Intensive note (Topic 15: Analytical chemistry)

Test for cations

Cation	Color	Addition of NaOH(aq) / KOH(aq)	Addition of NH_3(aq)
K^+	Colorless	No observable change	No observable change
Na^+	Colorless	No observable change	No observable change
Ca^{2+}	Colorless	White precipitate forms $Ca^{2+}(aq) + 2OH^-(aq) \rightarrow Ca(OH)_2(s)$	No observable change
Mg^{2+}	Colorless	White precipitate forms $Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$	White precipitate forms $Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$
Al^{3+}	Colorless	White precipitate forms and it dissolves in excess NaOH(aq) to give colorless solution $Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$ $Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$	White precipitate forms $Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$
Zn^{2+}	Colorless	White precipitate forms and it dissolves in excess NaOH(aq) to give colorless solution $Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(OH)_2(s)$ $Zn(OH)_2(s) + 2OH^-(aq) \rightarrow Zn(OH)_4^{2-}(aq)$	White precipitate forms and it dissolves in excess NH_3(aq) to give colorless solution $Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(OH)_2(s)$ $Zn(OH)_2(s) + 4NH_3(aq) \rightarrow Zn(NH_3)_4^{2+}(aq) + 2OH^-(aq)$
Fe^{2+}	Green	Green precipitate forms $Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$	Green precipitate forms $Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$
Fe^{3+}	Yellow	Brown precipitate forms $Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$	Brown precipitate forms $Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$
Pb^{2+}	Colorless	White precipitate forms and it dissolves in excess NaOH(aq) to give colorless solution $Pb^{2+}(aq) + 2OH^-(aq) \rightarrow Pb(OH)_2(s)$ $Pb(OH)_2(s) + 2OH^-(aq) \rightarrow Pb(OH)_4^{2-}(aq)$	White precipitate forms $Pb^{2+}(aq) + 2OH^-(aq) \rightarrow Pb(OH)_2(s)$
Cu^{2+}	Blue	Blue precipitate forms $Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$	Blue precipitate forms and it dissolves in excess NH_3(aq) to give deep blue solution $Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$ $Cu(OH)_2(s) + 4NH_3(aq) \rightarrow Cu(NH_3)_4^{2+}(aq) + 2OH^-(aq)$
Ag^+	Colorless	Dark brown precipitate forms $2Ag^+(aq) + 2OH^-(aq) \rightarrow Ag_2O(s) + H_2O(l)$	Dark brown precipitate forms and it dissolves in excess NH_3(aq) to give a colorless solution $2Ag^+(aq) + 2OH^-(aq) \rightarrow Ag_2O(s) + H_2O(l)$ $Ag_2O(s) + 4NH_3(aq) + H_2O(l) \rightarrow 2Ag(NH_3)_2^+(aq) + 2OH^-(aq)$
NH_4^+	Colorless	Colorless pungent smell gas forms which can turn moist red litmus paper blue $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$	No observable change

Flame color in flame test:

K^+: Lilac Na^+: Golden-yellow Ca^{2+}: Brick-red Cu^{2+}: Bluish-green

Test for anions

Anion	Testing reagent	Observation + Equation
Cl^-	Acidified $AgNO_3(aq)$	White precipitate forms. $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
Br^-	Acidified $AgNO_3(aq)$	Pale yellow precipitate forms $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
	$Cl_2(aq)$	Colorless solution turns brown. Upon addition of heptane, it turns orange-red. $Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$
I^-	Acidified $AgNO_3(aq)$	Yellow precipitate forms $Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$
	$Cl_2(aq)$	Colorless solution turns brown. Upon addition of heptane, it turns purple. $Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$
CO_3^{2-}	Dilute HCl(aq)	Colorless gas bubbles evolve which turn limewater from colorless to milky $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$ $CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$
OCl^-	Dilute HCl(aq)	Greenish-yellow gas forms which can turn moist blue litmus paper red and then white $OCl^-(aq) + Cl^-(aq) + 2H^+(aq) \rightarrow Cl_2(g) + H_2O(l)$
SO_3^{2-}	Dilute HCl(aq)	Colorless choking smell gas is produced which turns orange $K_2Cr_2O_7(aq)$ / H^+ to green $SO_3^{2-}(aq) + 2H^+(aq) \rightarrow SO_2(g) + H_2O(l)$ $3SO_2(g) + Cr_2O_7^{2-}(aq) + 2H^+(aq) \rightarrow 3SO_4^{2-}(aq) + 2Cr^{3+}(aq) + H_2O(l)$
	$Br_2(aq)$	Brown solution turns colorless $Br_2(aq) + SO_3^{2-}(aq) + 2H^+(aq) \rightarrow 2Br^-(aq) + SO_4^{2-}(aq) + H_2O(l)$
	Acidified $K_2Cr_2O_7(aq)$	Orange solution turns green $3SO_3^{2-}(aq) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3SO_4^{2-}(aq) + 2Cr^{3+}(aq) + 4H_2O(l)$
	Acidified $KMnO_4(aq)$	Purple solution turns colorless $5SO_3^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$
SO_4^{2-}	Acidified $BaCl_2(aq)$	White precipitate forms $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

Solubility table

Compound of	Solubility in water
NH_4^+, Na^+, K^+, NO_3^-, HCO_3^-	All are soluble
Cl^-, Br^-, I^-	All are soluble **(Except AgCl, AgBr, AgI, $PbCl_2$, $PbBr_2$, PbI_2)**
SO_4^{2-}	All are soluble **(Except $BaSO_4$, $CaSO_4$, $PbSO_4$)**
CO_3^{2-}	**All are insoluble** (Except Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$)
O^{2-} / OH^-	**All are insoluble** (Except Na_2O, K_2O, NaOH, KOH) CaO, MgO, $Ca(OH)_2$ and $Mg(OH)_2$ are slightly soluble.

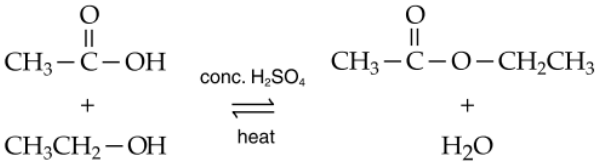
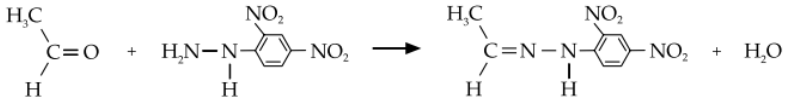
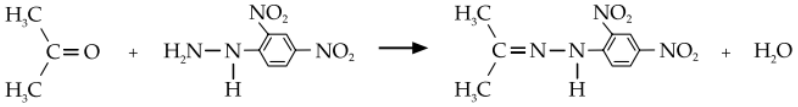
Test for gases

