Mastering Chemistry

Book 8

Topic 15 Analytical Chemistry

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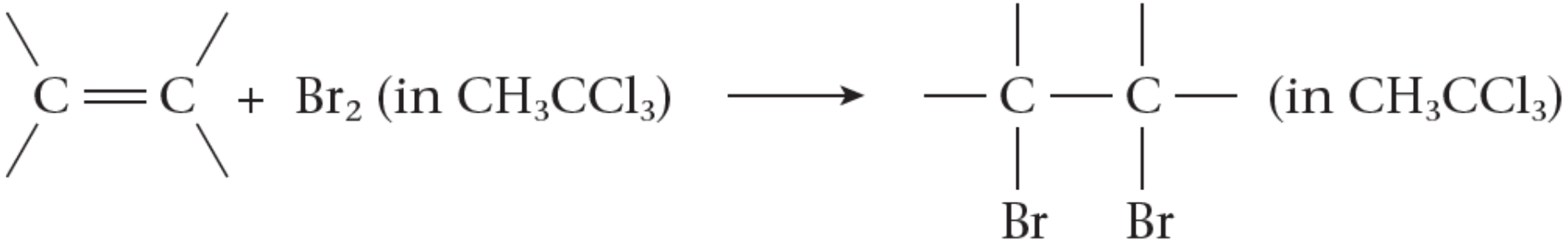
- Key terms
- Summary
- Unit Exercise

52.1 Specific chemical tests for functional groups (p.43)

- You are going to look at specific chemical tests for detecting the presence of the functional groups below:
  - carbon-carbon double bond (C=C);
  - alcohol functional group (–OH);
  - aldehyde functional group (–CHO);
  - ketone functional group (C=O);
  - carboxylic acid functional group (–COOH).

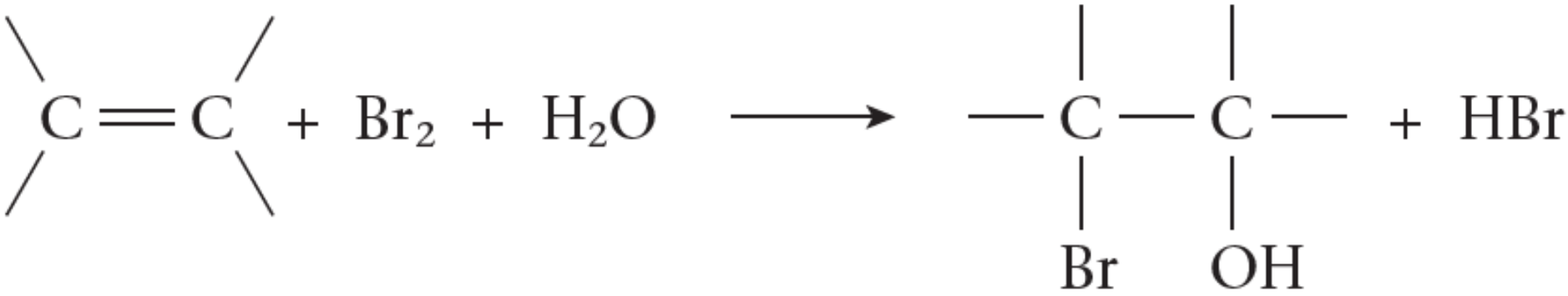
52.2 Test for carbon-carbon double bond (C=C) (p.44)

- When bromine dissolved in 1,1,1-trichloroethane is added to a carbon compound containing carbon-carbon double bond (C=C) at room temperature, the orange bromine solution becomes colourless quickly. This is because an addition reaction occurs.



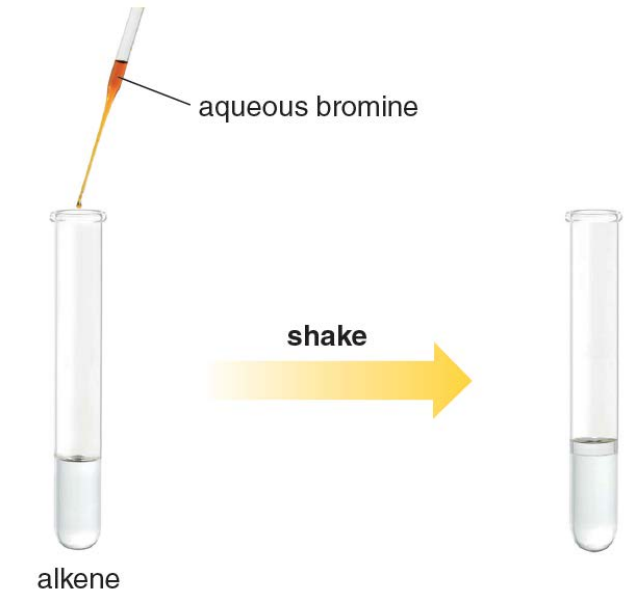
52.2 Test for carbon-carbon double bond (C=C) (p.44)

- Aqueous bromine becomes colourless quickly when mixed with a carbon compound containing carbon-carbon double bond.
- The test for carbon-carbon double bond often uses aqueous bromine rather than pure bromine.



52.2 Test for carbon-carbon double bond (C=C) (p.44)

- Method
  - Add aqueous bromine dropwise to the carbon compound under test slowly and shake the mixture.
  - When added to a carbon compound containing carbon -carbon double bond(s), the yellow-brown aqueous bromine becomes colourless quickly.



Add aqueous bromine dropwise to an alkene (left); the yellow-brown aqueous bromine becomes colourless quickly (right)

52.3 Tests for the alcohol functional group (–OH) (p.45)

Oxidation by acidified aqueous solution of potassium dichromate

- Primary alcohols are oxidised by acidified aqueous solution of potassium dichromate to aldehydes, which can be further oxidised to carboxylic acids.

$$\text{primary alcohol} \xrightarrow{\text{acidified } K_2Cr_2O_7(aq)} \text{aldehyde}$$

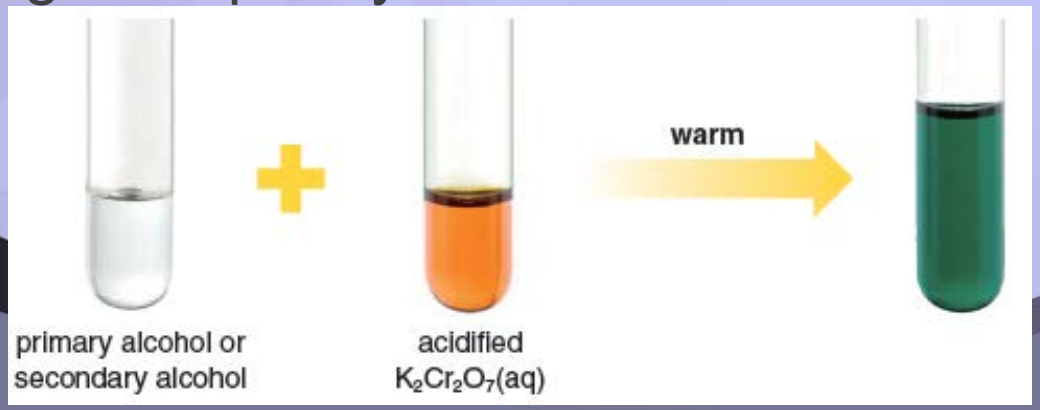
$$\text{aldehyde} \xrightarrow{\text{acidified } K_2Cr_2O_7(aq)} \text{carboxylic acid}$$

- Secondary alcohols are oxidised by acidified aqueous solution of potassium dichromate to ketones.

$$\text{secondary alcohol} \xrightarrow{\text{acidified } K_2Cr_2O_7(aq)} \text{ketone}$$

52.3 Tests for the alcohol functional group (–OH) (p.45)

- Tertiary alcohols are not oxidised by acidified aqueous solution of potassium dichromate.
- Method
  - Mix an acidified aqueous solution of potassium dichromate with the carbon compound under test.
  - Warm the mixture.
  - A primary alcohol or a secondary alcohol turns the acidified aqueous solution of potassium dichromate from orange to green quickly.



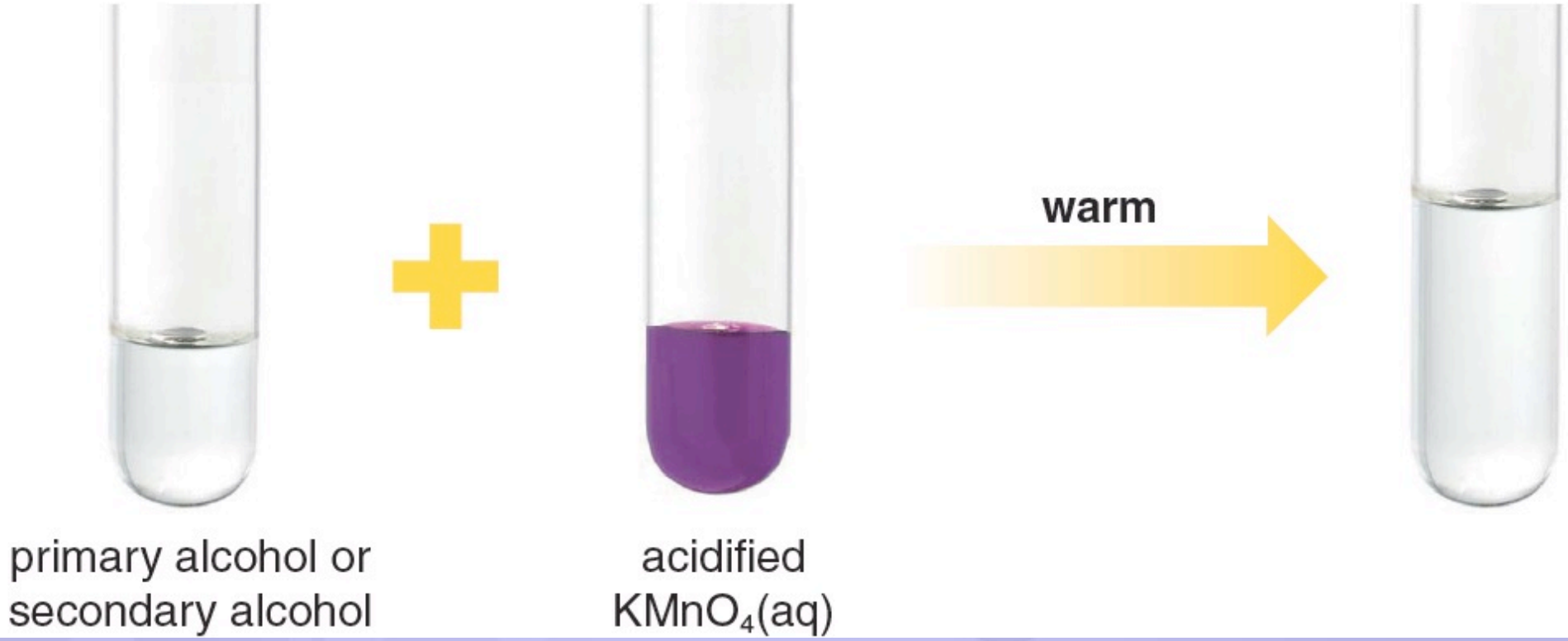
When warmed with acidified aqueous solution of potassium dichromate, primary or secondary alcohols turn the orange dichromate solution green

52.3 Tests for the alcohol functional group (–OH) (p.45)

Oxidation by acidified aqueous solution of potassium permanganate

- Acidified aqueous solution of potassium permanganate oxidises primary alcohols to carboxylic acids and oxidises secondary alcohols to ketones.
- Method
  - Mix an acidified aqueous solution of potassium permanganate with the carbon compound under test.
  - Warm the mixture.
  - A primary alcohol or a secondary alcohol turns the acidified aqueous solution of potassium permanganate from purple to colourless quickly.

52.3 Tests for the alcohol functional group (–OH) (p.45)



When warmed with acidified aqueous solution of potassium permanganate, primary or secondary alcohols turn the purple permanganate solution colourless

52.3 Tests for the alcohol functional group (–OH) (p.45)

Practice 52.1

Phosphorus pentachloride (PCl_5) can be used to test for the –OH group.

a) Describe what would be observed when phosphorus pentachloride is added to butan-1-ol.

Steamy fumes of hydrogen chloride

b) A tertiary alcohol, X, is an isomer of butan-1-ol. Suggest a chemical test to distinguish X and butan-1-ol. State the expected observation for each alcohol.

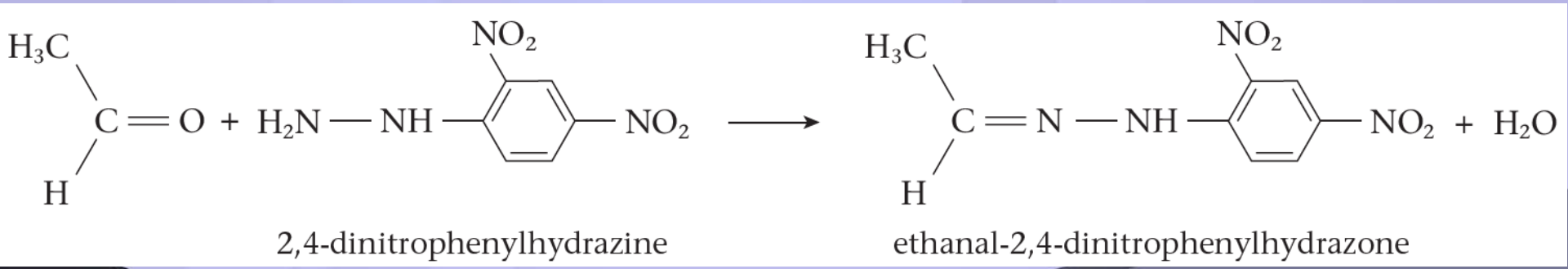
Any one of the following:

- Warm each alcohol with an acidified aqueous solution of potassium permanganate separately.
  Butan-1-ol gives a colour change from purple to colourless.
  X gives no observable change.
- Warm each alcohol with an acidified aqueous solution of potassium dichromate separately.
  Butan-1-ol gives a colour change from orange to green.
  X gives no observable change.

52.4 Tests for the aldehyde and ketone functional groups (–CHO and C=O) (p.47)

Test with 2,4-dinitrophenylhydrazine

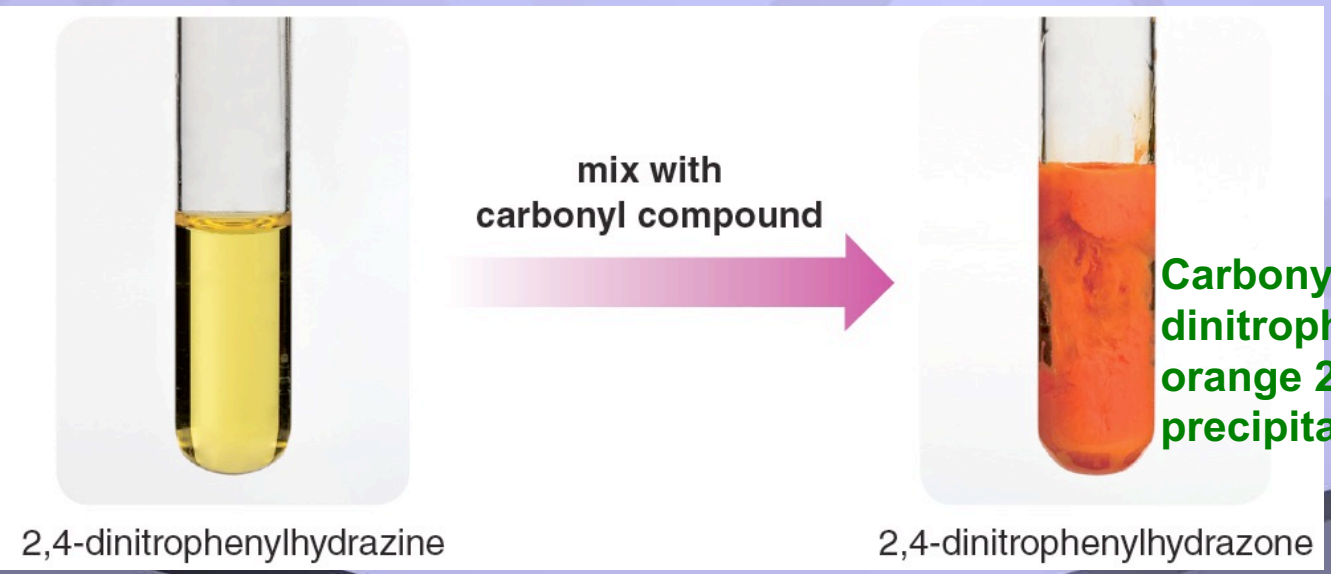
- The reagent reacts with carbonyl **2,4-dinitrophenylhydrazine (2,4-二硝基苯肼)** compounds to form 2,4-dinitrophenylhydrazones, which are bright red, orange or yellow precipitates.
- For example, ethanal reacts with 2,4-dinitrophenylhydrazine according to the equation below.



