratio. The R_f ratio can be compared to literature values to help determine the identity of the substance.

$$R_f = \frac{Distance\ covered\ by\ substance}{Distance\ covered\ by\ solvent\ front}$$

Checkpoint

- 1. A sample of sugar is mixed with some other organic compounds, given that sugar has the highest solubility in water of all the chemical species present in the mixture, outline a method to purify the sugar sample by recrystallisation.
- 2. An unknown sample X containing amino acids was analysed by paper chromatography. Amino acids X1, X2 and X3 are also added to the paper separately. Ninhydrin solution was sprayed on the chromatogram and some spots appeared purple.



a. Explain why ninhydrin solution was sprayed on the chromatogram before making observation about the result.

Amino acids are colourless in water, spraying ninhydrin can make the spots visible and hence we can deduce the R_f ratio of the acids.

- b. Explain why spots of different components of X travel across different distances. Different components have different solubilities in the solvent. The components with higher solubilities in the solvent travel across larger distances.
 - c. Calculate the Rf values of amino acid X2.

$$R_f \approx \frac{90}{210} = 0.429$$

e. Suppose the same mobile phase and stationary phase was used in column chromatography to separate the acids in X, which acid, A, B, or C will be collected first at the end of the column? Explain your answer in terms of the R_f ratio.

A will be collected first, the ratio R_f ratio of A is higher than B and C, so A travels faster in the mobile phase than B and C, so A will be collected first.

f. The above compounds are analysed again with thin layer chromatography, will the chromatogram produced be exactly the same? Explain your answer.

No, the stationary phase of the two experiments are different. The substances have different affinities/adsorptivity for different stationary phases, so their distance travelled in the mobile phase will be different.

3. A sample contains hept-1-ene and toluene (C₆H₅CH₃), their boiling points are given below:

	Hept-1-ene	Toluene
Boiling point (°C)	94	110

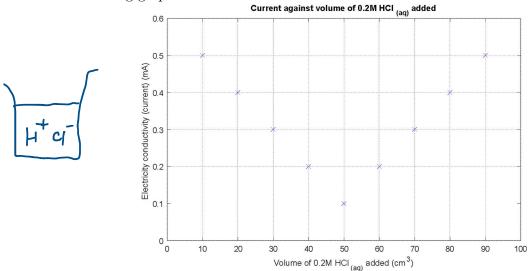
- a. A student tries to separate the two substances by simple distillation, however he could not obtain a pure heptane sample in the distillate, explain why this is the case and suggest one modification made to the extractions setup to increase the purity of the distillate.
- b. Suggest a chemical test to differentiate hept-1-ene and toluene, state the expected observations
- c. How can the student test whether the hept-1-ene sample obtained is of high purity or not?

Quantitative Methods of Analysis

Precipitation titration

In precipitation titration, an ionic solution undergoes a precipitation reaction. Due to the decrease in the concentration of mobile ions, the electricity conductivity of the solution mixture will decrease, resulting in the decrease in current passing through the circuit. After all of the original ions have completely reacted in the precipitation reaction, add more of the other solution used will increase the mobile ion concentration, and hence increase the electrical conductivity.

In this example, to determine the concentration of Ag^+ in a 25 cm³ $AgNO_{3(aq)}$ sample, 0.2M $HCl_{(aq)}$ is added to the sample at $10cm^3$ intervals. The current against volume of $HCl_{(aq)}$ added is recorded and the following graph is obtained.



a. Determine the endpoint of the reaction, i.e. what amount of $0.2 \text{ M HCl}_{(aq)}$ is required to fully react with $AgNO_{3(aq)}$.