Gas	Test	Observation + Equation
H_2 Colorless, odorless	Burning splint	It gives 'pop' sound with burning splint $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
O_2 Colorless, odorless	Glowing splint	It relights glowing splint
CO_2 Colorless, odorless	Bubble the gas into limewater	It turns limewater from colorless to milky $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$
*SO_2 Colorless, choking	Bubble the gas into acidified $K_2Cr_2O_7(aq)$	It turns acidified $K_2Cr_2O_7(aq)$ from orange to green $3SO_2(g) + Cr_2O_7^{2-}(aq) + 2H^+(aq) \rightarrow 3SO_4^{2-}(aq) + 2Cr^{3+}(aq) + H_2O(l)$
	Bubble the gas into $Br_2(aq)$	It turns $Br_2(aq)$ from brown to colorless $SO_2(g) + Br_2(aq) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2Br^-(aq)$
H_2O Colorless, odorless	Anhydrous copper(II) sulphate	It turns anhydrous copper(II) sulphate from white to blue $CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4 \cdot 5H_2O(s)$
	Dry cobalt(II) chloride paper	It turns dry cobalt(II) chloride paper from blue to pink $CoCl_2(s) + 6H_2O(l) \rightarrow CoCl_2 \cdot 6H_2O(s)$
NH_3 Colorless, pungent	Bring the gas close to an unstoppered bottle of conc. HCl(aq)	It forms a dense white fume with HCl(g) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
	Moist red litmus paper	It turns moist red litmus paper blue $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
HCl Colorless, pungent	Place a glass rod dipped with conc. $NH_3(aq)$ in the gas	It forms a dense white fume with $NH_3(g)$ $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
Cl_2 Greenish yellow, pungent	Moist blue litmus paper	It Turns moist blue litmus paper red and then white $Cl_2(g) + H_2O(l) \rightleftharpoons HCl(aq) + HOCl(aq)$ $OCl^- + dye \rightarrow Cl^- + (dye + O)$

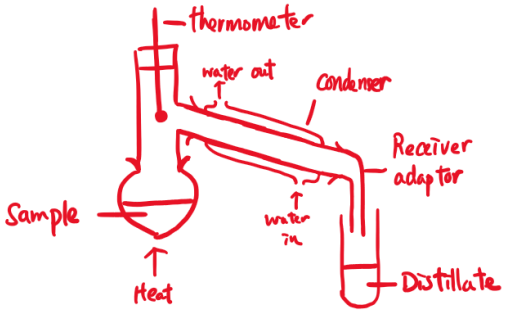
*$SO_2(g)$ can also turn limewater milky

$$SO_2(g) + Ca(OH)_2(aq) \rightarrow CaSO_3(s) + H_2O(l)$$

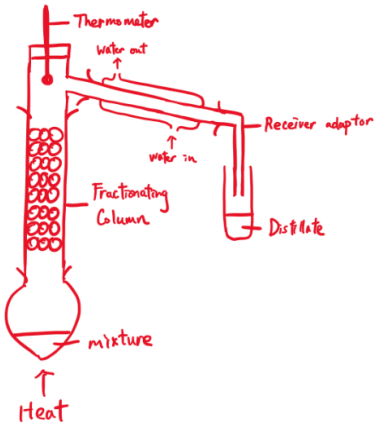
Test for functional groups

Functional group	Test	Observation + Equation
Carbon-carbon doble bond (C=C)	Br_2 (in organic solvent)	Orange solution turns colorless $CH_2=CHCH_3 + Br_2 \rightarrow CH_2BrCHBrCH_3$
	Acidified $KMnO_4$(aq).	Purple solution turns to colorless $CH_2=CHCH_3 + H_2O + [O] \rightarrow CH_2(OH)CH(OH)CH_3$
Hydroxyl (-OH) (1°, 2°)	Acidified $K_2Cr_2O_7$(aq), heat	Orange solution turns to green $CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$ $CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$
	Acidified $KMnO_4$(aq), heat	Purple solution turns to colorless $CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$ $CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$
Hydroxyl (-OH) (1°, 2°,3°)	Heat with CH_3COOH(l) in the presence of H_2SO_4(l)	Fruity smell ester forms 
Carbonyl (Aldehyde) (-CHO)	2,4-dinitrophenylhydrazine	Red / orange / yellow precipitate forms 
	Tollens' reagent	Silver mirror forms $CH_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow CH_3COO^- + 2Ag + 4NH_3 + 2H_2O$
	Acidified $K_2Cr_2O_7$(aq), heat	Orange solution turns to green $CH_3CHO + [O] \rightarrow CH_3COOH$
	Acidified $KMnO_4$(aq), heat	Purple solution turns to colorless $CH_3CHO + [O] \rightarrow CH_3COOH$
Carbonyl (Ketone) (-COC-)	2,4-dinitrophenylhydrazine	Red / orange / yellow precipitate forms 
Carboxyl group (-COOH)	Na_2CO_3(aq)	Colorless gas bubbles form $2CH_3COOH(aq) + Na_2CO_3(aq) \rightarrow 2CH_3COONa(aq) + CO_2(g) + H_2O(l)$

Distillation and fractional distillation



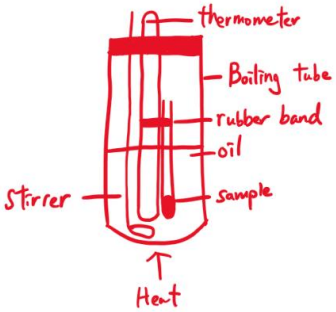
Simple distillation



Fractional distillation

- Distillation can be used to separate a mixture of miscible liquids with a great difference in boiling points. (> 25℃)
- Fractional distillation can be used to separate a mixture of miscible liquids with close boiling points. (10℃ – 25℃)
- Fractionating column: Packed with glass beads which provide a large surface area for repeated vaporization and condensation of the mixture.

Examining purity of a substance by melting point / boiling point test

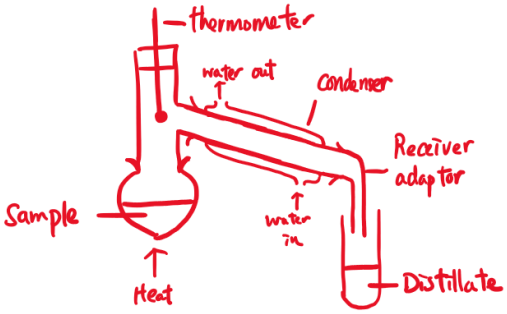


Melting point determination

How to show a solid sample is pure ice?

If it is pure ice, it should melt sharply at 0℃

(Impurities will lower the melting point of solid)



Boiling point determination

How to show a liquid sample is pure water?

If it is pure water, it should boil sharply at 100℃

(Impurities will raise the boiling point of liquid)

Recrystallization

In recrystallization, a crude (impure) solid product is dissolved in a minimum amount of hot solvent. Then the hot solution is filtered (to remove solid impurities) and cooled to allow crystals of the product to form (ideally pure product is crystallized).

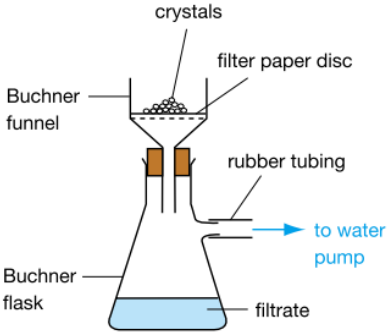
Step 1: Choose a solvent that dissolves the solid product but does not react with it.
The solubility of product should increase with temperature.