Studying the reactions of an aldehyde and a ketone with some reagents *Ref.*

52.4 Tests for the aldehyde and ketone functional groups (–CHO and C=O) (p.47)

- Method
  - Add a solution of 2,4-dinitrophenylhydrazine to the carbon compound under test.
  - A carbonyl compound gives a bright red, orange or yellow precipitate.



Carbonyl compound reacts with 2,4-dinitrophenylhydrazine to form an orange 2,4-dinitrophenylhydrazone precipitate

52.4 Tests for the aldehyde and ketone functional groups (–CHO and C=O) (p.47)

Tests for aldehyde functional group (—CHO)

- Aldehydes and ketones can be distinguished by a series of redox reactions. Aldehydes are oxidised readily to carboxylic acids; ketones are not oxidised easily.

Acidified aqueous solution of potassium dichromate

- Acidified aqueous solution of potassium dichromate turns from orange to green when warmed with an aldehyde. The aldehyde is oxidised to a carboxylic acid in the reaction.

52.4 Tests for the aldehyde and ketone functional groups (–CHO and C=O) (p.47)

Tollens' reagent

- **Tollens' reagent (托倫斯試劑)**, also called ammoniacal silver nitrate solution,
  contains the complex ion $[Ag(NH_3)_2]^+$. It is a colourless chemical that is made in a two-stage process:
  1 Add sodium hydroxide solution to silver nitrate solution until a brown precipitate is formed.
  2 Add dilute aqueous ammonia dropwise until the brown precipitate dissolves.
- Tollens' reagent is a weak oxidising agent and can react with an aldehyde but not a ketone.

52.4 Tests for the aldehyde and ketone functional groups (–CHO and C=O) (p.47)

- When an aldehyde reacts with Tollens' reagent, the silver ion is reduced and the aldehyde is oxidised.

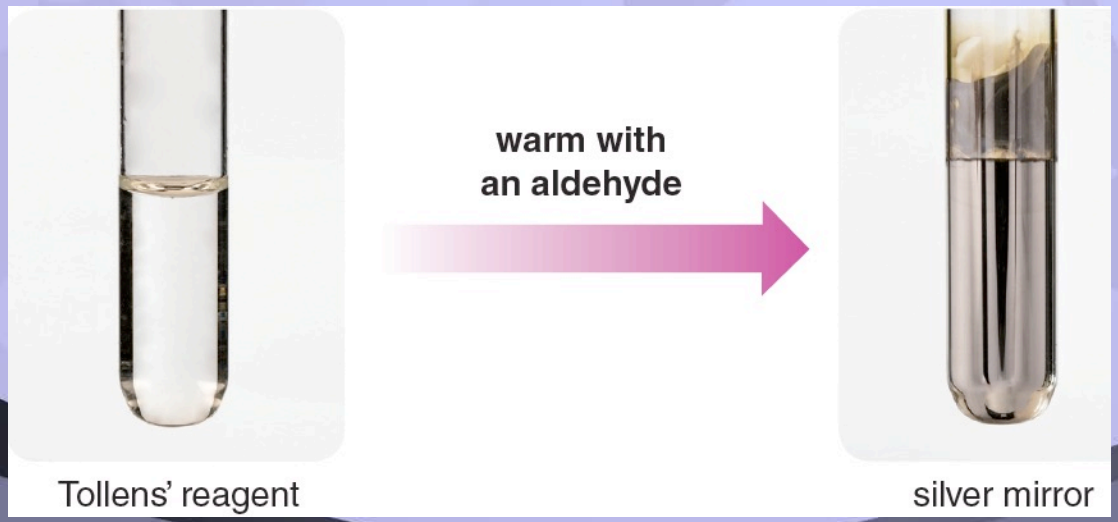
$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCOO^- + 2Ag + 4NH_3 + 2H_2O$$

colourless solution → carboxylate ion; silver mirror

- The silver metal is observed as a silver mirror on the inside of the reaction vessel.

52.4 Tests for the aldehyde and ketone functional groups (–CHO and C=O) (p.47)

- Method
  - Add a few drops of the carbon compound under test to 2 cm^3 of freshly prepared Tollens' reagent in a test tube.
  - Warm the mixture in a water bath at about 60 °C.
  - A silver mirror forms on the inside of the test tube if the carbon compound is an aldehyde.



Warming Tollens' reagent with an aldehyde gives a silver mirror

52.4 Tests for the aldehyde and ketone functional groups (–CHO and C=O) (p.47)

Practice 52.2

1 Two carbon compounds, X and Y, both with the molecular formula $C_5H_{10}O$, contain a carbonyl group.

a) Describe what you would observe when 2,4-dinitrophenylhydrazine is added to either of these compounds. Bright red / orange / yellow precipitate

b) It is suspected that X is an aldehyde and Y is a ketone. Outline a chemical test you could carry out to confirm this and describe the expected observation in each case.

Any one of the following:

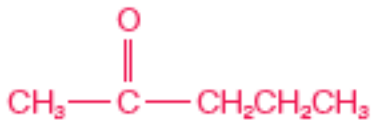
- Warm with Tollens' reagent.
  X gives a silver mirror on the inside of the reaction vessel.
  Y gives no observable change.
- Warm with an acidified aqueous solution of potassium dichromate.
  X turns the dichromate solution from orange to green.
  Y gives no observable change.

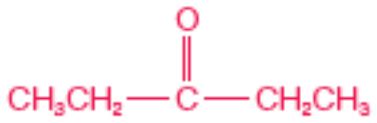
52.4 Tests for the aldehyde and ketone functional groups (–CHO and C=O) (p.47)

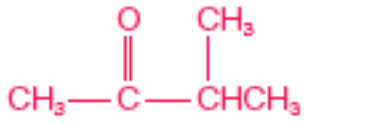
Practice 52.2 (continued)

1 c) Give the structural formulae of TWO possible isomers of Y which are ketones.

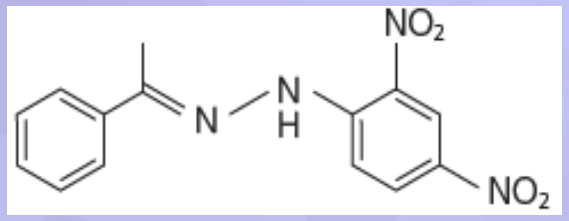
Any two of the following:



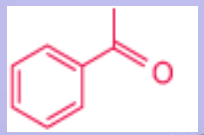




2 A carbon compound W reacts with 2,4-dinitrophenylhydrazine to form a yellow solid Z. The structure of Z is shown below:



Draw the structure of W.



52.5 Tests for the carboxylic acid functional group (p.50)

Test with aqueous solution of sodium hydrogencarbonate

- A carboxylic acid reacts with an aqueous solution of sodium hydrogencarbonate, liberating carbon dioxide gas.

$$RCOOH + NaHCO_3 \longrightarrow RCOO^-Na^+ + CO_2 + H_2O$$

- Method
  - Mix the carbon compound under test with an aqueous solution of sodium hydrogencarbonate.
  - Effervescence occurs if the carbon compound is a carboxylic acid.
  - The gas can be collected and bubbled into limewater which should turn milky, proving that the gas produced is carbon dioxide.

Effervescence occurs when a carboxylic acid is mixed with an aqueous solution of sodium hydrogencarbonate

52.5 Tests for the carboxylic acid functional group (p.50)

Ester formation

- A carboxylic acid can react with an alcohol to form an ester in the presence of a concentrated acid catalyst.

$$R_1COOH + R_2OH \overset{H^+}{\rightleftharpoons} R_1COOR_2 + H_2O$$

- Method
  - Mix the carbon compound under test with ethanol.
  - Use concentrated sulphuric acid as a catalyst. Heat the mixture.
  - A sweet, fruity smell from an ester can be detected if the carbon compound is a carboxylic acid.

52.5 Tests for the carboxylic acid functional group (p.50)

c) P is methanoic acid.
Q is a secondary alcohol as it forms a ketone upon oxidation. It is probably propan-2-ol.
X is 2-propyl methanoate.

Practice 52.3

Compound X ($C_4H_8O_2$) reacts with hot dilute sulphuric acid. Compounds P (CH_2O_2) and Q (C_3H_8O) are produced.
Tests are performed on P and Q and the results are as follows:
Test 1 P gives effervescence with $NaHCO_3(aq)$.
Test 2 Q is oxidised by acidified $K_2Cr_2O_7(aq)$. The oxidation product R gives an orange precipitate with 2,4-dinitrophenylhydrazine but gives a negative result when warmed with Tollens' reagent.

a) With reference to *Test 1*, suggest ONE functional group that P may have.
–COOH group

b) i) What is the purpose of using Tollens' reagent? Test for aldehyde group
ii) State the expected observation if an oxidation product gives a positive result with Tollens' reagent.
A silver mirror forms on the inside of the reaction vessel.
iii) Suggest one functional group that may be present in R. A ketone group

c) Draw a possible structure of X. Explain your answer.

52.6 Specific chemical tests for detecting the presence of functional groups (p.51)

- Specific chemical tests for detecting the presence of functional

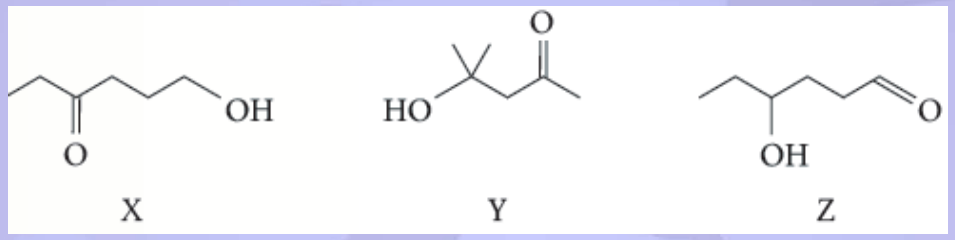
Functional group	Test	Observation(s)
−C=C−	add aqueous bromine to carbon compound slowly	yellow-brown aqueous bromine becomes colourless quickly
−OH (primary and secondary alcohols)	warm with acidified $K_2Cr_2O_7$(aq)	colour change from orange to green
	warm with acidified $KMnO_4$(aq)	colour change from purple to colourless (or very pale pink)
−CHO	treat with 2,4-dinitrophenylhydrazine	a bright red, orange or yellow precipitate forms
	warm with Tollens' reagent	silver mirror forms
	warm with acidified $K_2Cr_2O_7$(aq)	colour change from orange to green
$\rangle$C=O	treat with 2,4-dinitrophenylhydrazine	a bright red, orange or yellow precipitate forms
−COOH	mix with $NaHCO_3$(aq)	effervescence occurs; gas produced turns limewater milky
	warm with ethanol in the presence of concentrated sulphuric acid	a sweet, fruity smell is detected

3 **Identifying the functional groups in two unknown compounds *Ref.***

52.6 Specific chemical tests for detecting the presence of functional groups (p.51)

Q (Example 52.1)

The following compounds are isomers with molecular formula $C_6H_{12}O_2$.



Describe chemical tests you could carry out to distinguish among these compounds.

A

Warm each compound with Tollens' reagent. Only compound Z produces a silver mirror. Compounds X and Y give negative result.
Warm compounds X and Y with acidified $K_2Cr_2O_7(aq)$ separately. Only compound X gives a colour change from orange to green. Compound Y gives a negative result.

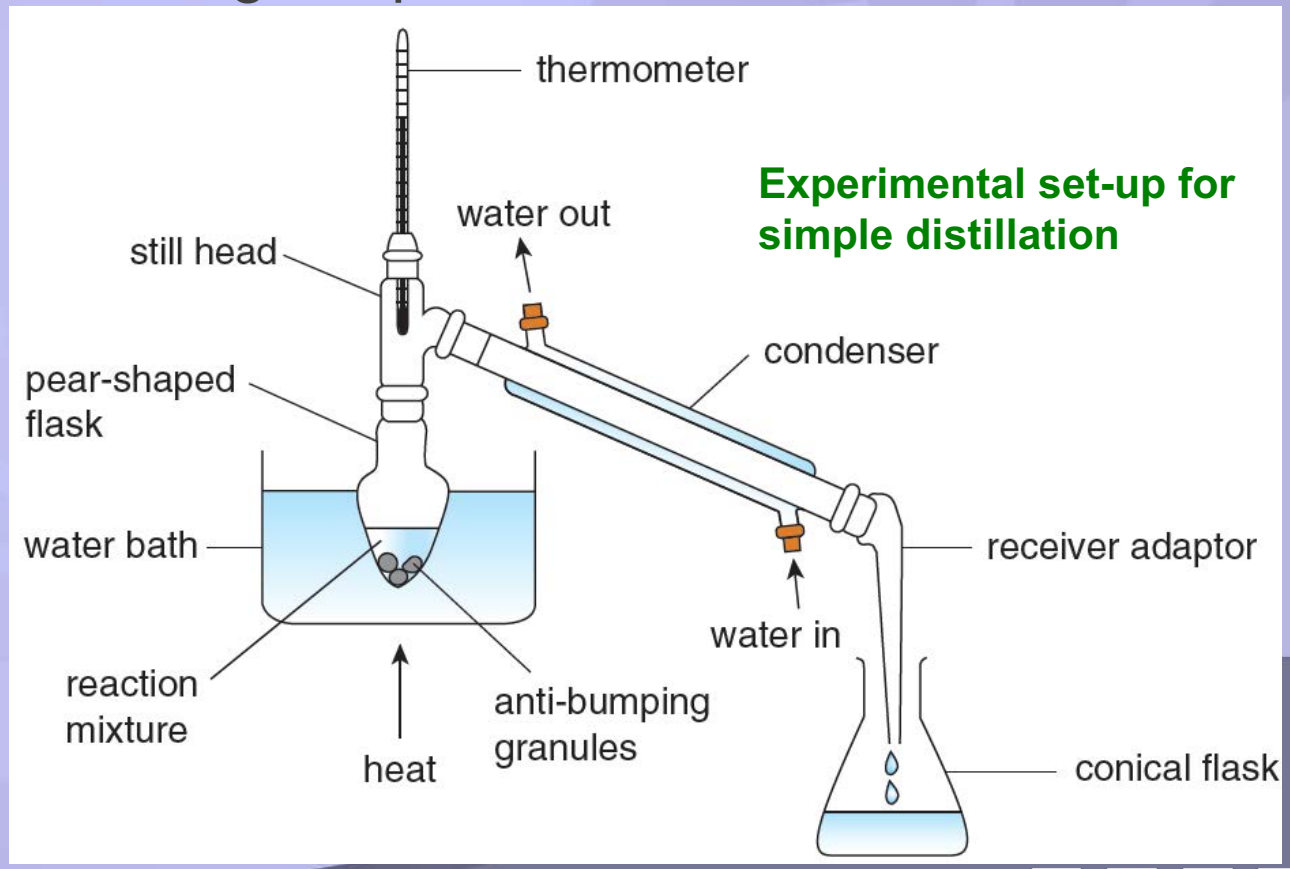
52.7 Common separation and purification methods (p.53)

- The result of any organic reaction will be a mixture of substances. The required product must be separated from the reaction mixture and then purified.
- The separation and purification methods used depend on whether the product is a solid or a liquid.