The endpoint is given by the lowest point in the curve, here the electrical conductivity is the lowest at $V = 50 \text{ cm}^3$. Therefore the endpoint of the reaction is at 50cm^3 of $HCl_{(aq)}$ added. Note: For non-symmetrical curves, you may need to extrapolate the two lines to find the lowest point.

b. Hence find $[Ag^{+}_{(aq)}]$ of the solution:

$$\mathrm{AgNO}_{3(\mathrm{aq})} + \mathrm{HCl}_{(\mathrm{aq})} \rightarrow \mathrm{AgCl}_{(\mathrm{s})} + \mathrm{HNO}_{3(\mathrm{aq})}$$

Mole ratio of Ag^+ : $Cl^- = 1:1$

Mole of Ag⁺ present in AgNO_{3(aq)} sample = (1)*(0.2)*(0.05) = 0.01 mole

 ${\rm [Ag^+]} = 0.01/0.025 = 0.4~{\rm mol~dm^{\text{-}3}}$

Cr 04

Mohr's method

Mohr's method is another way that precipitation reaction can be conducted if it involves chloride ions. In this reaction, Mohr's indicator – chromate indicator is added to the mixture. Silver nitrate solution is then added to the mixture which will form a white precipitate with $Cl^-_{(aq)}$. At the endpoint, when no more Cl^- is available, the chromate ions will react with silver ions to form a reddish brown precipitate (silver chromate). Hence the colour change at the endpoint is from white to reddish brown.

To determine the salt (NaCl) content in a particular brand of peanuts, 20g of peanuts is first grounded into a powder and then stirred in hot water so all of the water-soluble compounds dissolve in water. The sample is then diluted to $100 \mathrm{cm}^3$ and portions of $25 \mathrm{cm}^3$ of the solution are titrated against $0.10 \mathrm{M}$ AgNO_{3(aq)} In the test, $12.4 \mathrm{~cm}^3$ of $0.10 \mathrm{~M}$ AgNO_{3(aq)} was used to reach the end point of the reaction.

- a. State the colour change at the end point of the reaction From white to reddish brown.
- b. Find the percentage by mass of sodium chloride in the peanuts, clearly state your assumptions

Assume that all chloride ions are contributed by sodium chloride

$$\mathrm{Cl^-} + \mathrm{Ag^+} \rightarrow \mathrm{AgCl_{(s)}}$$

Mole ratio Cl^- : $Ag^+ = 1:1$

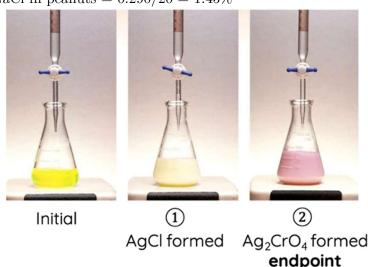
Mole Cl⁻ present in 25cm^3 dilute solution = $0.0124 * 0.10 = 1.24 * 10^{-3}$ mol

Mole Cl⁻ present in the original solution with the 20g peanuts

$$= 1.24 * 10^{-3} * 100/25 = 4.96 * 10^{-3}$$
 mole

Mass of NaCl in 20g peanuts = $4.96 * 10^{-3} * (23 + 35.5) = 0.290g$

% by mass of NaCl in peanuts = 0.290/20 = 1.45%



Redox titration

A redox titration uses a redox reaction with a visible endpoint to conduct quantitative analysis.

1. Determine the content of Fe²⁺ in a supplement tablet

Tablets of total mass 30g is grounded up into a powder and dissolved in water. The solution is then diluted to 250cm^3 and split into 25cm^3 portions. 0.06 M acidified potassium permanganate is added to the solution mixture until the endpoint is reached. It was found that 14.2 cm^3 of 0.06 M KMnO_{4(aq)}/H⁺_(aq) is needed for the reaction to reach its endpoint

- a. Is an indicator needed to indicate the endpoint? What is the colour change at the endpoint? An indicator is not needed since acidified potassium permanganate is purple in colour on its own. The solution mixture will change colour from colourless to pink at the endpoint.
 - b. The manufacturer claims the iron content of the tablets to be over 10%, is his claim correct?

$$\begin{array}{c} {\rm MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O} \\ {\rm Fe^{2+} \rightarrow Fe^{3+} + e^-} \end{array}$$

Overall chemical equation: $\rm MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

Mole of MnO_4 : $Fe^{2+} = 1:5$

Mole of Fe^{2+} present in the $25cm^3$ diluted portions:

= 0.0142 * 0.06 * 5 = 4.26 * 10
$$^{-3}$$
 mol

Mole of Fe²⁺ present in 30g of the tablets = $4.26 * 10^{-3} * 10 = 0.0426$ mol

Mass of Fe in 30g of the tablets = 0.0426 * 55.8 = 2.37g

Iron content (% by mass of Fe) = 2.37/30 * 100% = 7.92% < 10%

He is wrong!