Step 2: Dissolve the crude product in minimum amount of hot solvent. Filter to remove insoluble impurities.
(Fluted filter paper is used to increase the surface area for filtration)

Step 3: The hot filtrate is cooled slowly to form crystals

Step 4: Collect the crystals by suction filtration (under reduced pressure)

Step 5: Wash the crystals with little cold solvents. Dry the crystals with filter paper



Suction filtration

Liquid-liquid extraction

Liquid-liquid extraction (solvent extraction) is a method used in the separation of carbon compounds involving separating funnel.

Example 1

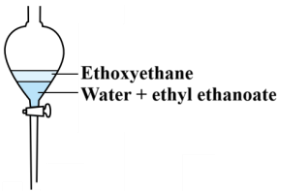
Outline the steps to obtain ethyl ethanoate from an aqueous solution of ethyl ethanoate by liquid-liquid extraction.

Step 1: Ethoxyethane (an organic solvent) is added to the mixture in a separating funnel. Two separate layers form.

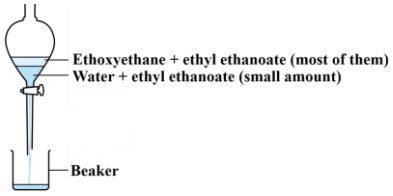
Step 2: After shaking, the organic layer (containing ethoxyethane and most of the ethyl ethanoate) is collected and the aqueous layer (containing water and small amount of ethyl ethanoate) is discarded

Step 3: The ethyl ethanoate in the organic layer can be further purified by distillation (and collected as second distillate).

Step 1

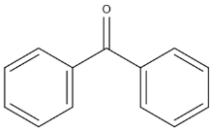


Step 2

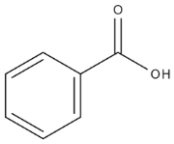


Example 2A

You are provided with a mixture of **X** and **Y** dissolved in hexane. The structures of **X** and **Y** are shown below:



Compound X (melting point = 47 °C)



Compound Y (melting point = 121 °C)

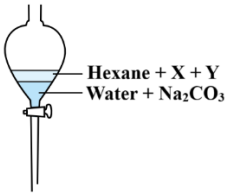
Outline the steps to obtain **pure solid X** from this mixture by liquid-liquid extraction

Step 1: Na_2CO_3(aq) is added to the mixture in a separating funnel

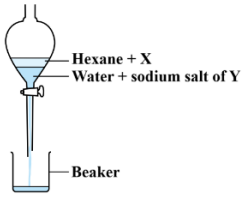
Step 2: After shaking, the organic layer (containing hexane and **X**) is collected and the aqueous layer (containing water and **sodium salt of Y**) is discarded

Step 3: Pure solid **X** can be collected by evaporating hexane.

Step 1



Step 2



Outline the steps to obtain **pure solid Y** from this mixture by liquid-liquid extraction

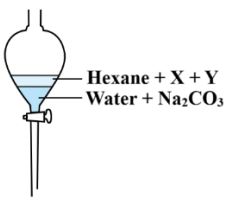
Step 1: Na_2CO_3(aq) is added to the mixture in a separating funnel

Step 2: After shaking, the aqueous layer (containing water and **sodium salt of Y**) is collected and the organic layer (containing hexane and **X**) is discarded

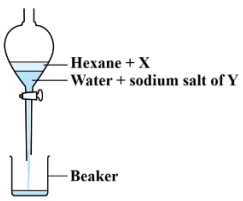
Step 3: Add dilute H_2SO_4(aq) to the aqueous layer collected until no more precipitate (i.e. **solid Y**) is produced

Step 4: Solid **Y** can be obtained by filtration

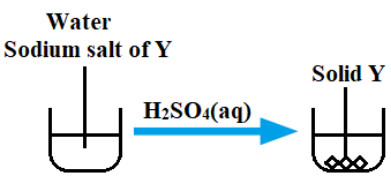
Step 1



Step 2



Step 3

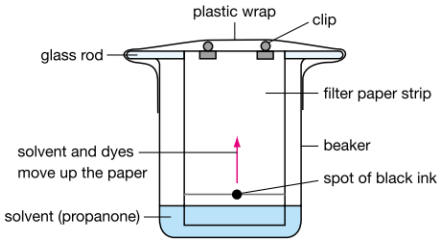


Chromatography

Different substances can be separated by chromatography as they have different solubilities in the mobile phase and have different degrees of adsorption onto the stationary phase.

A. Paper chromatography

Example: Separating different dyes in a sample of black ink



Mobile phase:

Solvent (propanone)

Stationary phase:

Thin film of water bound to the fibres of filter paper

B. Thin-layer chromatography and column chromatography

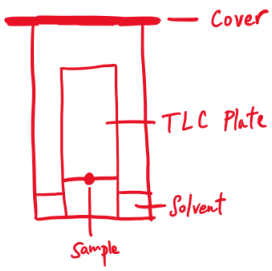
Example: Identifying different pigments in a ketchup sample

Mobile phase:

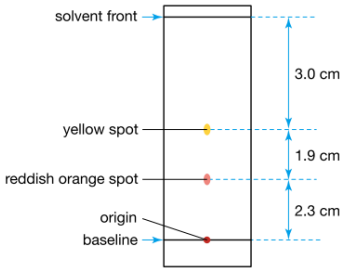
Solvent

Stationary phase:

Thin layer of silica (SiO_2) coated on a TLC plate



TLC experimental set-up



Chromatogram

$R_f = \frac{\text{Distance travelled by the component from the baseline}}{\text{Distance travelled by the solvent from the baseline}}$	R_f of yellow spot = (1.9 + 2.3) / (3.0 + 1.9 + 2.3) = 0.58 R_f of reddish-orange spot = (2.3) / (3.0 + 1.9 + 2.3) = 0.32

The identity of a component can be found by:

- Comparing its R_f value with those recorded in a data book
- Comparing its R_f value with those of the known reference compounds

For colorless components:

- Placing the plate under UV light can make the colorless spots visible
- For amino acids, the TLC plate can be sprayed by a chemical called ninhydrin to give purple spots.

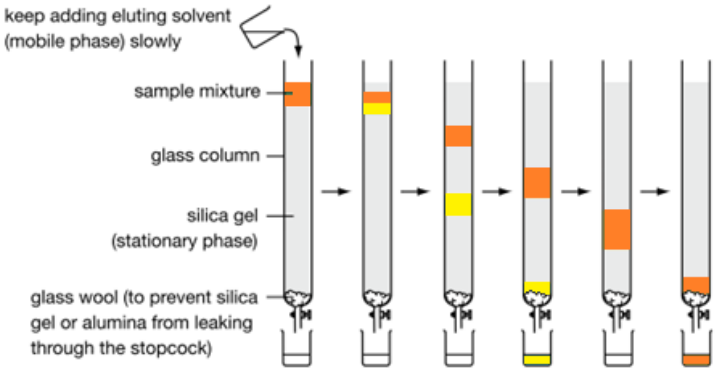
The above pigment can be separated and obtained for further use by **column chromatography.**

Mobile phase:

Solvent (same as the above TLC experiment)

Stationary phase:

Silica (same as the above TLC experiment)



Yellow spot will run out from the bottom of the column first as it has a higher R_f value

C. Gas chromatography (GC)

Gas chromatography is primarily used in identifying volatile compounds in environmental, medical and forensic studies.