Type of product	Separation and purification methods to employ
Liquid product	• distillation • fractional distillation • liquid-liquid extraction
Solid product	• recrystallisation • chromatography

52.8 Simple distillation (p.53)

- Simple distillation is a common method for separating a crude liquid product from the reaction mixture if the liquid product has a much lower boiling temperature than other substances in the mixture.



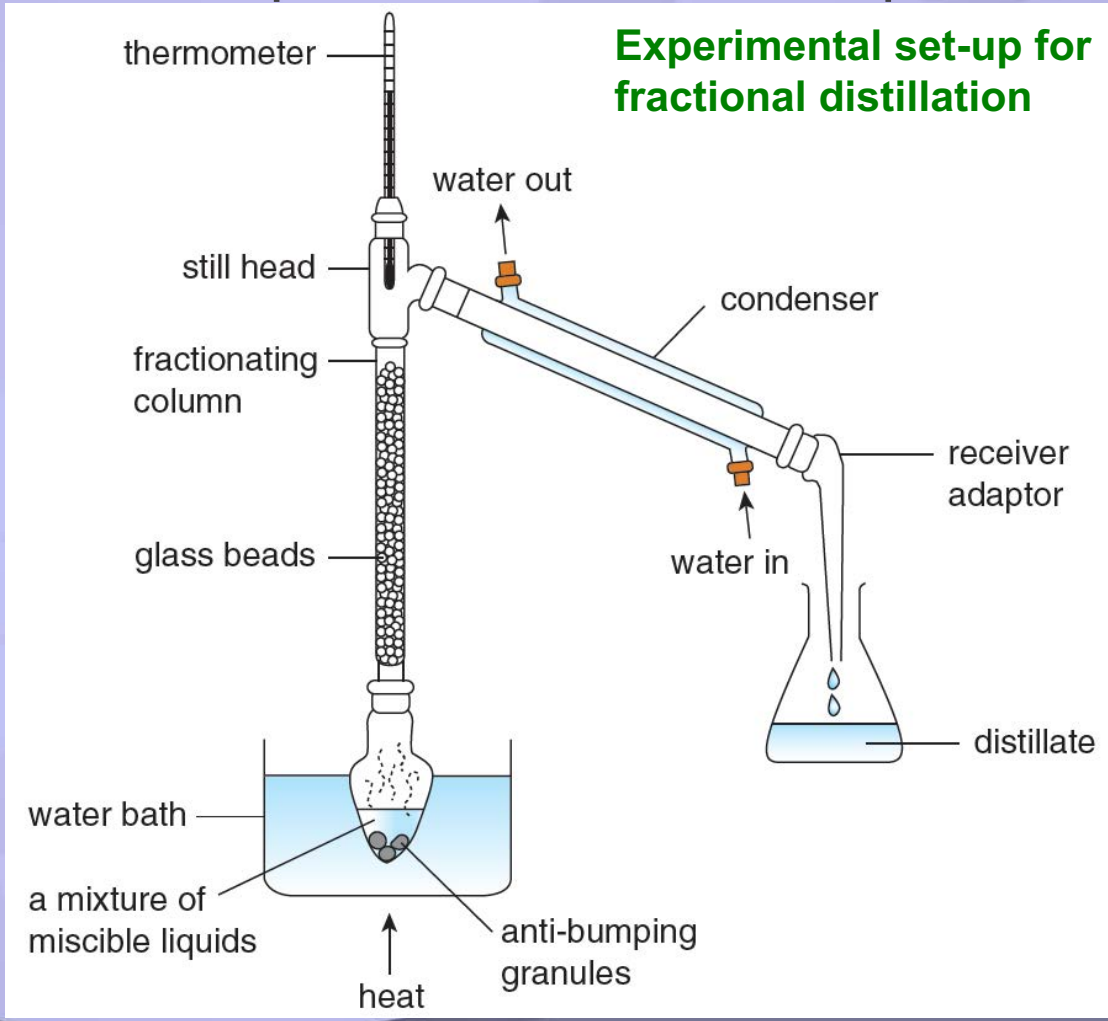
Experimental set-up for simple distillation

52.8 Simple distillation (p.53)

- Heat the mixture until it boils gently.
- When the vapour temperature is approximately 2 °C below the boiling point of the liquid you are about to collect, put the collecting flask in place.
- Collect the distillate until the temperature of the vapour rises above the boiling point of the liquid you are collecting.
- Stop heating.
- Simple distillation can also be used to separate two volatile liquids (with a large difference in boiling points) that form a solution.

52.9 Fractional distillation (p.54)

- Fractional distillation separates mixtures of liquids with close boiling points.



52.9 Fractional distillation (p.54)

- The column is filled with glass beads, acting as surfaces on which the vapour from the mixture can condense and the condensed liquid can vaporise when meeting hot vapour passing up the column.
- The vapour becomes richer and richer in the most volatile liquid in the mixture as it rises up the column.
- The most volatile liquid with the lowest boiling point distils over first, then the liquid with the next lowest boiling point and so on.

52.9 Fractional distillation (p.54)

Practice 52.4

In an experiment, ethanoic acid was prepared by heating ethanol with excess acidified $K_2Cr_2O_7(aq)$ under reflux.

a) What is meant by 'heating under reflux'? (Consider the physical changes that occur.)

Boil the mixture.
Condense / cool the vapour to return it to the reaction flask.

b) Write the half equation for the reduction of dichromate ion.

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

c) What would be the colour of the reaction mixture after it was heated under reflux?

Green

d) A solution containing both water and ethanoic acid was produced by distillation of the final reaction mixture.

i) Explain why the other products and any excess reactants were left behind in the distillation flask.

They are ionic compounds. / They have high boiling points.

ii) Suggest a method to separate pure ethanoic acid (boiling point: 118 °C) from water.

Any one of the following:

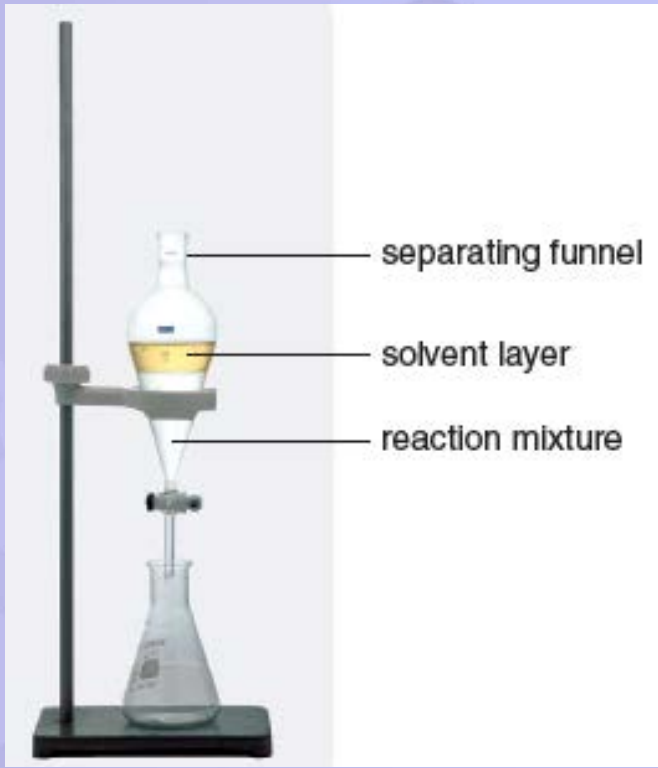
- Fractional distillation
  Water distils off first; then ethanoic acid.
- Absorb the water by using a drying agent.

52.10 Liquid-liquid extraction (p.55)

- **Liquid-liquid extraction (液液萃取)** (also called solvent extraction) involves using a solvent to extract the desired liquid product from the other substances in the reaction mixture.
- There are several solvents that can be used, but the choice depends mainly on these features.
  - The solvent added should be immiscible (i.e. not mix) with the solvent containing the desired product.
  - The desired product should have a higher solubility in the solvent added than in the reaction mixture.

52.10 Liquid-liquid extraction (p.55)

- Here is a summary of the process of liquid-liquid extraction.
  1 Place the reaction mixture in a separating funnel, and then add the chosen solvent — it should form a separate layer.



During the extraction, add a solvent to the reaction mixture, giving two layers of liquids

52.10 Liquid-liquid extraction (p.55)

2 Place the stopper and gently shake the contents of the funnel for a while.

Hold the stopper and the tap firmly when shaking

3 Allow the contents to settle into two layers.

4 Remove the stopper and open the tap to allow the lower layer to drain into a flask. Then pour the upper layer into a separate flask.

52.10 Liquid-liquid extraction (p.55)

- The desired product has been removed from the reaction mixture, but is now mixed with the added solvent. You can use simple distillation or fractional distillation to separate the desired product from the solvent used.
- If necessary, the product can be further purified by simple distillation.

52.10 Liquid-liquid extraction (p.55)

Q (Example 52.2)

Consider a solution of compounds X and Y in dichloromethane.

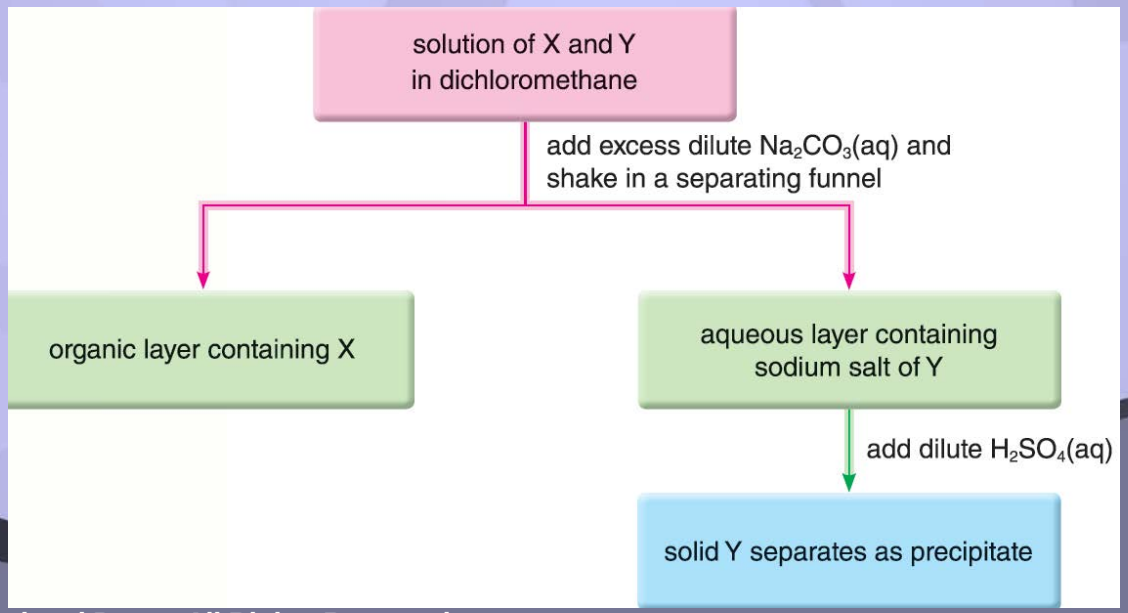
You are provided with dilute $Na_2CO_3(aq)$ and dilute $H_2SO_4(aq)$. Outline an experimental procedure, based on solvent extraction, to separate solid Y from a solution of X and Y in dichloromethane.

52.10 Liquid-liquid extraction (p.55)

Q (Example 52.2) (continued)

A

Add excess dilute $Na_2CO_3(aq)$ to the solution of X and Y in dichloromethane. Shake the mixture in a separating funnel. Allow the mixture in the separating funnel to settle. Collect the aqueous layer containing sodium salt of Y.
Add dilute $H_2SO_4(aq)$ to the aqueous layer until no more precipitate forms. Obtain solid Y by filtration.
The flow diagram below summarises the procedure used.



52.10 Liquid-liquid extraction (p.55)

Practice 52.5

The procedure below is used to extract caffeine from tea.

Step 1 Add 25 g of tea, 10 g of calcium carbonate and 250 cm^3 of water to a large beaker.

Step 2 Boil the mixture gently for 15 minutes.

Step 3 Filter the mixture.

Step 4 Separate caffeine from the aqueous mixture using solvent extraction, with dichloromethane as the solvent.

Step 5 Dry the solution of caffeine in dichloromethane obtained in *Step 4*.

Step 6 Remove the dichloromethane.

(Density of dichloromethane = 1.32 g cm^{-3})

a) i) Draw a diagram of the apparatus used in *Step 4*, labelling the organic and aqueous layers that would be observed at the end of *Step 4*.

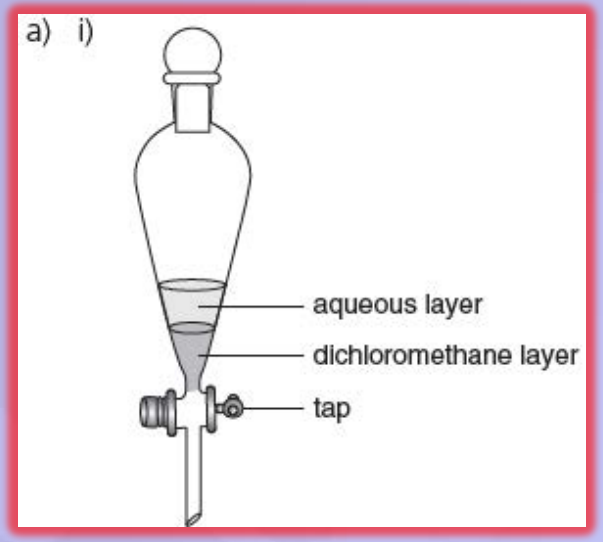
ii) Outline how to carry out the solvent extraction in *Step 4*, including the necessary safety precautions.

b) Name a suitable drying agent for drying the solution of caffeine in *Step 5*.

c) Suggest a suitable way to remove the dichloromethane.

52.10 Liquid-liquid extraction (p.55)

Practice 52.5 (continued)



a) ii) Shake the aqueous mixture with dichloromethane in a separating funnel.
Open the tap of the separating funnel regularly to release the pressure built up inside the funnel.
Allow the contents to settle into two layers.
Open the tap to allow the lower layer to drain into a flask.

b) Any one of the following:
- Anhydrous calcium chloride
- Anhydrous magnesium sulphate
- Anhydrous sodium sulphate

c) Distillation / fractional distillation

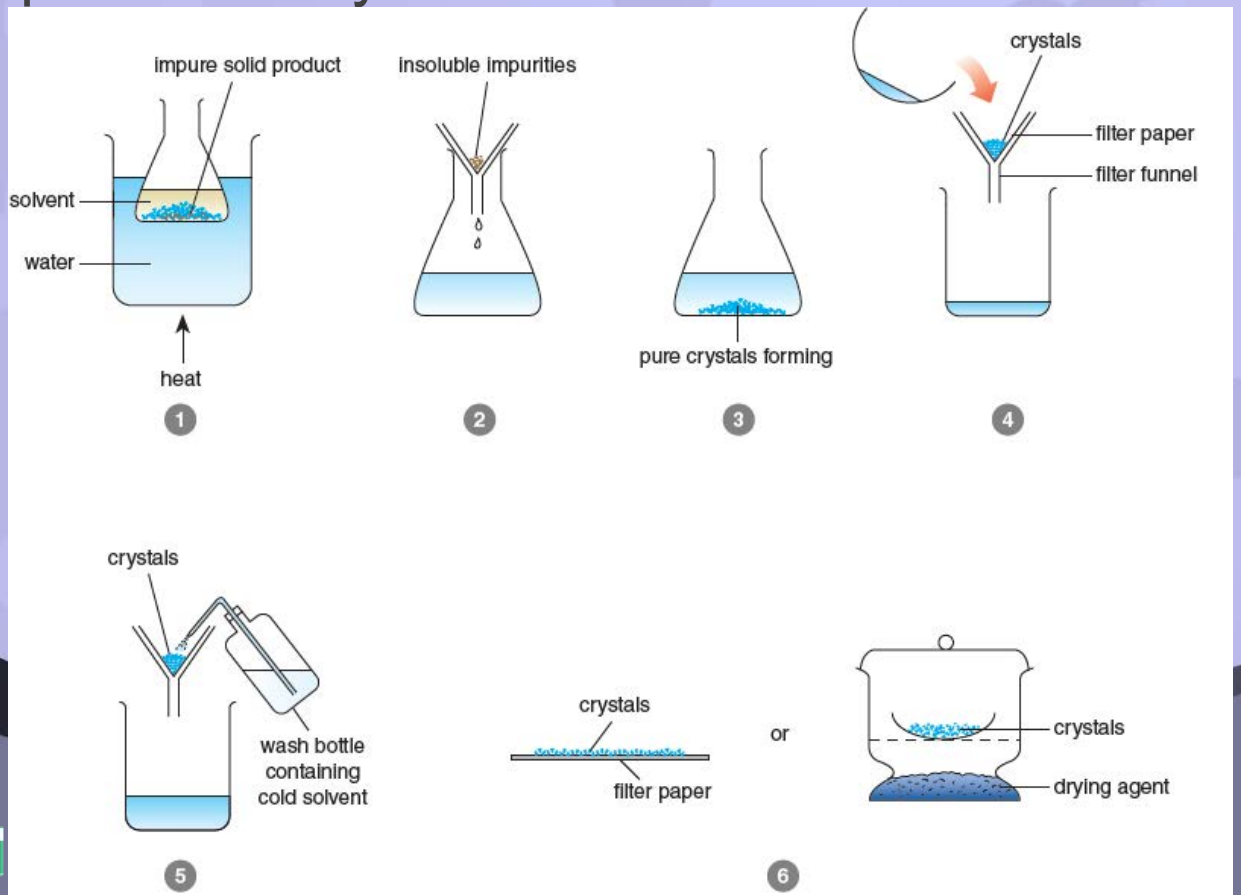
52.11 Recrystallisation (p.58)

- A solid product is removed from the reaction mixture by filtration. It is then purified by recrystallisation.
- A solvent has to be found in which the solid product is soluble when the solvent is hot, but insoluble (or very much less soluble) when the solvent is cold.
- Follow the steps below in the process.
  1 Dissolve the impure solid in the minimum volume of hot solvent.
  2 Filter the hot mixture to remove any insoluble impurities. Retain the filtrate.
  3 Leave the filtrate to cool until crystals form, leaving the soluble impurities in solution.
  4 Collect the crystals by filtration.