A sample of the steel (0.0900 g) was reacted with excess dilute sulphuric acid. The solution required 15.0 cm³ of 0.0200 M acidified potassium permanganate solution for complete reaction. Calculate the percentage by mass of iron in the steel sample.

Vitamin C is also known as ascorbic acid AA (C6H8O6). Its concentration in a fruit juice can be found by volumetric analysis.

Step 1: Acidify 25.0 cm3 of a sample of fruit juice with dilute sulphuric acid. Dissolve about 1 g of potassium iodide in the solution.

Step 2: Add 2-3 cm3 of starch solution.

Step 3: Titrate the mixture with standard solution KIO3(aq).

The following reactions occur in the process.

- IO3– (aq) ions react with I– (aq) to form iodine.
- Ascorbic acid reduces the iodine formed to I– (aq) ions.
 - (a) State an assumption in this experiment.

 Only ascorbic acid can reduce iodine to form iodide ions.
 - (b) The mixture is titrated with standard solution KIO3(aq) directly. State the colour change at the end point of the titration in step 3.

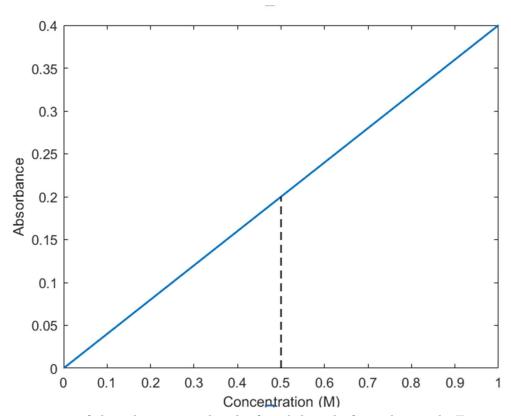
 From colourless to blue-black.
 - (c) Write an ionic equation for the reaction between IO₃ (aq) and I (aq) to form iodine.
 - (d) The reaction of ascorbic acid with iodine can be represented by the following equation: C₆H₈O₆ + I₂ → C₆H₆O₆ + 2H⁺ + 2I⁻ In the above experiment, 25.0 cm3 of the sample solution required a mean titre of 17.60 cm3 of 0.0118 mol dm-3 KIO3(aq). Calculate the mass of ascorbic acid in 1.00 dm3 of the sample solution. (molar mass of ascorbic acid = 176.0 g mol-1) (Stoichiometric ratio of KIO3 to I2 = 1 : 3)

Instrumental methods of analysis

Instrumental methods of analysis involves using digital instruments to accurately measure certain properties of a sample. Instrumental methods are generally quicker, more accurate and require less chemicals.

Colorimetry

In a coloured solution, the absorbance / colour intensity of the solution is directly proportional to the concentration of the solution.

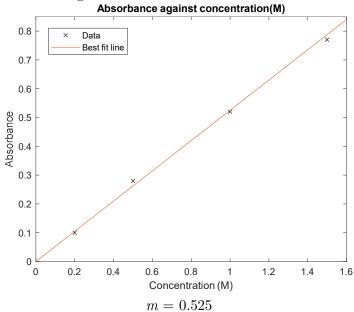


The concentration of the solution can then be found directly from the graph. For instance, the concentration of the solution at absorbance = 0.2 is 0.5 M.

A colorimeter has been calibrated to find the concentration of an orange solution X. The following table shows the absorbances of four solutions of X with different concentrations.

Solution	Concentration/ mol dm-3	Absorbance
1	0.2	0.1
2	0.5	0.28
3	1	0.52
4	1.5	0.77

a. Plot a graph of absorbance against concentration.



b. A solution of X of unknown concentration has an absorbance of 0.45. What is its concentration?

c. What colour filter should be used in this experiment? Explain your answer. Blue, orange solution strongly absorbs blue light.