Determining the concentration of chloride ions by Mohr's method

In an experiment to determine the concentration of chloride ions in a water sample, 25.0 cm^3 of the water sample is diluted to 250.0 cm^3 with distilled water. 25.0 cm^3 portions of the diluted solution are then titrated against 0.0200 M $AgNO_3(aq)$ using $K_2CrO_4(aq)$ as an indicator. 12.50 cm^3 of $AgNO_3(aq)$ is required to reach the end point.

(a) State the expected observation at the end point of the titration. Explain your answer with the aid of a chemical equation.

Answer: Reddish-brown precipitate of silver chromate forms.

$$2Ag^+(aq) + CrO_4^{2-}(aq) \rightleftharpoons Ag_2CrO_4(s)$$

(b) Explain why Mohr's method should be carried out in a pH range of 6.5–9.0.

Answer: If the pH is too high, $Ag^+(aq)$ will react with $OH^-(aq)$ to give $Ag_2O(s)$

$$2Ag^+(aq) + 2OH^-(aq) \rightarrow Ag_2O(s) + H_2O(l)$$

If the pH is too low, $CrO_4^{2-}(aq)$ will react with $H^+(aq)$ to give $Cr_2O_7^{2-}(aq)$

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$$

In both cases, more $Ag^+(aq)$ are consumed before the end point is reached. The titration results would give a higher than expected chloride ion concentration.

(c) Calculate the molarity of chloride ions in the water sample.

Answer: $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

$^nAg^+ = (12.5/1000) \times 0.02 = 2.5 \times 10^{-4}$

$^nCl^-$ in 25.0 cm^3 diluted sample = 2.5×10^{-4}

$^nCl^-$ in 250.0 cm^3 diluted sample = $2.5 \times 10^{-4} \times 250/25 = 2.5 \times 10^{-3} = {}^nCl^-$ in 25.0 cm^3 original water sample

Molarity of Cl^- = $(2.5 \times 10^{-3}) / (25/1000) = 0.01$ M

Determining the percentage by mass of iron in commercial iron tablets

An experiment is carried out to determine the iron content in a brand of iron tablets. 5.50 g of ground iron tablets is dissolved in excess $H_2SO_4(aq)$ and the solution is diluted to 250.0 cm^3 with distilled water. 25.0 cm^3 portions of the diluted solution are then titrated against 0.0500 M $KMnO_4(aq)$. An average volume of 15.70 cm^3 of $KMnO_4(aq)$ is required to reach the end point.

(a) State the color change at end point. Explain your answer.

Answer: Solution turns from yellow (due to Fe^{3+}) to pale pink (due to MnO_4^-). (No indicator is needed in this titration)

(b) Calculate the percentage by mass of iron in the iron tablets. (Relative atomic mass: Fe = 55.8)

Answer: $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$

$^nMnO_4^- = (15.7/1000)(0.05) = 7.85 \times 10^{-4}$

$^nFe^{2+}$ in 25.0 cm^3 solution = $7.85 \times 10^{-4} \times 5 = 3.925 \times 10^{-3}$

$^nFe^{2+}$ in 250.0 cm^3 solution = $3.925 \times 10^{-3} \times 250/25 = 0.03925 = {}^nFe$ in 5.50 g tablet.

Percentage by mass of iron in the tablet = $(0.03925 \times 55.8) / (5.5) \times 100\% = 39.8\%$

Determining the concentration of hypochlorite ions in a chlorine bleach

25.00 cm^3 of the bleach was first diluted to 250.0 cm^3. 25.00 cm^3 of the diluted solution was added to a conical flask containing excess $H_2SO_4(aq)$ and excess KI(aq). The reaction mixture obtained was titrated with 0.0512 M $Na_2S_2O_3(aq)$ using starch solution as indicator. The mean volume of $Na_2S_2O_3(aq)$ required to reach the end point was 21.02 cm^3.

(a) State the color change at end point. Explain your answer.

Answer: From dark blue (due to starch-I_2 complex) to colorless (all $I_2(aq)$ is consumed by $Na_2S_2O_3(aq)$)

(b) Explain why the starch solution should not be added too early

Answer: If the starch solution is added too early, $I_2(aq)$ will react with starch to form a water-insoluble complex which reduces the amount of I_2 in the reaction mixture. $I_2(aq)$ determined will be lower than the actual value.

(c) Calculate the concentration of NaOCl, in g dm^{-3}, in the bleach. (Formula mass of NaOCl = 74.5)

Answer: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

$^nS_2O_3^{2-}(aq) = (21.02/1000) \times 0.0512 = 1.076 \times 10^{-3}$

$^nI_2(aq) = 1.076 \times 10^{-3} \times 1/2 = 5.381 \times 10^{-4}$

$OCl^-(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow Cl^-(aq) + I_2(aq) + H_2O(l)$

$^nOCl^-$ in 25.00 cm^3 diluted sample = 5.381×10^{-4}

$^nOCl^-$ in 250.0 cm^3 diluted sample = $5.381 \times 10^{-4} \times 250/25 = 5.381 \times 10^{-3} = {}^nOCl^-$ in 25.00 cm^3 original sample

Concentration of NaOCl in mol $dm^{-3} = (5.381 \times 10^{-3}) / (25/1000) = 0.215$ mol dm^{-3}

Concentration of NaOCl in g $dm^{-3} = 0.215 \times 74.5 = 16.0$ g dm^{-3}

Determining the mass of ascorbic acid in a fruit juice

$I_2(aq)$ is generated by mixing 5.0 cm^3 of 1.0 M KI(aq), 5.0 cm^3 of 0.050 M $KIO_3(aq)$ and 25.0 cm^3 of 1.0 M $H_2SO_4(aq)$. Then 25.0 cm^3 sample of the grapefruit juice is added to the $I_2(aq)$ produced. The resultant mixture (containing excess $I_2(aq)$ is titrated with 0.100 M $Na_2S_2O_3(aq)$, using starch solution as the indicator. 13.20 cm^3 of $Na_2S_2O_3(aq)$ is required to reach the end point.

(a) Explain why standard $I_2(aq)$ cannot be prepared by weighing $I_2(s)$ and dissolving it in a known volume of KI(aq).

Answer: $I_2(s)$ is volatile

(b) Calculate the concentration of ascorbic acid (vitamin C), in mg cm^{-3}, in the sample of grapefruit juice.
(Molecular mass of ascorbic acid ($C_6H_8O_6$) = 176)

Answer: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

^{n}excess I_2 = (mole of $S_2O_3^{2-}$) x 1/2 = (13.2/1000)(0.1)(1/2) = 6.6×10^{-4}

$5I^-(aq) + IO_3^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$

All $^nI_2$ generated = $^nIO_3^-$ x 3 = (5/1000)(0.05)(3) = 7.5×10^{-4}

$C_6H_8O_6(aq) + I_2(aq) \rightarrow C_6H_6O_6(aq) + 2I^-(aq) + 2H^+(aq)$

$^nI_2$ reacted with ascorbic acid = $7.5 \times 10^{-4} - 6.6 \times 10^{-4} = 9.0 \times 10^{-5} = {}^nC_6H_8O_6$ in 25.0 cm^3 sample

Mass ascorbic acid in mg = $9.0 \times 10^{-5} \times 176 \times 1000 = 15.84$ mg

Concentration of ascorbic acid in mg $cm^{-3} = 15.84 / 25 = 0.6336$ g cm^{-3}

(c) State one assumption in the experiment.