52.11 Recrystallisation (p.58)

5 Wash the crystals with a small amount of cold solvent to remove any of the filtrate which contains dissolved impurities.

6 Allow the solvent to evaporate from the crystals in the air or place the crystals in a desiccator.



Steps of recrystallisation

52.11 Recrystallisation (p.58)

- A minimum volume of hot solvent is used to dissolve the solid product, making a saturated solution.
- The solution is cooled and the solubility of the compound drops, causing it to recrystallise from the solution.
- Impurities remain dissolved in the solution.
- A minimum volume of hot solvent is used to ensure that as much of the solid product is obtained as possible.

52.11 Recrystallisation (p.58)

Practice 52.6

A crude sample of benzoic acid is purified by recrystallisation using water as a solvent. The steps are listed below.

Step 1 Dissolve the impure solid in the minimum volume of hot water.
Step 2 Filter the solution quickly.
Step 3 Allow the filtrate to cool.
Step 4 Filter the crystals formed from the remaining solution.
Step 5 Wash the crystals with a little cold water.
Step 6 Leave the crystals to dry.

Give reasons for each of the following steps.

a) The minimum volume of hot water is used in *Step 1*.

Any one of the following:
- Otherwise too much benzoic acid remains in the solution.
- If excess water is used, crystals might not form.

b) The filtrate is cooled in *Step 3* before the crystals are filtered off.

Yield of benzoic acid would be lower if the filtrate is warm. / Solubility of benzoic acid in a warm solvent is higher.

c) The crystals are washed with cold water in *Step 5*.

Wash away soluble impurities.

52.12 Chromatography (p.60)

- There are now a range of chromatography techniques that can be used to
  - separate and identify the components of a mixture of chemicals;
  - check the purity of a chemical;
  - identify the impurities in a chemical preparation;
  - purify a chemical product.

52.12 Chromatography (p.60)

Principles of chromatography

- All types of chromatography have a **stationary phase (固定相)** and a **mobile phase (流動相)**.
  - The stationary phase does not move and is normally a solid or a liquid supported on a solid.
  - The mobile phase does move, and is normally a liquid or a gas.
- Chromatography depends on the movement of the mobile phase through the stationary phase.
- A small amount of the mixture to be analysed is added to the stationary phase.
- The mobile phase moves through the stationary phase, carrying the components of the mixture with it.
- A mixture can be separated because the components distribute themselves differently between the stationary and mobile phases, according to their affinity for each phase.

52.13 Paper chromatography (PC) (p.61)

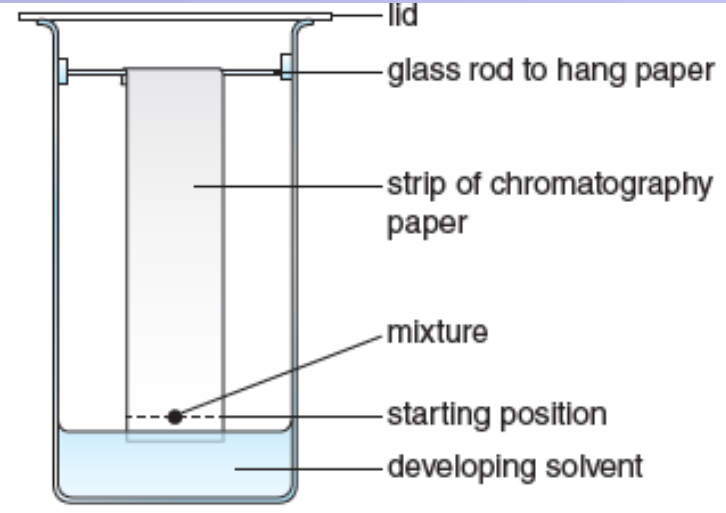
- In paper chromatography, the stationary phase is the water trapped in the fibres of the chromatography paper, and the mobile phase is a **developing solvent (展開劑)**.

Producing a paper chromatogram

- Dissolve the mixture to be analysed in a solvent. This solvent is usually not the same as the mobile phase.
  1 Spot the solution under test on a pencil line 1 cm from the base of the chromatography paper. Pencil is used because it will not run into the solvent.
  2 Add the developing solvent to a chromatography tank and covers it with a lid. Let the tank stand for a while to allow the air inside become saturated with the solvent vapour.

52.13 Paper chromatography (PC) (p.61)

3 Place the prepared paper in the tank, checking that the spot is above the level of the solvent.



A chromatography tank (the sample spot on the paper must be above thelevel of the solvent)

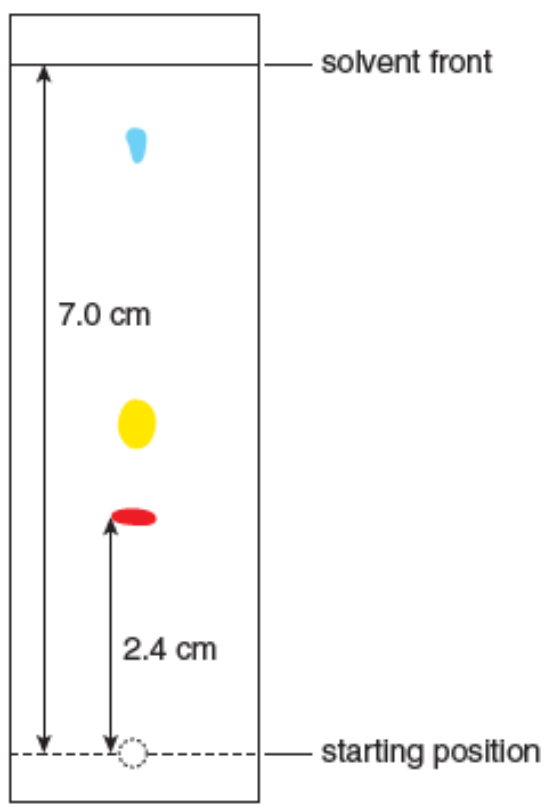
4 The solvent rises up the paper, carrying the components of the mixture with it.

5 Take the paper from the tank when the solvent gets near the top. Mark the position of the **solvent front (溶劑前沿)**. The resulting paper is called a **chromatogram (色層譜)**.

52.13 Paper chromatography (PC) (p.61)

Interpreting a chromatogram

- From the chromatogram shown below, the black ink contains three different dyes.

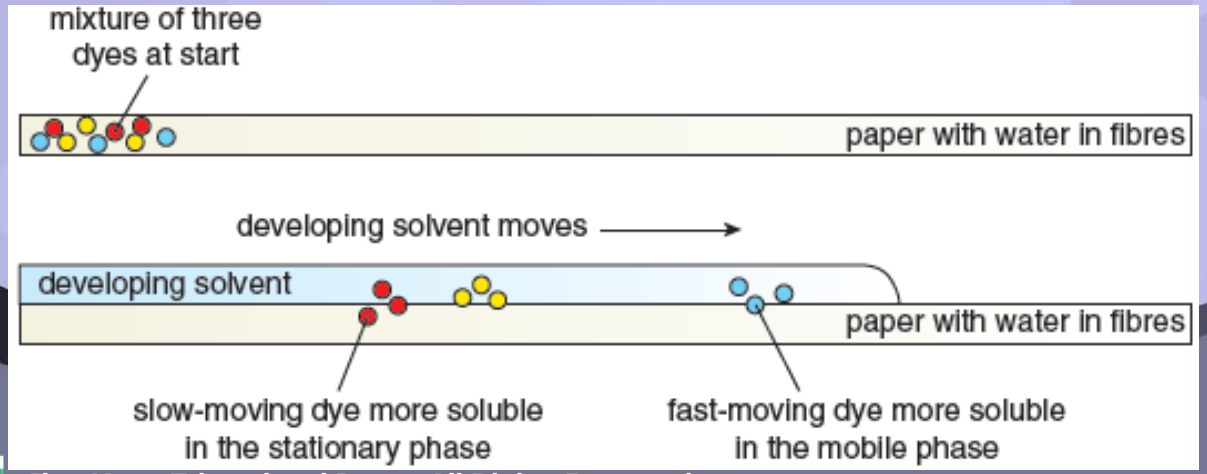


A paper chromatogram obtained when a black ink is analysed

52.13 Paper chromatography (PC) (p.61)

Interpreting a chromatogram

- Separation of dyes occurs because of the different relative solubilities of the dyes in the developing solvent (i.e. the mobile phase) and in the water in the fibres of the paper (i.e. the stationary phase).
- Dyes that are more soluble in the mobile phase than in the stationary phase move rapidly up the paper, while those that are more soluble in the stationary phase are not carried as far up the paper.



The principles of paper chromatography

52.13 Paper chromatography (PC) (p.61)

Identifying the component of a mixture by using retention factor

- The distance a component travels relative to the solvent is called the **retention factor (比移值)** (symbol: R_f).

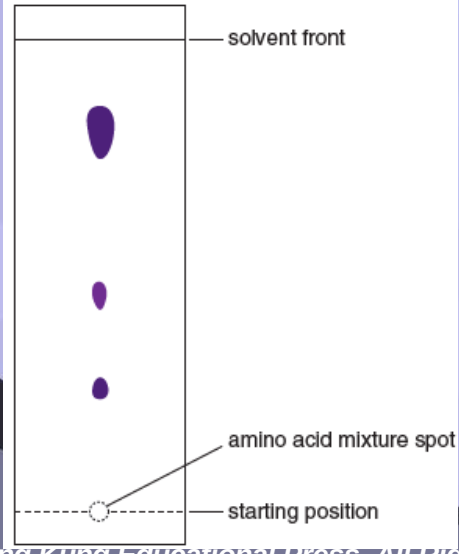
$$R_f = \frac{\text{distance travelled by the component}}{\text{distance travelled by the solvent}}$$

- Data tables list retention factors for a wide variety of chemicals, using particular solvents under stated conditions. These allow the identification of unknown components by comparison with these retention factors.
- Spots of solutions of chemicals suspected of being present in the unknown mixture can be run on the same chromatography paper and a direct comparison can be made.

52.13 Paper chromatography (PC) (p.61)

Making colourless components on a chromatogram visible

- Coloured components on a chromatogram are easy to see. Colourless components can be made visible by using ultraviolet radiation or by spraying with a chemical reagent that will react with the components to form coloured products.
- A general visualising agent for most carbon compounds is iodine. When the paper is placed in a tank containing iodine vapour, the iodine is absorbed by the carbon compounds in the spots, turning them brown.



The components of an amino acid mixture are visible after spraying with ninhydrin

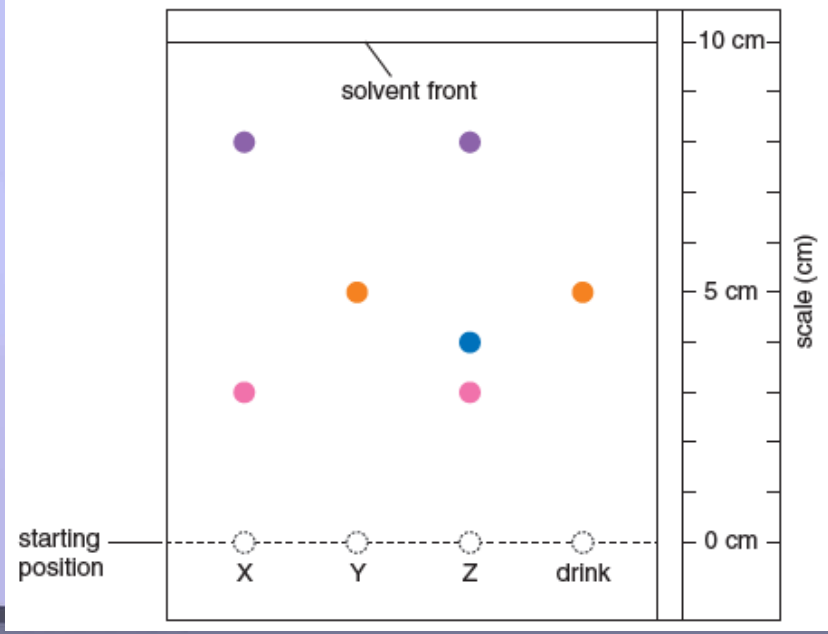
Using paper chromatography for the separation and identification of amino acids ***Ref.***

52.13 Paper chromatography (PC) (p.61)

Practice 52.7

Some food colourings are a mixture of coloured substances. Paper chromatography can be used to separate the coloured substances in food colourings.

A student carried out an experiment to test which food colouring was present in a drink. Samples of three food colourings (X, Y and Z) were also used. The chromatogram obtained is shown below.



52.13 Paper chromatography (PC) (p.61)

Practice 52.7 (continued)

a) Name the mobile phase and stationary phase in this paper chromatography.

Mobile phase: developing solvent
Stationary phase: water trapped in the fibres of the chromatography paper

b) Describe the principle underlying the separation of coloured substances in the food colourings by paper chromatography.

Separation of coloured substances in the food colouring occurs because of the different relative solubilities of the coloured substances in the mobile phase and in the stationary phase.

c) State all the food colourings that contain more than one coloured substance. X and Z

d) Food colouring X is banned.
Explain how the student could tell that the drink tested did NOT contain the banned food colouring X.