IR Spectroscopy

For carbon compounds, different functional groups will resonate (greatly absorb energy) at different frequencies. By finding these resonance frequencies, we can determine the functional groups or even structures of carbon compounds. For those who are curious, here is how wavenumber and frequency are related (physics):

Wavenumber
$$k = \frac{2\pi}{\lambda}$$

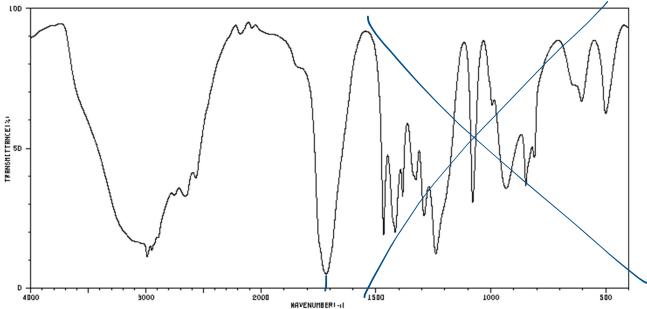
$$c = f\lambda = c_0 \text{ (speed of light)}$$

$$k = \frac{2\pi f}{c_0} = \frac{\omega}{c_0}$$

From $k = \frac{2\pi}{\lambda}$, the unit of the wavenumber can thus seen to be cm⁻¹. Different functional groups have the following characteristic absorption wavenumber ranges:

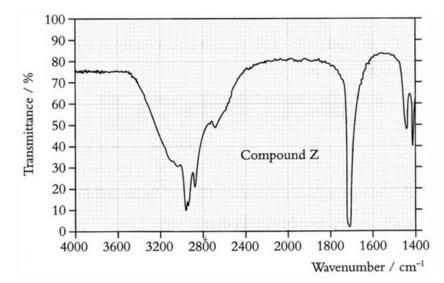
Bond	Compound type	Wavenumber (cm ⁻¹)
C=C	Alkenes	1610 to 1680
C=O	Aldehydes, ketones, carboxylic acids and derivatives	1680 to 1800
C≡C	Alkynes	2070 to 2250
C≡N	Nitriles	2200 to 2280
О-Н	Acids (hydrogen-bonded) [WIDE PEAK]	2500 to 3300
C-H	Alkanes, alkenes, arenas	2840 to 3095
О-Н	Alcohols, phenols (hydrogen-bonded) [WIDE PEAK]	3230 to 3670
N-H	Amines [WIDE PEAK]	3350 to 3500

Exercise: What functional group does the following compound have?



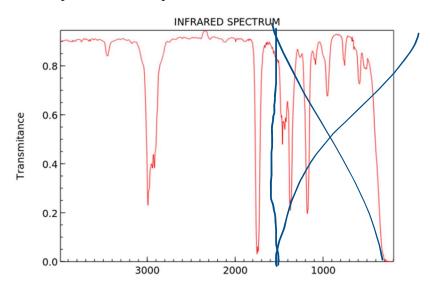
Note that acid and ester groups still have the peak at 1680 to 1800cm⁻¹ which corresponds to C=O bond. The above is actually the IR spectrum for propanoic acid.

- 2. A carbon compound Z with a relative molecular mass of 88.0 was found to contain 54.54% carbon, 36.36% oxygen and 9.10% hydrogen by mass.
 - a. Determine the molecular formula of compound Z.
 - b. Based on the result from (a) and the its infra-red spectrum is shown below, draw a possible structure of compound Z. Explain your answer



Compound A has molecular formula C₄H₈O.

a. Below is the infrared spectrum of compound A:



- i. One of the axes of the infrared spectrum is missing. Label the missing axis.
- ii. Compound A could NOT form a silver mirror when heated with Tollens' reagent. Deduce the structure of compound A.

	*	
Bond	Compound type	Wavenumber (cm ⁻¹)
C=C	Alkenes	1610 to 1680
C=O	Aldehydes, ketones, carboxylic acids and derivatives	1680 to 1800
C≡C	Alkynes	2070 to 2250
C≡N	Nitriles	2200 to 2280
О-Н	Acids (hydrogen-bonded) [WIDE PEAK]	2500 to 3300
С-Н	Alkanes, alkenes, arenas	2840 to 3095
О-Н	Alcohols, phenols (hydrogen-bonded) [WIDE PEAK]	3230 to 3670
N-H	Amines [WIDE PEAK]	3350 to 3500

In the IR spectrum, the peak at 1680-1800 cm⁻¹ corresponds to a C=O bond.