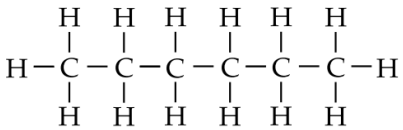
Answer: Ascorbic acid is the only substance in the grapefruit juice that reacts with iodine.

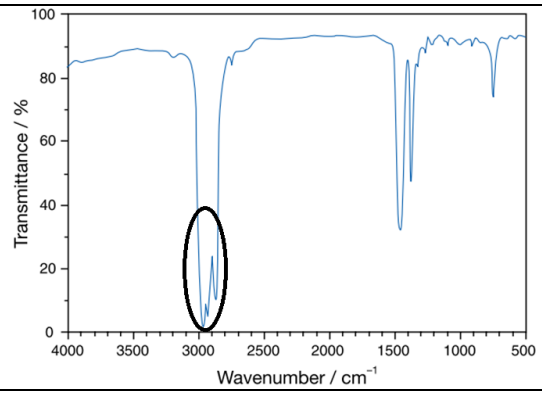
Infrared spectroscopy (IR)

When molecules absorb infra-red radiation of certain characteristic frequencies corresponding to the vibrational frequencies of a specific bond in the molecule, this gives rise to an absorption peak in an infra-red spectrum.

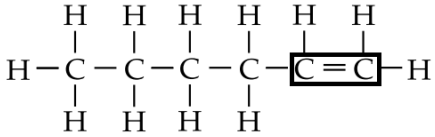
Bond	Compound type	Wavenumber / cm^{-1}
C=C	Alkenes	1610 – 1680
C=O	Aldehydes, ketones, carboxylic acids and derivatives	1680 – 1800
C≡C	Alkynes	2070 – 2250
C≡N	Nitriles	2200 – 2280
O–H	Acid (Hydrogen-bonded)	2500 – 3300
C–H	Alkanes, alkenes, arenes	2840 – 3095
O–H	Alcohols, phenols (hydrogen-bonded)	3230 – 3670
N–H	Amines	3350 – 3500

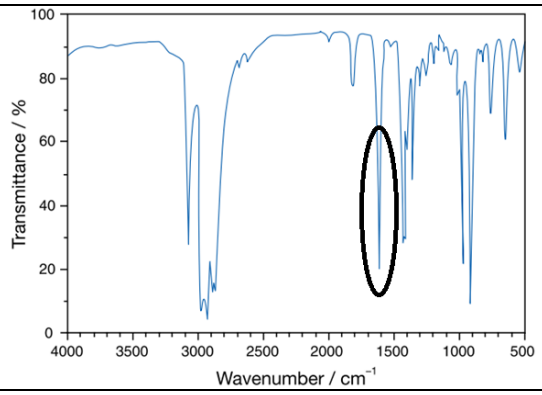
The region from 400 to 1500 cm^{-1} is a region called the fingerprint region. A compound can be identified by comparing its fingerprint region with that of a known compound.



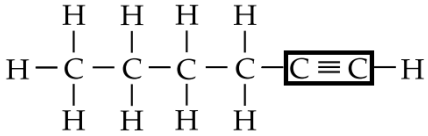


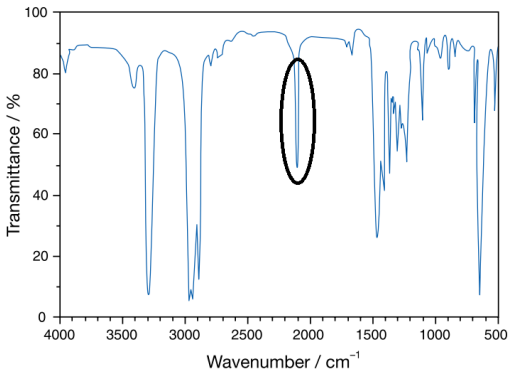
Presence of **a sharp absorption peak** at around **2950 cm^{-1}** indicates the **presence of C–H bond**



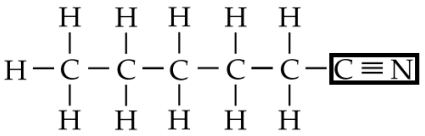


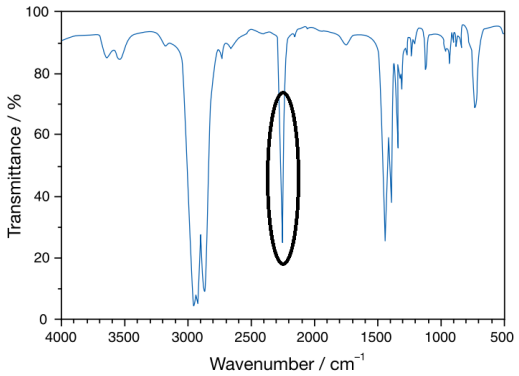
Presence of **a sharp absorption peak** at around **1610 cm^{-1}** indicates the **presence of C=C bond**



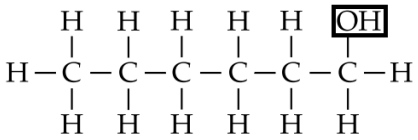


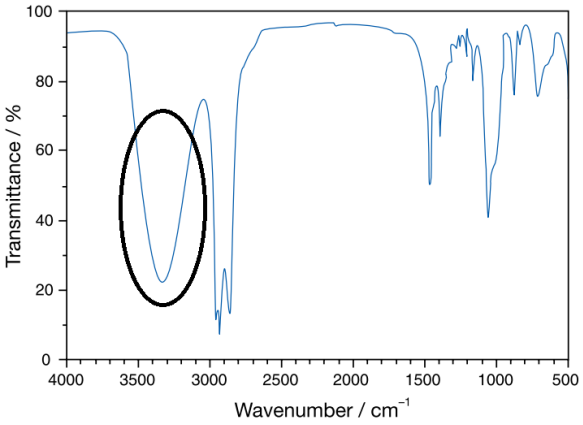
Presence of **a sharp absorption peak** at around **2120 cm^{-1}** indicates the **presence of C≡C bond**



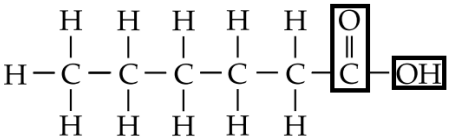


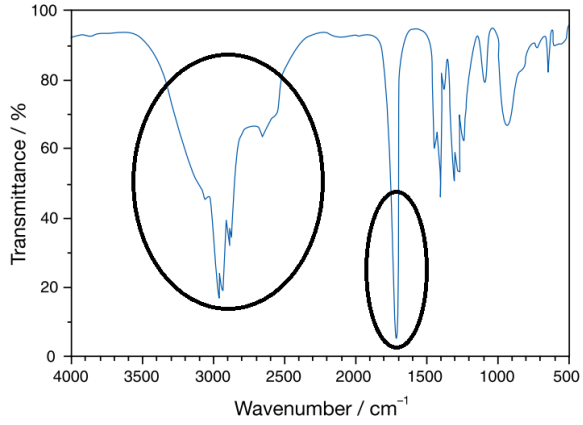
Presence of **a sharp absorption peak** at around **2250 cm^{-1}** indicates the **presence of C≡N bond**