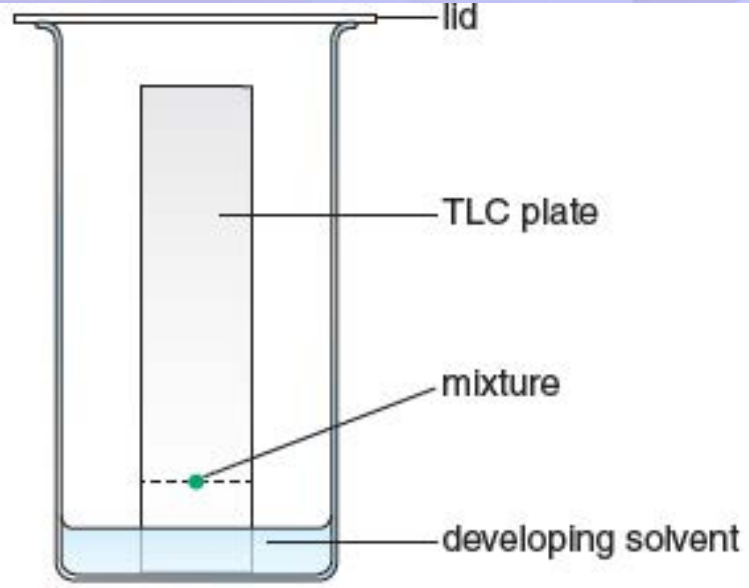
The drink did not have spot(s) corresponding to spot(s) of X.

e) Calculate the R_f value for the coloured substance in food colouring Y.

$$R_f = \frac{5\text{ cm}}{10\text{ cm}} = 0.5$$

52.14 Thin layer chromatography (TLC) (p.66)

- Thin layer chromatography uses a thin layer of either alumina (Al_2O_3) or silica gel (SiO_2), which is supported on a glass or plastic plate. The thin layer is the stationary phase.
- The sample is spotted onto the plate and placed in a developing solvent. The container is covered with a lid.



The apparatus used for thin layer chromatography (TLC)

52.14 Thin layer chromatography (TLC) (p.66)

- Both alumina and silica gel can adsorb chemicals onto their surfaces.
- Components in the mixture separate because
  - they differ in the extent to which they are soluble in the mobile phase;
  - they are adsorbed by the stationary phase to different extents.
- The better adsorbed components travel more slowly up the TLC plate.

52.14 Thin layer chromatography (TLC) (p.66)

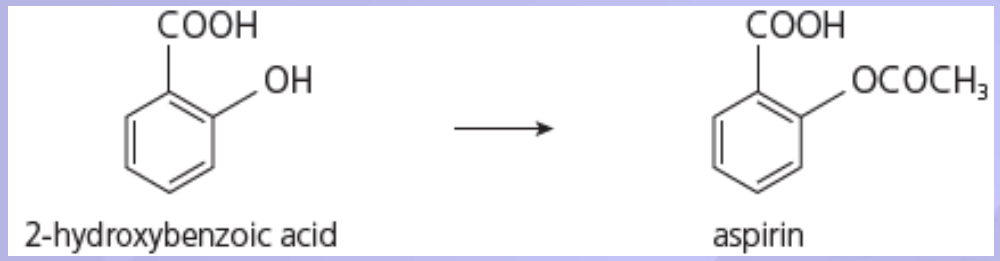
- Thin layer chromatograms are analysed by calculating the value for the retention factor R_f for each component.
- Each component can be identified by comparing its R_f value with known values recorded using the same solvent system and stationary phase.
- The separated components can be recovered by scraping the areas containing the spots into a suitable solvent.
- Thin layer chromatography is quicker than paper chromatography and can be used on smaller samples, making it useful in forensic science, where it can be used to identify drugs and explosive residues.

52.14 Thin layer chromatography (TLC) (p.66)

Practice 52.8

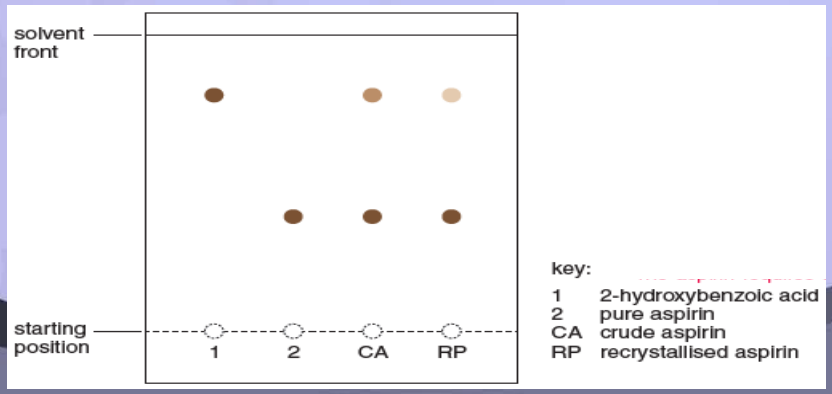
Identifying the major components of a painkiller by thin layer chromatography *Ref.*

A student prepared aspirin from 2-hydroxybenzoic acid in the laboratory.



The crude aspirin was purified by recrystallisation. The student investigated the composition of both the crude and recrystallised aspirin using thin layer chromatography (TLC).

Separate samples of 2-hydroxybenzoic acid, pure aspirin, the crude aspirin and the recrystallised aspirin were applied to a chromatography plate. The chromatography was run.



52.14 Thin layer chromatography (TLC) (p.66)

Practice 52.8 (continued)

a) Describe how the student would carry out the experiment to produce the chromatogram.

Spot the samples onto a plate covered with a thin layer of either alumina or silica gel.
Place the plate in a tank containing a developing solvent.
Allow the developing solvent to rise up the plate, carrying the components of the samples with it.
Remove the plate from the tank when the solvent gets near the top of the plate.
Dry the plate.

b) Explain why the spots of 2-hydroxybenzoic acid and pure aspirin travel different distances up the chromatogram.

2-hydroxybenzoic acid and pure aspirin
- differ in the extent to which they are soluble in the developing solvent (mobile phase);
- are adsorbed by the alumina or silica gel (stationary phase) to different extents.

c) Analyse the chromatogram.

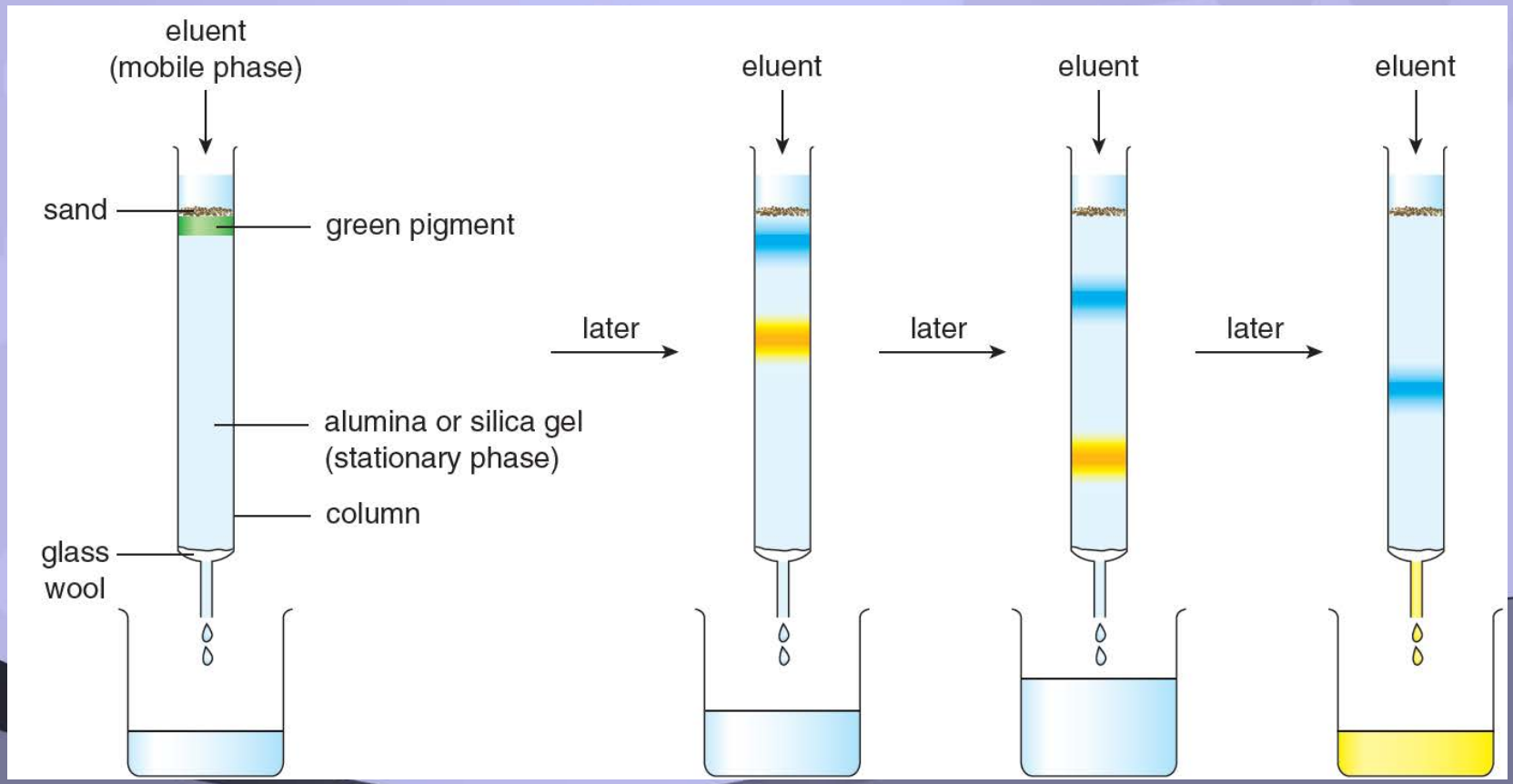
The crude aspirin contains both aspirin and unreacted 2-hydroxybenzoic acid.
The recrystallised aspirin contains less unreacted 2-hydroxybenzoic acid (the spot is less intense) compared with crude aspirin.
The aspirin requires further purification.

52.15 Column chromatography (CC) (p.68)

- Column chromatography uses a powder, such as alumina or silica gel as the stationary phase. This is packed into a narrow tube — the column.
- The mixture to be separated is dissolved in a suitable solvent and placed on the top of the column.
- Fresh solvent is added to the column. The solvent moves through the column and the components in the mixture separate depending on their different solubilities in the solvent (mobile phase) and their different adsorption by the stationary phase.
- The process is called **elution (洗提)** and the solvent added is called the **eluent (洗提液)**.

52.15 Column chromatography (CC) (p.68)

- The separation of two pigments in a green pigment. Add eluent to the column until the bands have been eluted and collect each component separately.



52.15 Column chromatography (CC) (p.68)

- For colourless components, add fluorescent dyes to them and you can see their movement under ultraviolet light.
- Column chromatography has the advantage that fairly large amounts can be separated and collected. It is not used to identify the components of a mixture.
- The stationary and mobile phases, and the applications of the three types of chromatography.

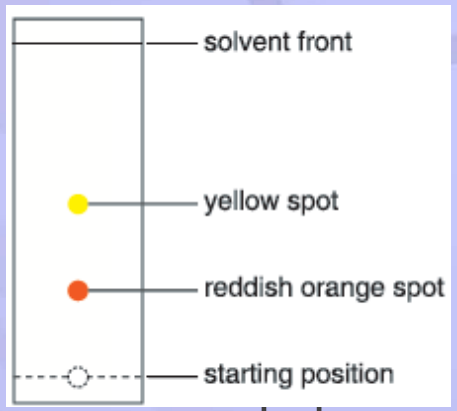
Type of chromatography	Stationary phase	Mobile phase	Application	
			Separation and identification	Separation for further use
Paper	water in the paper fibres	liquid solvent	✔	
Thin layer	thin layer of alumina or silica gel coated onto a plate	liquid solvent	✔	
Column	alumina or silica gel in vertical glass column	liquid solvent		✔

52.15 Column chromatography (CC) (p.68)

Q (Example 52.3)

The main pigments in a brand of tomato paste are lycopene (reddish orange) and β-carotene (yellow). In order to isolate lycopene from the tomato paste, thin layer chromatography (TLC) and column chromatography were carried out.

a) The result of TLC is shown below:



Explain why the two pigments have different R_f values.

b) With reference to the result of TLC, explain whether the second-collected coloured fraction in the column chromatography is lycopene or β-carotene, if the same stationary phase and mobile phase are used.

52.15 Column chromatography (CC) (p.68)

Q (Example 52.3) (continued)

A

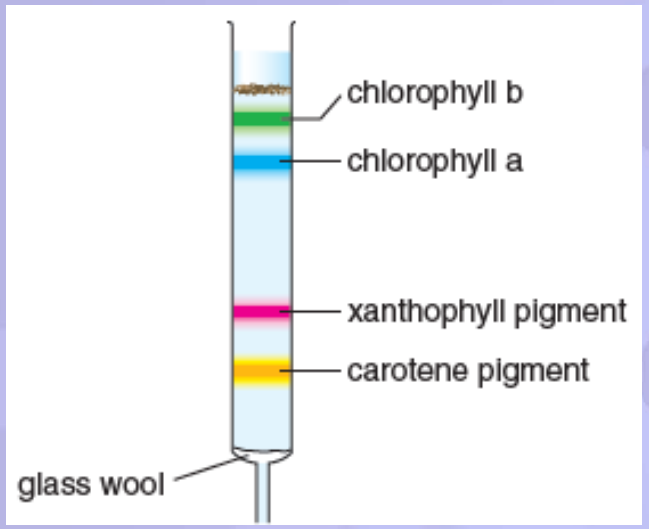
a) The two pigments have different solubilities in the mobile phase and different adsorption by the stationary phase.
The better adsorbed reddish orange pigment travels up more slowly.

b) Lycopene (the reddish orange pigment) is the second-collected coloured fraction.
The better adsorbed lycopene takes a longer time to reach the bottom of the column.

52.15 Column chromatography (CC) (p.68)

Practice 52.9

1 The diagram shows the separation of pigments in a plant extract by column chromatography using hexane as the eluent.



a) The separation depends on the different solubilities of the components in hexane and the different adsorption of the components by the stationary phase.

b) If the eluent is changed, the solubilities of the components in the eluent may change, and hence more, less or even no separation could occur. The order in which the components appears in column may also change.

c) Chlorophyll b
The most adsorbed chlorophyll b travels most slowly up the TLC plate.

a) Briefly describe the principle underlying the separation of the pigments by using column chromatography.

b) Explain how changing the eluent would affect the separation process.

c) In another experiment, the pigments in plant extract are separated by using thin layer chromatography, using the same stationary phase and the same mobile phase. Which of the pigments would have the smallest R_f value? Explain your answer.

52.15 Column chromatography (CC) (p.68)

Practice 52.9 (continued)

2 Rose petals contain a useful organic compound X. X can dissolve in warm hexane, and can be extracted from the petals by using hexane.

X obtained from the extraction may contain other organic impurities. Suggest a method for separating X from these impurities.

Column chromatography / thin layer chromatography

52.16 Choosing appropriate methods for separating substances in a mixture (p.72)

- It is important that you choose the appropriate method for separating the substances in a mixture.
- For example, 1-chloropentane can be prepared by adding excess phosphorus pentachloride to pentan-1-ol:

$$CH_3(CH_2)_3CH_2OH(l) + PCl_5(s) \longrightarrow CH_3(CH_2)_3CH_2Cl(l) + HCl(g) + POCl_3(l)$$

- Phosphorus trichloride oxide, $POCl_3$, has a boiling temperature of 105 °C, which is very similar to that of 1-chloropentane (108 °C). Therefore, it is not possible to separate the two by distillation of the reaction mixture.
- Liquid-liquid extraction is needed for extracting 1-chloropentane from the reaction mixture.

52.16 Choosing appropriate methods for separating substances in a mixture (p.72)

Q (Example 52.4)

A student proposed using simple distillation to separate hex-1-ene from a mixture of hex-1-ene and water.
The proposed method was considered inappropriate.
Outline a suitable procedure for separating hex-1-ene from a mixture of hex-1-ene and water. Explain your answer.
Some data of hex-1-ene and water are given in the table below.

Data	hex-1-ene	water
Boiling point (°C)	63	100
Density (g cm^{-3})	0.68	1.0

52.16 Choosing appropriate methods for separating substances in a mixture (p.72)

Q (Example 52.4) (continued)

A

Hex-1-ene and water are immiscible liquids. The mixture can be separated by using a separating funnel.

Place the mixture in a separating funnel. Two layers appear, with the denser water forming the lower layer.

Allow the layers to settle. Run off and dispose of the water layer.

Collect the hex-1-ene layer.

52.16 Choosing appropriate methods for separating substances in a mixture (p.72)

Practice 52.10

1 A liquid mixture consists of two organic compounds X and Y. The boiling point of X is 79.3 °C while that of Y is 82.6 °C. Explain why fractional distillation is NOT a suitable method to separate X from the mixture.