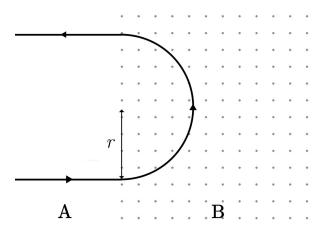
The absence of a wide peak at 2500-3300cm⁻¹ indicates that the compound does not contain a carboxyl group. Since the compound only has 1 O atom, it cannot be an ester.

Compound A does not form a silver mirror when heated with Tollens' reagent, so it must not be an aldehyde, hence compound A is a ketone.

Compound A is butanone.

Mass spectrometry

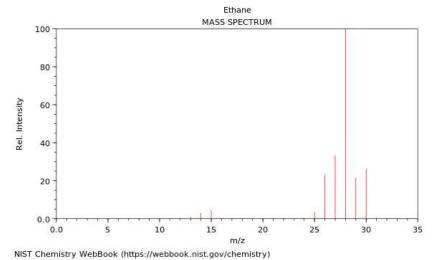
The sample is first turned into a gas and ionised to create molecular ions and fragment ions and then accelerated to a certain velocity and ran through a magnetic field to determine their m/q ratio as follows:



Molecular ions are positively charged and undergo a circular path motion in the magnetic field (the diagram is actually for an electron). The radius of the path can tell us the m/q ratio.

$$r = \frac{mv}{Bq}$$

For our case in chemistry, m/q is just the relative atomic mass since all ions have an equal charge of 1+. The results are then shown on the mass spectrum.



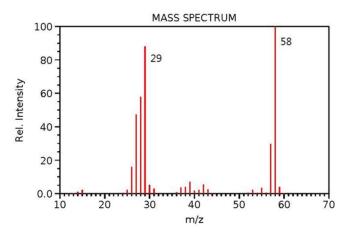
For instance, ethane has the following mass spectrum, the peak at m/q (also called m/z) = 28 corresponds to the molecular $CH_3CH_3^+$ ion. Can you figure out why there are peaks at m/q = 26, 27, 29 and 30?

The minor peak at m/q = 15 corresponds to the fragment CH_3^+ ion. The combination of the molecular ion peak and fragment ion peak can provide us with further insight of the molecule's structure. Quite often, we will combine it with IR spectroscopy to fully confirm on the molecule's identity.

A carbonyl compound has a molecular formula C3H6O.

a. Draw TWO possible structures for the compound.

b. Consider the following mass spectrum of the compound.



i. Draw the structure of ions correspond to the labelled peaks in the spectrum.

1. Draw the structure of ions correspond to the labelled peaks in the spectrum.		
m/q	Corresponding Ion(s)	
58		
29		

ii. Hence state the systematic name of the compound

Common ions to look out for in mass spectrums

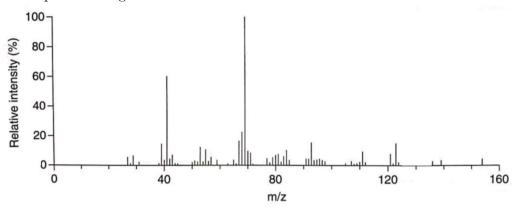
m/q	Corresponding ion
15	$ m CH_3^+$
29	CHO ⁺
43	CH ₃ CO ⁺
43	CH ₃ CH ₂ CH ₂ ⁺
77	$C_6H_5^+$ (Benzene ring)
91	$\mathrm{C_6H_5CH_2}^+$

The characteristic smell of pine wood is due partly to the presence of a group of compounds called terpenes. One of the simpler terpenes is a compound called geraniol, which is an oily liquid at room temperature and pressure. The structure of geraniol is shown below.

a. Calculate the molar mass of geraniol.

(Relative atomic masses: H = 1.0, C = 12.0, O = 16.0)

b. The mass spectrum of geraniol is shown below.



i. Explain why this mass spectrum can be used to confirm the molar mass of geraniol.

- ii. Identify the fragment ion that is responsible for the peak at m/z=69. (Relative atomic masses : $H=1.0,\,C=12.0,\,O=16.0$)
- iii. Suggest **TWO** chemical tests to confirm that geraniol is an alcohol but neither an aldehyde nor a ketone by combining their results.