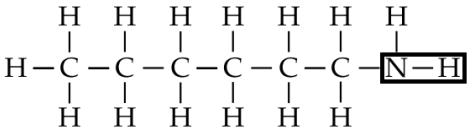
Presence of **a board absorption peak** at around **3330 cm^{-1}** indicates the **presence of O–H bond (alcohol)**

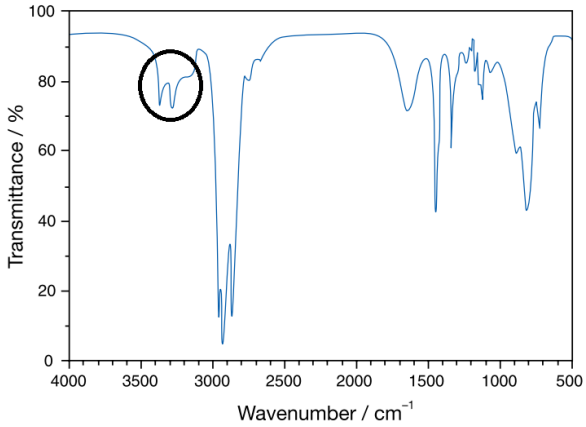




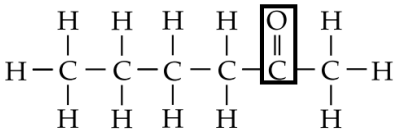
Presence of **a sharp absorption peak** at around **1710 cm^{-1}** indicates the **presence of C=O bond**

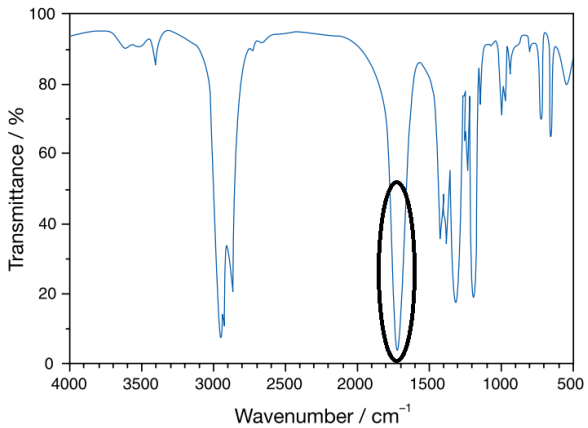
Presence of **a board absorption peak** at around **2960 cm^{-1}** indicates the **presence of O–H bond (alcohol)**





Presence of **absorption peaks** at around **3290 cm^{-1} and 3370 cm^{-1}** indicates the **presence of N–H bond**





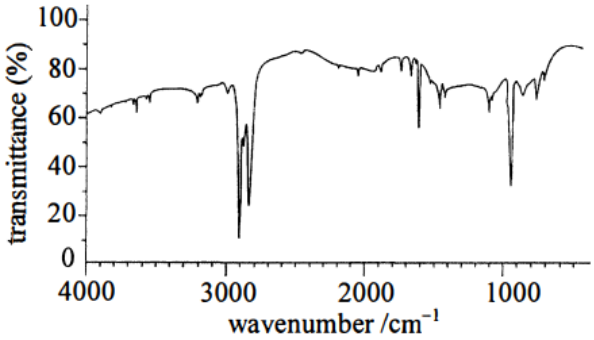
Presence of **a sharp absorption peak** at around **1720 cm^{-1}** indicates the **presence of C=O bond**

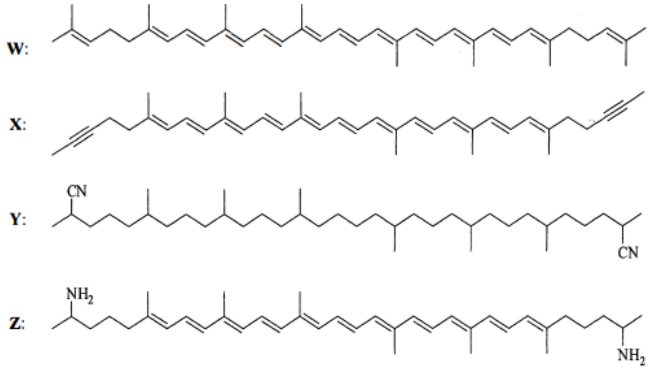
Note that some compounds CANNOT be distinguished from their respective infra-red spectra by referring to the characteristic Infra-red absorption wavenumber range only if they have same functional groups. It is because their infra-red spectra will give the same characteristics absorption peak(s). (e.g. Hexanal and hexan-2-one, propan-1-ol and propan-2-ol)

They can be distinguished by comparing their fingerprint region with that of a known compound.

Example 1

The infra-red spectrum of compound A, and the structures of organic compound W, X, Y and Z are shown below:





By referring to the Characteristic Infra-red Absorption Wavenumber Ranges (Stretching modes) given in the table below ONLY, suggest whether W, X, Y or Z may be the structure of A. Explain your answer.

Answer: **Presence of a sharp absorption peak at 1630 cm^{-1}** suggesting it **contains C=C group**, ruling out the possibility of Y.

Absence of absorption peak at 2070 – 2250 cm^{-1} suggesting it **does not contain C≡C group**, ruling out the possibility of X.

Absence of absorption peak at 3350 – 3500 cm^{-1} suggesting it **does not contain N–H group**, ruling out the possibility of Z. Therefore W is lycopene

Example 2

Characteristic Infra-red Absorption Wavenumber Ranges (Stretching modes)

Bond	Compound type	Wavenumber range / 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
O–H	Acids (hydrogen-bonded)	2500 to 3300
C–H	Alkanes, alkenes, arenes	2840 to 3095
O–H	Alcohols, phenols (hydrogen-bonded)	3230 to 3670
N–H	Amines	3350 to 3500

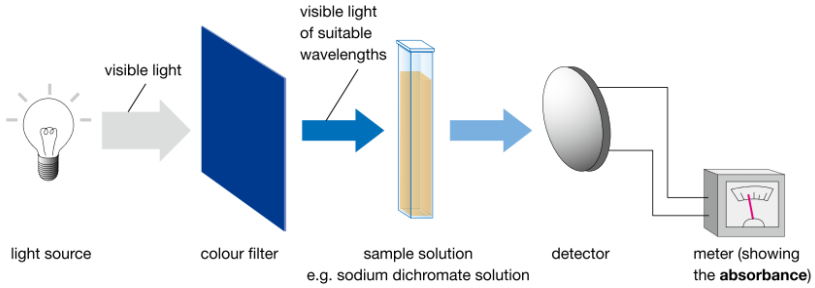
(a) With reference to the information given in the table above, suggest whether infra-red spectroscopy can be used to distinguish between propan-1-ol and propanal.

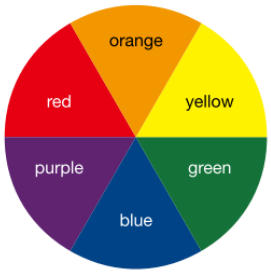
Answer: The IR spectrum of propan-1-ol shows a strong absorption peak in the region from 3230 – 3670 cm^{-1} (corresponding to O-H group of propan-1-ol), while the IR spectrum of propanal does not show this peak. The IR spectrum of propanal shows a strong absorption peak in the region from 1680 – 1800 cm^{-1} (corresponding to C=O group of propanal), while the IR spectrum of propan-1-ol does not show this peak.