Their boiling points are too close.

2 Outline how pentane can be obtained from a mixture of pentane, decane and water by physical methods. (Boiling points: pentane = 36 °C, decane = 174 °C, water = 100 °C)

Use a separating funnel to remove water (the lower liquid layer) from the mixture.
The upper layer remaining in the funnel contains pentane and decane.
Carry out distillation on the upper layer.
Pentane distils off first.

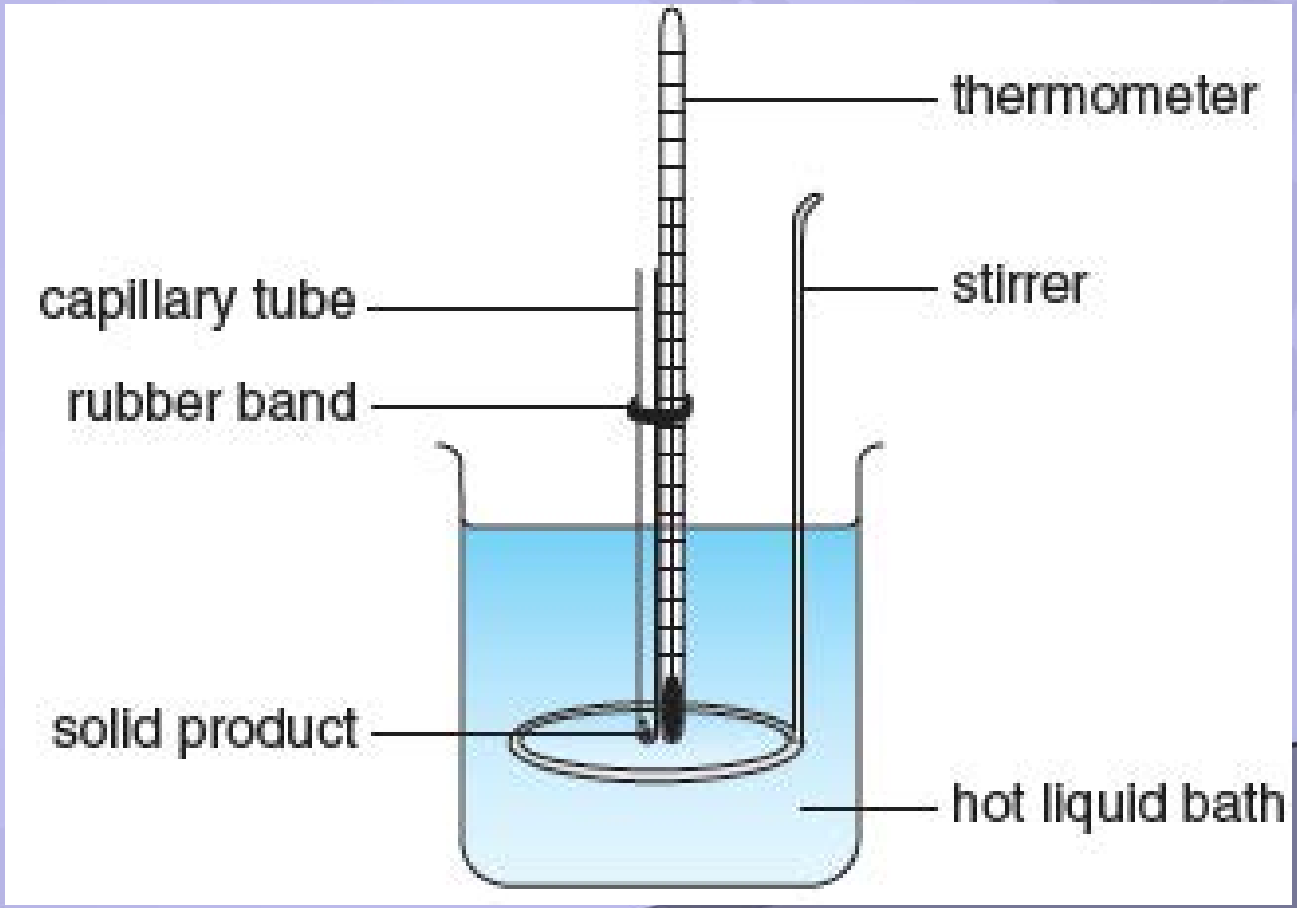
52.17 Checking the purity of a product (p.73)

- A pure substance melts and boils over a very small temperature range while a mixture does not.
- Impurities tend to lower the melting point of a substance and raise its boiling point.
- After the separation and purification of the products from organic preparations, you can check the purity of a solid product by determining its melting point, and the purity of a liquid product by determining its boiling point.

52.17 Checking the purity of a product (p.73)

Melting point determination

- The apparatus for measuring the melting point of a solid product.



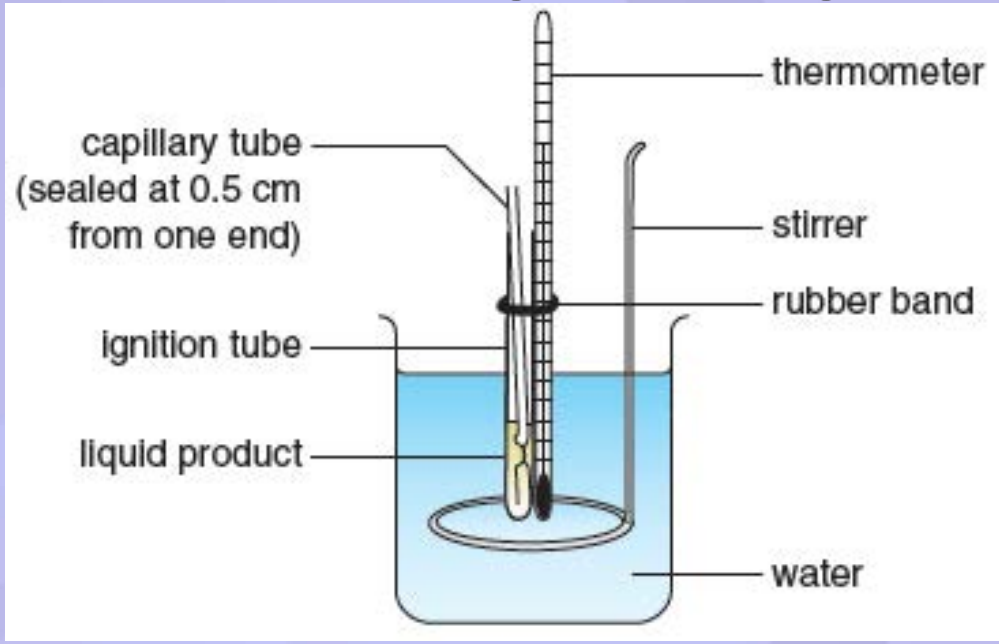
52.17 Checking the purity of a product (p.73)

- The method is as follows:
  - Insert some of the solid product into a capillary tube and then attach the tube open end upwards to a thermometer with a rubber band.
  - Place the thermometer into a bath of liquid. The liquid must boil at a higher temperature than the melting temperature of the solid product being tested.
  - Slowly heat the liquid bath with constant stirring. Notice the temperature at which the solid product starts and finishes melting.
- Compare the experimental value to the published value for the melting point. The presence of impurities in a substance broadens its melting temperature range. A pure compound will melt within 0.5 °C of the true melting point.

52.17 Checking the purity of a product (p.73)

Boiling point determination

- The apparatus for measuring the boiling point of a liquid product.



- If a large amount of the sample is available, the boiling point can be measured using simple distillation apparatus.

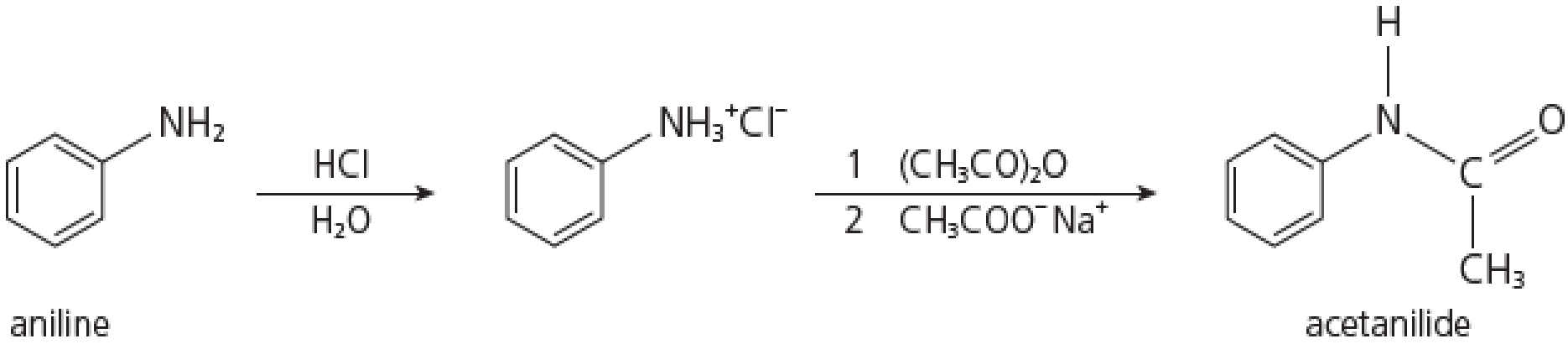
52.17 Checking the purity of a product (p.73)

- A pure liquid product will boil over a very small range of temperature, whereas an impure one will boil over a considerable range.
- The method is as follows:
  - Place a small amount of the liquid product in the ignition tube and, using a rubber band, attach it to the thermometer.
  - Insert a capillary tube sealed at 0.5 cm from one end into the liquid.
  - Clamp the thermometer in the beaker of water.
  - Slowly heat the water, stirring all the time. When the stream of bubbles coming out of the capillary tube is rapid and continuous, stop heating.
  - Allow the beaker of water to cool, stirring continuously. The bubbles slow down. The boiling point of the liquid product is reached when the bubbles stop.

52.17 Checking the purity of a product (p.73)

Practice 52.11

Acetanilide can be synthesised from aniline according to the following reaction scheme:



The crude solid product is separated from the reaction mixture.

52.17 Checking the purity of a product (p.73)

Practice 52.11 (continued)

a) Suggest how you can purify the crude solid product by using recrystallisation from an ethanol-water mixture.

Dissolve the crude solid product in the minimum volume of hot solvent.
Filter the hot mixture.
Leave the filtrate to cool to obtain acetanilide.
Filter off the acetanilide and wash with a small amount of cold solvent.

b) Suggest how you can verify whether the recrystallised sample of acetanilide is pure.

Any one of the following:

- Determine the melting point of the product and compare with the published value for the melting point.
- Determine the melting point of the product. A sharp melting point indicates that the product is pure.

Key terms (p.76)

2,4-dinitrophenylhydrazine	2,4-二硝基苯肼	column chromatography	柱色層法
Tollens' reagent	托倫斯試劑	developing solvent	展開劑
liquid-liquid extraction	液液萃取	solvent front	溶液前沿
stationary phase	固定相	chromatogram	色層譜
mobile phase	流動相	retention factor	比移值
paper chromatography	紙色層法	elution	洗提
thin layer chromatography	薄層色層法	eluent	洗提液

Summary (p.77)

1 The table below summarises results of chemical tests for some functional groups.

Functional group	Test	Observation(s)
–C=C–	add aqueous bromine to carbon compound slowly	yellow-brown aqueous bromine becomes colourless quickly
–OH (primary and secondary alcohols)	warm with acidified $K_2Cr_2O_7$(aq)	colour change from orange to green
	warm with acidified $KMnO_4$(aq)	colour change from purple to colourless (or very pale pink)
–CHO	treat with 2,4-dinitrophenylhydrazine	a bright red, orange or yellow precipitate forms
	warm with Tollens' reagent	silver mirror forms
	warm with acidified $K_2Cr_2O_7$(aq)	colour change from orange to green
$\diagdown\!\!\diagup C{=}O$	treat with 2,4-dinitrophenylhydrazine	a bright red, orange or yellow precipitate forms
–COOH	mix with $NaHCO_3$(aq)	effervescence occurs; gas produced turns limewater milky
	warm with ethanol in the presence of concentrated sulphuric acid	a sweet, fruity smell is detected

Summary (p.77)

2 The table below summarises common separation and purification methods for liquid and solid products.

Type of product	Method	Remark(s)
Liquid product	distillation	• If a crude liquid product has a much lower boiling temperature than other substances in the reaction mixture, separate it by distillation.
	fractional distillation	• Separate mixtures of liquids with close boiling points by fractional distillation.
	liquid-liquid extraction	• Use a solvent to extract the desired liquid product from the reaction mixture.
Solid product	recrystallisation	• A solvent has to be found in which the solid product is soluble when the solvent is hot, but insoluble when the solvent is cold.
	chromotography	• This method involves a stationary phase and a mobile phase. • A mixture can be separated because the components distribute themselves differently between the stationary and mobile phases, according to their affinity for each phase.

Summary (p.77)

3 The table below summarises the stationary and mobile phases, and the working principle of three types of chromatography.

Type of chromatography	Stationary phase	Mobile phase	Working principle
Paper	water in the paper fibres	liquid solvent	Separation occurs because each component has different solubilities in the mobile phase and in the stationary phase.
Thin layer	thin layer of alumina or silica gel coated onto a plate	liquid solvent	Separation occurs because each component has a different solubility in the mobile phase and a different adsorption by the stationary phase.
Column	alumina or silica gel in vertical glass column	liquid solvent	

Summary (p.77)

4 As long as the same solvent and type of chromatographic paper are used, a component in a mixture can be identified from its retention factor R_f.

$$R_f = \frac{\text{distance travelled by the component}}{\text{distance travelled by the solvent}}$$

5 The purity of a solid product may be checked by its melting point and that of a liquid product by its boiling point.

Unit Exercise (p.79)

Note: Questions are rated according to ascending level of difficulty (from 1 to 5):

 question targeted at level 3 and above;

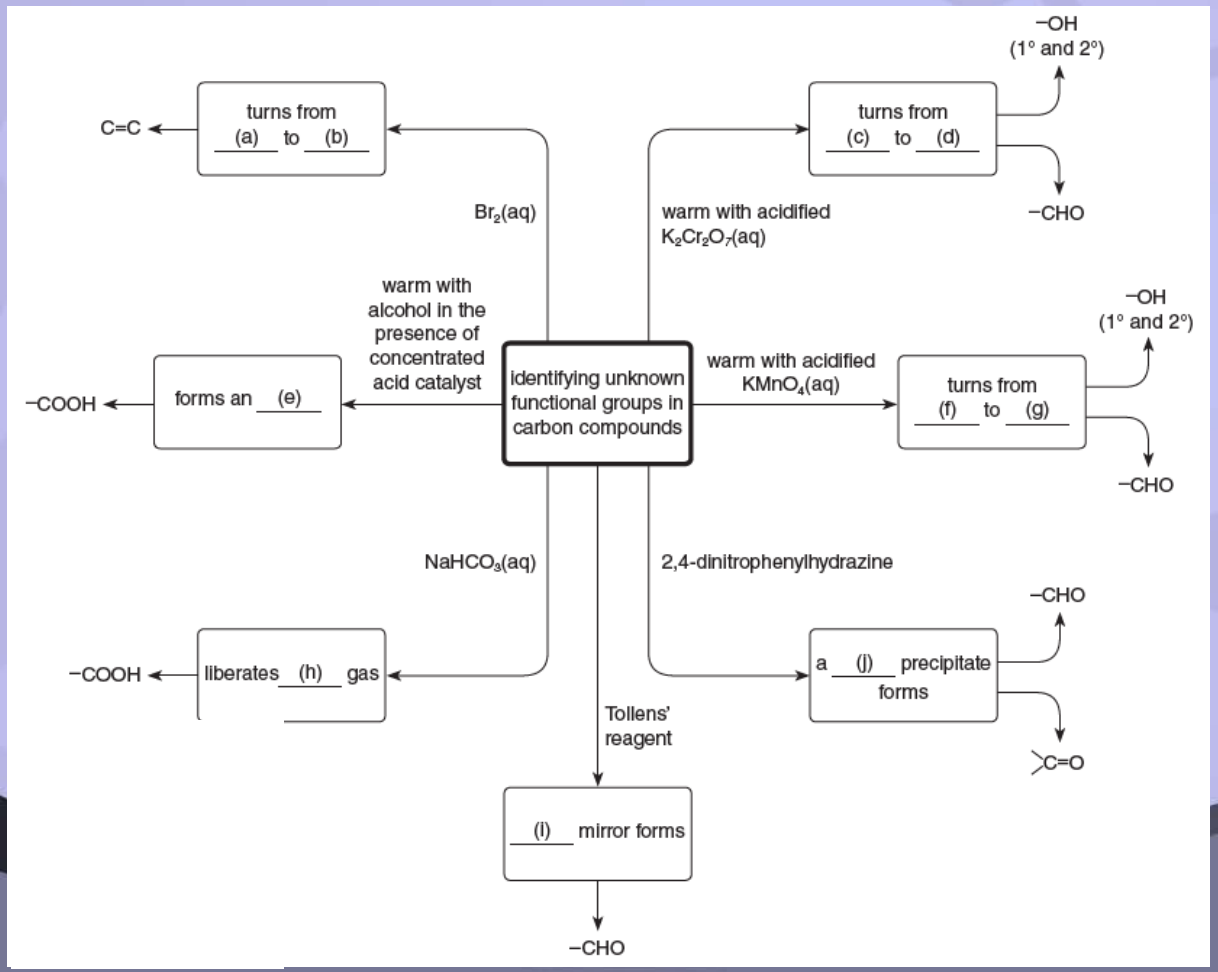
 question targeted at level 4 and above;

 question targeted at level 5.