(b) With reference to the information given in the table above, suggest whether infra-red spectroscopy can be used to distinguish between propanal and propanone.

Answer: Both compounds show a characteristic absorption in the wavenumber range (1680 – 1800 cm^{-1}) which is characteristic of C=O bond of carbonyl group. As the two compounds do not possess other different functional groups, they cannot be differentiated from each other using the given information

Colorimeter

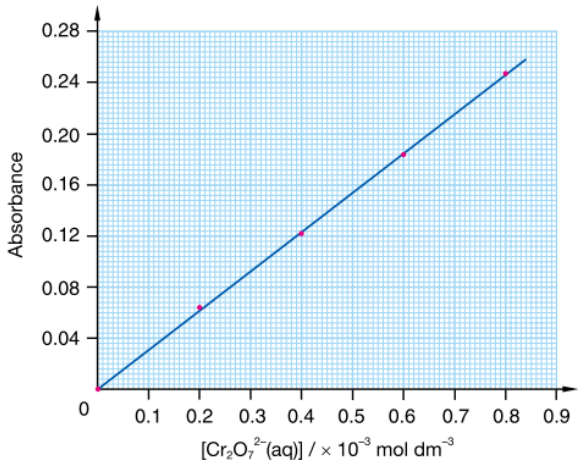




- Visible light of suitable wavelengths is passed through the colored sample solution. The sample solution absorbs a part of the light and transmits the remaining part of the light. This shows the fraction of light absorbed (absorbance).
- The higher the concentration of colored species, the higher the absorbance. Note that absorbance has no unit.
- The color of the color filter should be the complementary color of the colored sample. For example, yellow filter is chosen for purple $KMnO_4(aq)$ as it absorbs yellow light in a large extent.
- Colorimetry is more appropriate than volumetric analysis in determining the concentration of a very dilute solution. Modern instruments can measure the low level of substances accurately

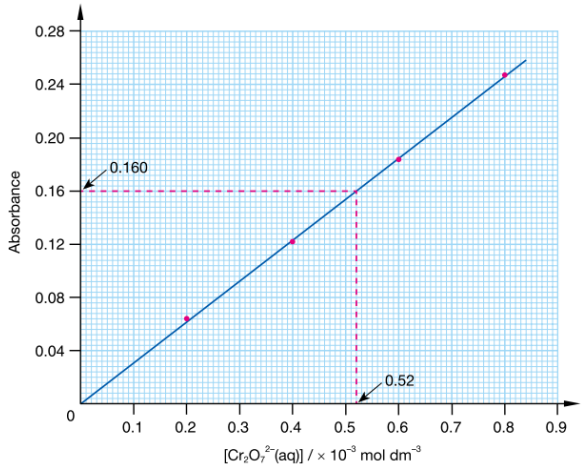
Determining the concentration of a colored species from a calibration curve

Step 1: Constructing a calibration curve



- A series of standard $K_2Cr_2O_7(aq)$ with different concentrations are first prepared.
- The absorbance of each of these solutions is then measured with a colorimeter (using blue filter).
- Using the above data, plot a calibration curve which shows the variation of absorbance with the concentration of $Cr_2O_7^{2-}(aq)$
- The absorbance should be directly proportional to the concentration of $Cr_2O_7^{2-}(aq)$

Step 2: Determining the concentration of a sample from the calibration curve



- Measure the absorbance* of the unknown solution using the same colorimeter. (e.g. The absorbance recorded is 0.160)
- Draw a horizontal line corresponding to the absorbance of 0.160 until the line meets the calibration curve.
- The concentration of the sample can be obtained from the calibration curve (in this case, 0.52 x 10^{-3} mol dm^{-3})

* If the concentration of a coloured species in the sample is too high, we may need to dilute the sample solution so that the concentration of the coloured species falls within the range of the calibration curve.

Mass spectrometry

In mass spectrometry, the sample is first vaporized to gaseous form and bombarded by fast-moving electrons. Electrons are knocked out from molecules of the sample, forming positive ions, called molecular ions (M^+).

$$M(g) + e^- \rightarrow M^+ + 2e^-$$

Molecular ions may further split into fragment ions. The positive ions (both molecular ions and fragment ions) are accelerated by electric field and deflected by a magnetic field. In general, ions with a lower mass-to-charge ratio (m/z or m/e) are deflected more and vice versa. By varying the strengths of the electric field and the magnetic field, ions of different m/z are separated and brought to the detector, producing electrical signals proportional to the number of ions detected. These signals are recorded and presented in a mass spectrum.

Common fragments (R = alkyl group)

R^+	RCO^+	$C_6H_5CH_2^+$

Common fragment ions and their m/z

m/z	15	29	43	57	71	77	91	105
Chemical species	CH_3^+	HCO^+ $C_2H_5^+$	CH_3CO^+ $C_3H_7^+$	$CH_3CH_2CO^+$ $C_4H_9^+$	$CH_3CH_2CH_2CO^+$	$C_6H_5^+$	$C_6H_5CH_2^+$	$C_6H_5CO^+$ $C_6H_5CH_2CH_2^+$

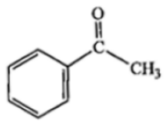
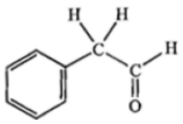
If the m/z of a peak is equal to common m/z – 2 (e.g. 27, 55, 103), it likely contains a C=C bond (with 2 H atoms less)

If the difference between 2 peaks = 17: Formed by stripping off a -OH

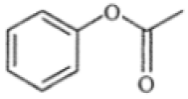
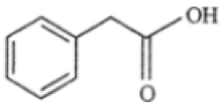
If the difference between 2 peaks = 31: Formed by stripping off a $-OCH_3$

If the difference between 2 peaks = 45: Formed by stripping off a -COOH

Example 1

	
m/z = 15 (CH_3^+)	**m/z = 29 (HCO^+)**
m/z = 43 (CH_3CO^+)	**m/z = 91 ($C_6H_5CH_2^+$)**
m/z = 105 ($C_6H_5CO^+$)	

Example 2

	
m/z = 15 (CH_3^+)	m/z = 17 (OH^+)
m/z = 43 (CH_3CO^+)	m/z = 45 ($COOH^+$)
m/z = 93 ($C_6H_5O^+$)	**m/z = 91 ($C_6H_5CH_2^+$)**
m/z = 121 ($C_6H_5OCO^+$)	m/z = 119 ($C_6H_5CH_2CO^+$)

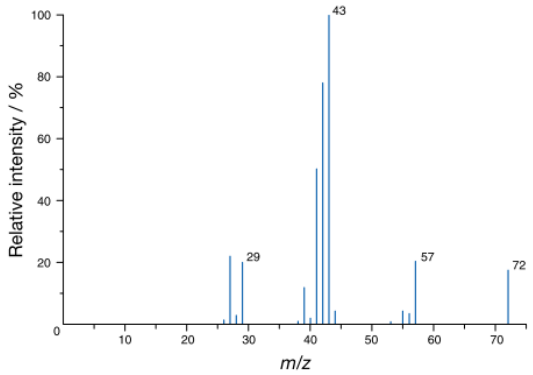
Example 3

Illustrate how $CH_3CH_2CHO(l)$ and $CH_3COCH_3(l)$ can be distinguished from their respective mass spectra.

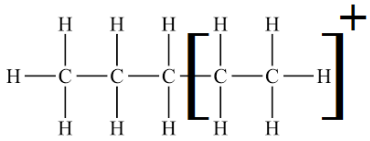
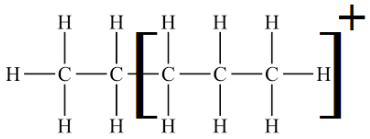
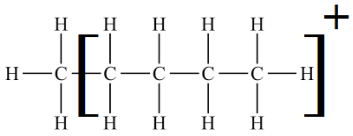
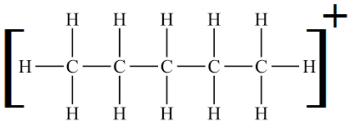
Answer: In the mass spectrum of CH_3CH_2CHO, a significant peak appears at m/z = 29 corresponding to CHO^+ / $CH_3CH_2^+$ (OR a significant peak appears at m/z = 57 corresponding to $CH_3CH_2CO^+$), while this peak does not appear in the mass spectrum of CH_3COCH_3

In the mass spectrum of CH_3COCH_3, a significant peak appears at m/z = 43 corresponding to CH_3CO^+, while this peak does not appear in the mass spectrum of CH_3CH_2CHO.

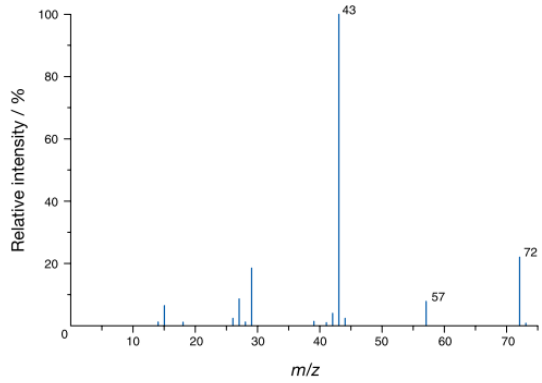
Fragmentation of alkane (Cleavage on C-C to give R^+ is preferred)



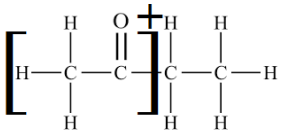
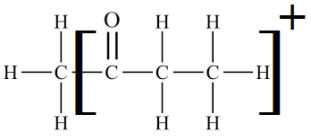
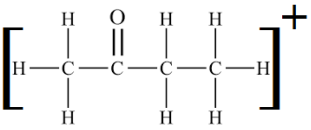
Mass spectrum of pentane

m/z	ions
29 $CH_2CH_3^+$ (stripping off $-CH_2CH_2CH_3$)	
43 $CH_2CH_2CH_3^+$ (stripping off $-CH_2CH_3$)	
57 $CH_2CH_2CH_2CH_3^+$ (stripping off $-CH_3$)	
72 $CH_3CH_2CH_2CH_2CH_3^+$ (molecular ion peak)	

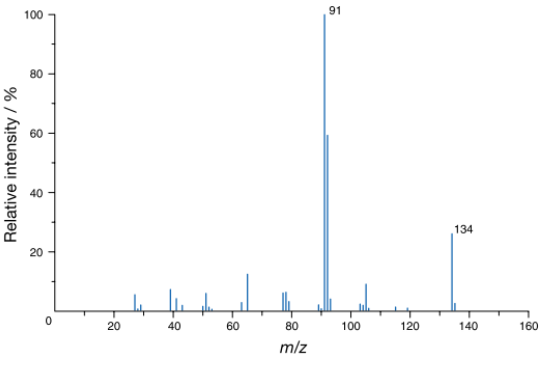
Fragmentation of aldehydes and ketones (Cleavage next to C=O to give RCO^+ is preferred)



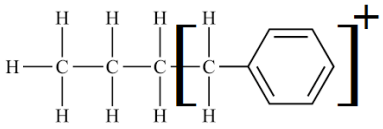
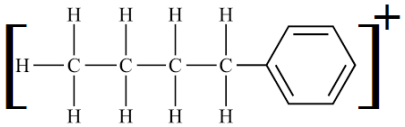
Mass spectrum of butanone

m/z	ions
43 CH_3CO^+ (stripping off $-CH_2CH_3$)	
57 $CH_3CH_2CO^+$ (stripping off $-CH_3$)	
72 $CH_3CH_2COCH_3^+$ (molecular ion peak)	

Fragmentation of alkylbenzene and their derivatives ($C_6H_5CH_2^+$ preferred)



Mass spectrum of butylbenzene

m/z	ions
91 $C_6H_5CH_2^+$ (stripping off $-CH_2CH_2CH_3$)	
134 $C_6H_5CH_2CH_2CH_2CH_3^+$ (molecular ion peak)	

Analytical methods and their applications in our society

Colorimetry	- **Determining concentrations of food coloring**	
	- **Determining urea concentration in urine** Urea is a colorless compound. To measure the urea content in urine, a reagent that forms a coloured complex specifically with urea is added	
Volumetric analysis (VA)	- **Determining sulphur dioxide content in white wine**	
	- **Errors in titration experiments:** Titration errors are unavoidable in volumetric analysis but they can be reduced by repeating the titration several times. This can give more reliable titration results	
	Uncertainty arising from the apparatus or chemicals used	
	- Balance readings	- Volumes of volumetric flasks and pipettes
	- Graduation marks on burettes	- Purity of primary standards
	Titration errors	
	- Error in burette reading	- Error in reading of liquid volume
	- End point error	
Thin-layer chromatography (TLC)	- **Identifying fake drugs** - **Identifying toxins present in the body**	
Infrared spectroscopy (IR)	- **Identifying impurities in drugs**	- **Deducing flammable liquid residues**
	- **Monitoring carbon monoxide level in air**	- **Monitoring formaldehyde level in air**
Gas chromatography-mass spectrometry (GC-MS)	- **Monitoring dioxin level in air** Dioxins are produced during the combustion of Cl-containing compounds. They are carcinogenic. GC-MS is a very accurate and highly sensitive analytical method to determine the low level of dioxin. (GC: Separation of different substances, MS: Identification of the separated substances)	
Gas chromatography (GC)	- **Determining alcohol content in blood or urine** - **Investigating abuse of illegal or banned drugs (e.g. ketamine)** - **Separating different compounds in flammable liquid residues left in a fire scene** - **Determining urea concentration in urine**	
Breathalyser	- **Determining alcohol content in breath**	
Mass spectrometry (MS)	- **Deducing flammable liquid residues (e.g. petrol)** - **Identifying proteins present specifically in cancer cells**	
Iodine sublimation	- **Identifying fingerprints** The suspected object is placed in a closed container with $I_2(s)$ inside. The container is then heated. $I_2(s)$ sublimes to give $I_2(g)$ which dissolves in the oil of the fingerprint, turning the pattern brown. The 'brown' fingerprint is then photographed before it fades. To help prevent fading, a 1% starch solution can be sprayed onto the fingerprint	