Unit Exercise (p.79)

PART I KNOWLEDGE AND UNDERSTANDING

1 Complete the following concept maps.

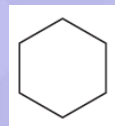


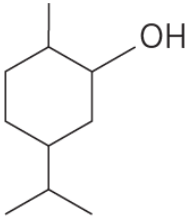
a) yellow-brown
b) colourless
c) orange
d) green
e) ester
f) purple
g) colourless
h) carbon dioxide
i) silver
j) bright red / orange / yellow

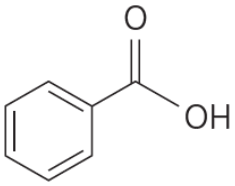
Unit Exercise (p.79)

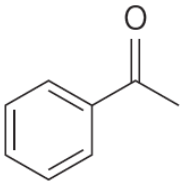
PART II MULTIPLE CHOICE QUESTIONS

2 Which of the following compounds would form an orange precipitate with 2,4-dinitrophenylhydrazine?

A 

B 

C 

D 

Answer: D

Unit Exercise (p.79)

3 Compound X is treated with warm acidified aqueous solution of potassium dichromate. The resulting product gives an orange precipitate with 2,4-dinitrophenylhydrazine but no observable change with Tollens' reagent.

What could X be?

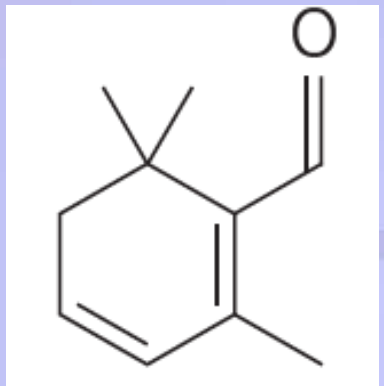
A Pentan-1-ol
B Pentan-2-ol
C Pentanal
D 2-methylbutan-2-ol

Explanation:
X is a secondary alcohol as it gives a ketone upon oxidation.

Answer: B

Unit Exercise (p.79)

4 Safranal is one of the substances that contributes to the aroma of saffron.



Separate samples of safranal were tested with aqueous bromine, 2,4-dinitrophenylhydrazine and Tollens' reagent.

Unit Exercise (p.79)

4 (continued)

What are the final observations when safranal is tested with each of those reagents?

	Aqueous bromine	2,4-dinitrophenylhydrazine	Tollens' reagent
A	yellow-brown solution	orange solution	yellow solution
B	colourless solution	orange precipitate	silver mirror
C	yellow-brown solution	orange solution	silver mirror
D	colourless	orange precipitate	yellow solution

Explanation:
Safranal is an aldehyde with a carbon-carbon double bond.

Answer: B

Unit Exercise (p.79)

5 Consider the two carbon compounds X and Y:

$CH_3CH(OH)CH_2CHO$	$CH_3COCH_2CH_2OH$
X	Y

Which of the following reagents can be used to distinguish between them?

A Acidified aqueous solution of potassium dichromate
B Dilute sulphuric acid
C Phosphorus pentachloride
D Tollens' reagent

Answer: D

Explanation:
X gives a silver mirror when warmed with Tollens' reagent while Y does not.

Unit Exercise (p.79)

6 For which purpose is distillation used?

A To allow a liquid to boil without the loss of vapour
B To purify a liquid product
C To remove an involatile impurity
D To allow further reaction without the loss of product

(OCR Advanced Subsidiary, Chem. B (Salters), H033/01, May 2017, 5)

Answer: B

Unit Exercise (p.79)

7 In the first stage of the synthesis of methyl 3-nitrobenzoate, methyl benzoate, $C_6H_5COOCH_3$, is prepared by the reaction of benzoic acid with methanol in the presence of concentrated sulphuric acid. When the reaction is complete, the sulphuric acid is neutralized by the addition of aqueous sodium carbonate. The simplest way of obtaining the impure methyl benzoate from this mixture will be

A refluxing.
B solvent extraction.
C filtration.
D recrystallisation.

Answer: B

(Edexcel IAL, Advanced, Unit 5, WCH05/01, Jun. 2014, 19)

Unit Exercise (p.79)

8 Ninhydrin is used in thin layer chromatography to help with the identification of amino acids. This is because the ninhydrin

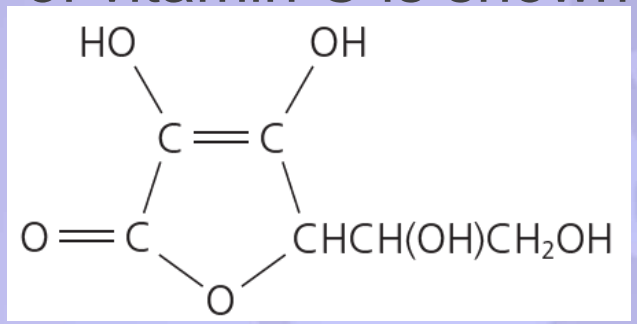
A reacts with amino acids to form a compound which has an intense colour.
B reacts with amino acids to form compounds each of which has a characteristic colour.
C increases the separation of the amino acids on the chromatogram.
D ensures that the mobile phase maintains a nearly constant pH for all the amino acids.

(Edexcel Advanced GCE, Unit 5, 6CH05/01R, Jun. 2014, 16)

Answer: A

Unit Exercise (p.79)

9 The structure of vitamin C is shown below.



Which of the following properties is vitamin C likely to have?

(1) It is soluble in water.
(2) It decolourises aqueous bromine rapidly.
(3) It gives a silver mirror with Tollens' reagent.

A (1) and (2) only
B (1) and (3) only
C (2) and (3) only
D (1), (2) and (3)

Explanation:
(3) Vitamin C does NOT contain an aldehyde group. Hence it would NOT give a silver mirror with Tollens' reagent.

Answer: A

Unit Exercise (p.79)

10 In which of the following reactions are the carbon compounds oxidised?

(1) $CH_3CH_2{=}CH_2$ + acidified aqueous solution of potassium permanganate
(2) CH_3CH_2CHO + Tollens' reagent
(3) CH_3COCH_3 + 2,4-dinitrophenylhydrazine reagent

A (1) and (2) only
B (1) and (3) only
C (2) and (3) only
D (1), (2) and (3)

Answer: A

Explanation:

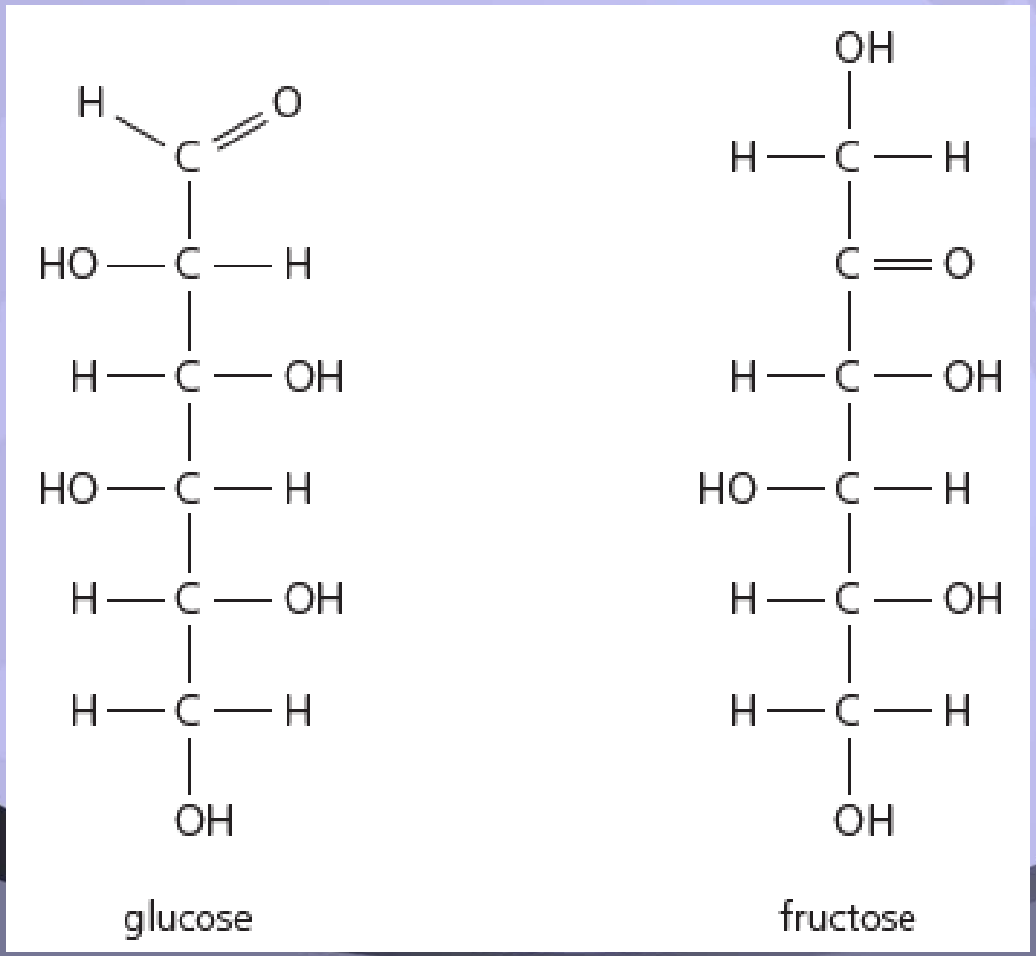
(1) In the reaction between $CH_3CH_2{=}CH_2$ and acidified $KMnO_4(aq)$, $KMnO_4(aq)$ is reduced to $Mn^{2+}(aq)$.

(2) In the reaction between CH_3CH_2CHO and Tollens' reagent, silver ion is reduced to silver.

Unit Exercise (p.79)

PART III STRUCTURED QUESTIONS

11 The structures of glucose and fructose are shown below.



Unit Exercise (p.79)

11 (continued)

a) Glucose and fructose are 'structural isomers'. What is meant by this term?

Structural isomers are two or more compounds that have the same molecular formula but the atoms are bonded together in different orders (i.e. with different structures). (1)

b) State what will be observed when glucose is warmed with Tollens' reagent;

i) treated with 2,4-dinitrophenylhydrazine.

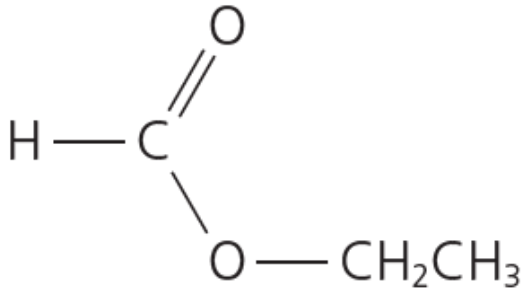
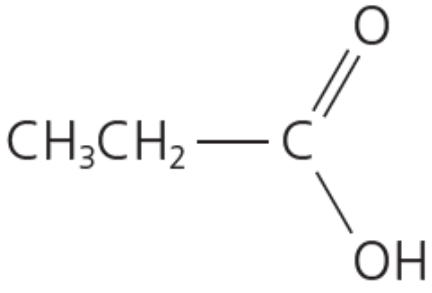
A silver mirror forms on the inside of the reaction vessel. (1)

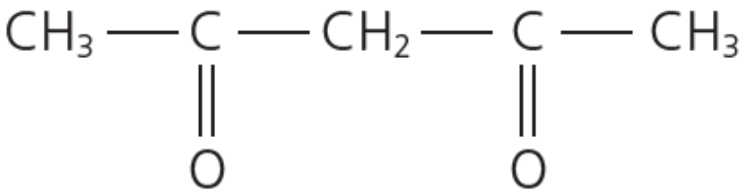
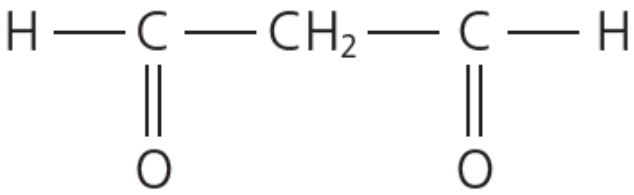
ii) treated with 2,4-dinitrophenylhydrazine.

A bright red / orange / yellow precipitate forms.

Unit Exercise (p.79)

12 Suggest a chemical test to distinguish one compound from the other in each of the following pairs. Your answer should include the reagents used and the expected observations for both compounds.

a)  and 

b)  and 

Unit Exercise (p.79)

12 (continued)

a) Any one of the following:

- Mix each compound separately with $NaHCO_3(aq)$. (1)
  CH_3CH_2COOH gives effervescence.
  $HCOOCH_2CH_3$ gives no observable change. } (1)
- Warm each compound separately with ethanol in the presence of concentrated H_2SO_4. (1)
  CH_3CH_2COOH gives an ester with a sweet fruity smell.
  $HCOOCH_2CH_3$ gives no observable change. } (1)

b) Any one of the following:

- Warm each compound separately with Tollens' reagent. (1)
  $CHOCH_2CHO$ gives a silver mirror.
  $CH_3COCH_2COCH_3$ gives no observable change. } (1)
- Warm each compound separately with acidified $K_2Cr_2O_7(aq)$. (1)
  $CHOCH_2CHO$ gives a colour change from orange to green.
  $CH_3COCH_2COCH_3$ gives no observable change. } (1)

Unit Exercise (p.79)

13 a) Suggest a chemical test to show the presence of each of the following:

i) HCl(g)

ii)  functional group

b) Which of the following chemicals is most suitable for drying ethyl ethanoate?
anhydrous magnesium sulphate,
concentrated sulphuric acid,
solid sodium hydroxide

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).

(HKDSE, Paper 2, 2014, 3(a)(i)–(ii))

Unit Exercise (p.79)

14 In an experiment, propanal is warmed with Tollens' reagent.

a) State the expected observation.

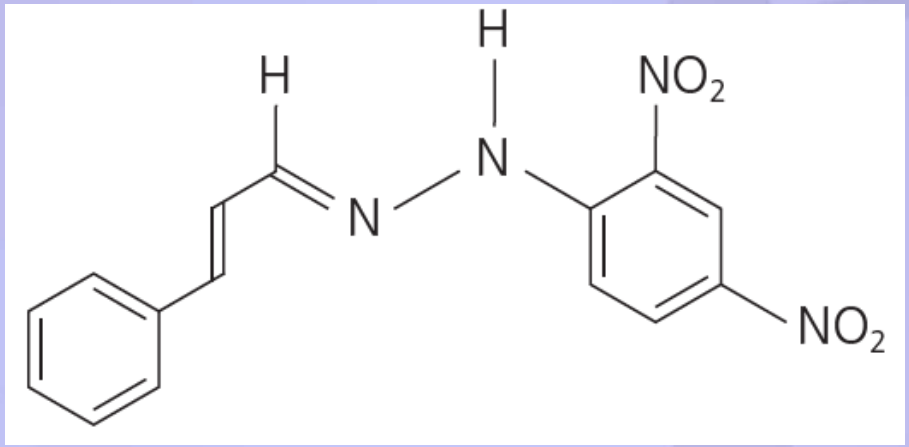
A silver mirror forms on the inside of the reaction vessel. (1)

b) Draw the structure of the organic product formed.

$CH_3CH_2COO^-$ (1)

Unit Exercise (p.79)

15 An organic compound X reacts with 2,4-dinitrophenylhydrazine to form a yellow solid Z. The structure of Z is shown below:



Given that the molecular formula of X is C_9H_8O, draw the structure of X.

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).

(HKDSE, Paper 2, 2017, 1(a)(iii))

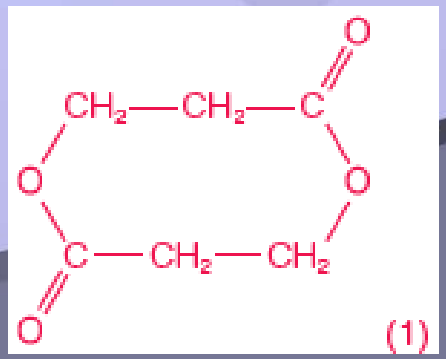
Unit Exercise (p.79)

16 The molecular formula of X is $C_3H_6O_3$. The carbon atoms in X are bonded directly to one another.
X gives effervescence when shaken with $Na_2CO_3(aq)$.
When X is heated under reflux with acidified $K_2Cr_2O_7(aq)$, the product, Y, gives no observable change with 2,4-dinitrophenylhydrazine.

a) Give the structural formula of X. $HOCH_2CH_2COOH$ (1)

b) Give the structural formula of Y. $HOOCCH_2COOH$ (1)

c) When X is warmed with a little concentrated sulphuric acid, a small amount of a cyclic compound, Z, is formed. Z has the molecular formula $C_6H_8O_4$.
Draw the structure of Z.



(1)

Unit Exercise (p.79)

17 Alcohol X is heated with acidified $K_2Cr_2O_7(aq)$ under reflux. X is oxidised.

a) State the colour change observed. From orange to green (1)

b) The oxidation results in the formation of either a ketone or a carboxylic acid.

Suggest a chemical test to show that the oxidation product is a

i) ketone;

ii) carboxylic acid.

Give your expected observation in each case.

i) Mix the product with 2,4-dinitrophenylhydrazine. (1)
A bright red / orange / yellow precipitate forms. (1)

ii) Any one of the following:

- Mix the product with $NaHCO_3(aq)$. (1)
  Effervescence occurs. (1)
- Warm the product with ethanol in the presence of concentrated H_2SO_4. (1)
  An ester with a sweet fruity smell is formed. (1)

c) Tests show that X is oxidised to a ketone. What type of alcohol is X? Secondary alcohol (1)

Unit Exercise (p.79)

18 Four unlabelled reagent bottles each contains one of the colourless liquids listed below:

$CH_3CH_2CH_2CH_2OH$

$CH_3CH_2COOCH_3$

$CH_3CH_2CH_2COOH$

$CH_2=CHCH_2COOH$

Suggest chemical tests to distinguish the four liquids.

Test with $NaHCO_3(aq)$

Mix each liquid with $NaHCO_3(aq)$ separately. (1)

$CH_3CH_2CH_2COOH$ and $CH_2=CHCH_2COOH$ give effervescence.

The other two liquids give a negative result. (1)

Test with $Br_2(aq)$

Add $Br_2(aq)$ to each of $CH_3CH_2CH_2COOH$ and $CH_2=CHCH_2COOH$ slowly. (1)

$CH_2=CHCH_2COOH$ gives a colour change from yellow-brown to colourless.

$CH_3CH_2CH_2COOH$ gives a negative result. (1)

Test with acidified $K_2Cr_2O_7(aq)$

Warm each of the two other liquids with acidified $K_2Cr_2O_7(aq)$ separately. (1)

$CH_3CH_2CH_2CH_2OH$ gives a colour change from orange to green.

$CH_3CH_2COOCH_3$ gives a negative result. (1)

Unit Exercise (p.79)

19 Outline how hex-1-ene can be obtained from a mixture of hex-1-ene, octane and water by physical methods.

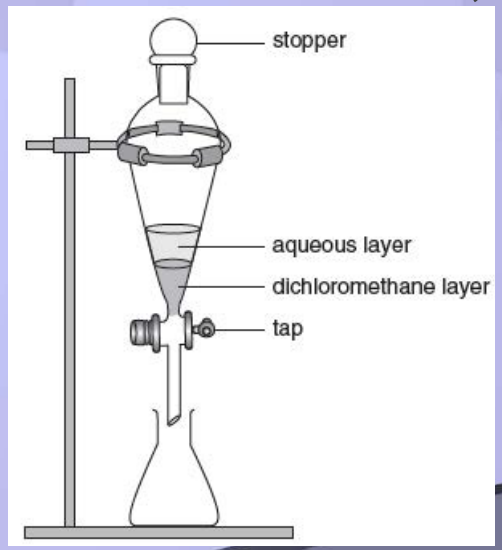
(Boiling points: hex-1-ene = 63 ˚C, octane = 125 ˚C, water = 100 ˚C)

(HKDSE, Paper 2, 2013, 3(a))

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).

Unit Exercise (p.79)

20 Cloves are dried, unopened flower buds of an evergreen tree that grows in tropical climates.
Clove oil is extracted from dried cloves and a mixture of clove oil and water is obtained. This mixture is placed in a separating funnel and 50 cm^3 of liquid dichloromethane is added. The mixture is shaken and allowed to stand, giving two layers as shown below.



Most of the clove oil dissolves in the dichloromethane.

Unit Exercise (p.79)

20 (continued)

a) Describe how the dichloromethane layer is obtained free from the aqueous layer.

Remove the stopper and open the tap.

Run off the dichloromethane layer until the interface just reaches the tap / lower layer removed. (1)

Close the tap.

b) The dichloromethane, which boils at 40 °C and produces a toxic vapour, is then evaporated off to leave clove oil.

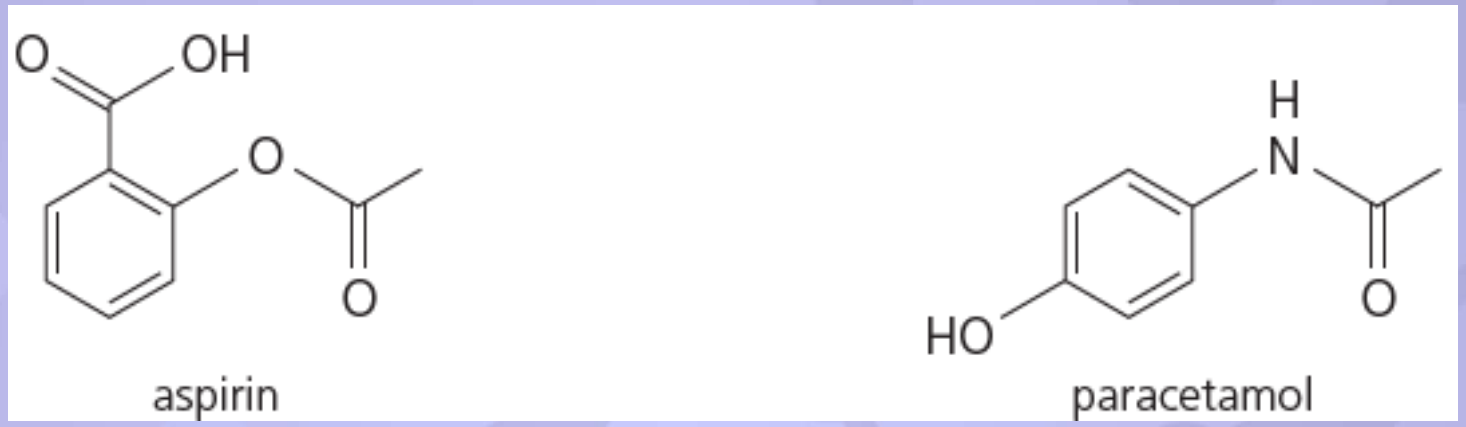
Suggest a suitable method and the equipment used for removing the dichloromethane from the mixture.

Distillation (1)

Use hot water bath / electric heating mantle. (1)

Unit Exercise (p.79)

21 Aspirin and paracetamol are widely used painkiller.



a) A student added small amounts of powdered aspirin and powdered paracetamol separately to aqueous solution of sodium carbonate.
Describe what would be observed in each case and explain the difference in the observations.

Aspirin gives effervescence.
Paracetamol gives no observable change. (1)
Aspirin contains a –COOH group while paracetamol does not. (1)

Unit Exercise (p.79)

21 (continued)

b) An aspirin sample S was contaminated with an organic base Y.

i) Suggest how aspirin can be isolated from the aspirin sample S by using an organic solvent dichloromethane and an aqueous solution of sodium hydroxide.

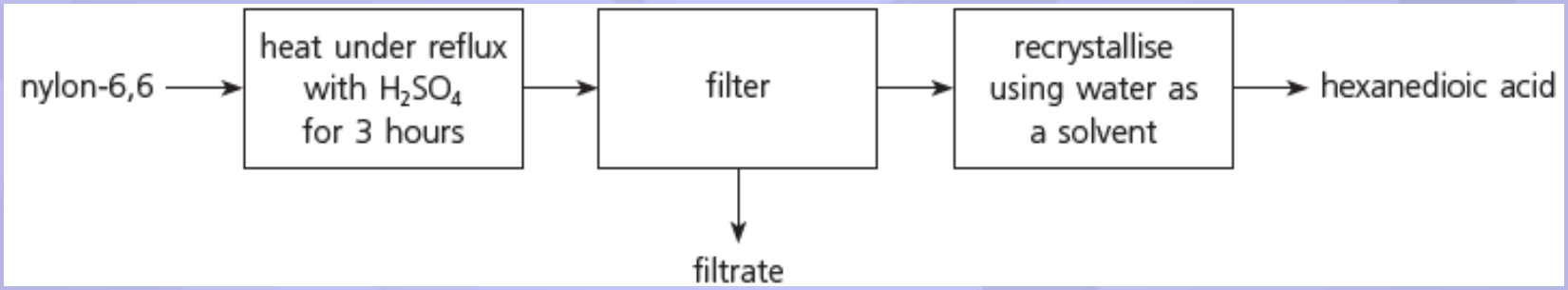
Dissolve the sample in the organic solvent dichloromethane. (1)
Shake the solution obtained with the aqueous solution of sodium hydroxide in a separating funnel. (1)
Collect the aqueous layer.
Add dilute hydrochloric acid to the aqueous layer to regenerate the aspirin and (1)
then collect the aspirin formed by filtration. (1)

ii) Suggest how you can identify that the solid obtained is pure.

Measure the melting point of the solid obtained. (1)
A sharp melting point indicates that the solid is pure. (1)

Unit Exercise (p.79)

22 a) Scientists are investigating how best to recycle nylon-6,6. One approach is to break the polymer down into its monomers which can be reused. The following flow chart shows how hexanedioic acid can be produced from nylon-6,6.



i) What is meant by 'heating under reflux'?

ii) Describe the main steps involved in carrying out the recrystallisation of hexanedioic acid using water as a solvent.

In your account, describe what property of hexanedioic acid this process depends upon.

Unit Exercise (p.79)

22 (continued)

b) The student adds excess sodium hydroxide solution to the filtrate. The student notices that the mixture develops a 'fishy' smell characteristic of an amine.
Suggest the structural formula of the compound responsible for the 'fishy' smell.

(OCR Advanced Level Chem. B (Salters), Sample Question Paper, H433, 2016, 1(a)(i), (iii), (b))

Unit Exercise (p.79)

22 (continued)

a) i) Boil a mixture. (1)
Condense / cool the vapour to return it to the reaction vessel. (1)

ii) Dissolve the crystals in the minimum volume of hot water. (1)
Filter the hot mixture. (1)
Leave the filtrate to cool to obtain crystals. (1)
Filter off the crystals and wash with cold water. (1)
Property of hexanedioic acid: It is more soluble in hot water than in cold water. (1)

b) $H_2N(CH_2)_6NH_2$ (1)

Unit Exercise (p.79)

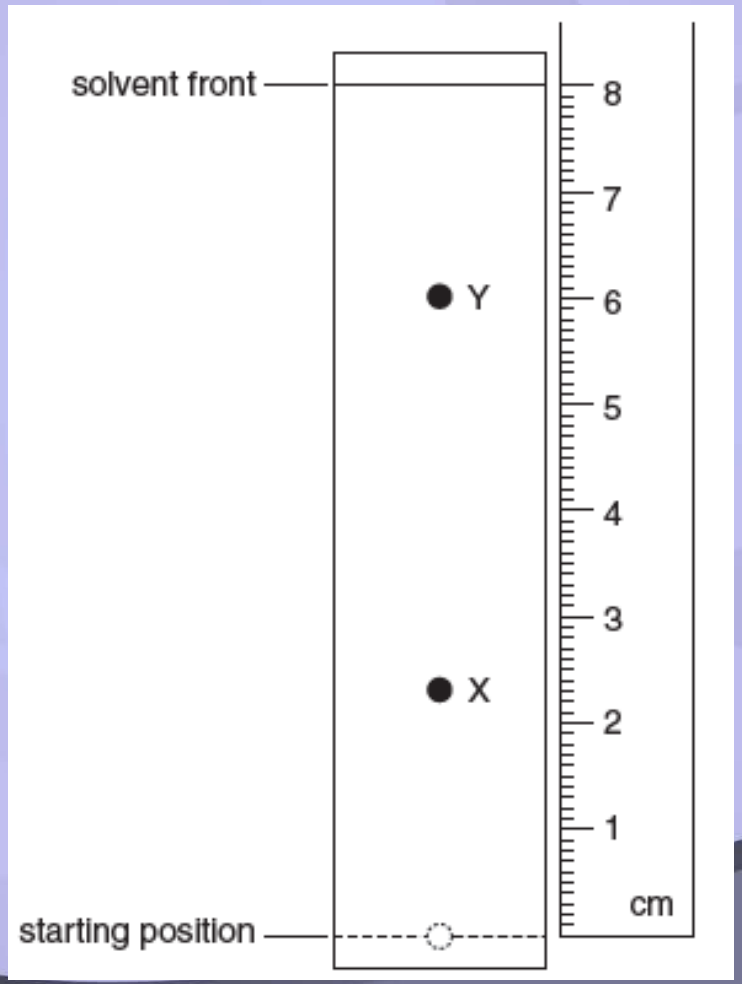
23 What is meant by the '*R*f value' of a substance in a paper chromatogram?

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).

(HKDSE, Paper 2, 2018, 3(a)(iii))

Unit Exercise (p.79)

24 Thin layer chromatography (TLC) is used to analyse a mixture of two amino acids. The result is shown below.



Unit Exercise (p.79)

24 (continued)

a) Briefly describe the principle underlying the separation of amino acids X and Y by using thin layer chromatography.

b) Suggest ONE method that can be used to make the spots on the TLC plate visible.

c) The R_f values for some amino acids, recorded under identical conditions, are shown in the table below.

Amino acid	R_f
Serine	0.21
Glycine	0.29
Alanine	0.55
Proline	0.64
Tyrosine	0.75
Valine	0.82

Determine the identity of the amino acids in the mixture.

Unit Exercise (p.79)

24 (continued)

a) Amino acids X and Y separate because
- they differ in the extent to which they are soluble in the mobile phase; (1)
- they are adsorbed by the stationary phase to different extents. (1)

b) Spray with ninhydrin. (1)

c) R_f for amino acid X = $\frac{2.3}{8.0}$ = 0.29 (1)

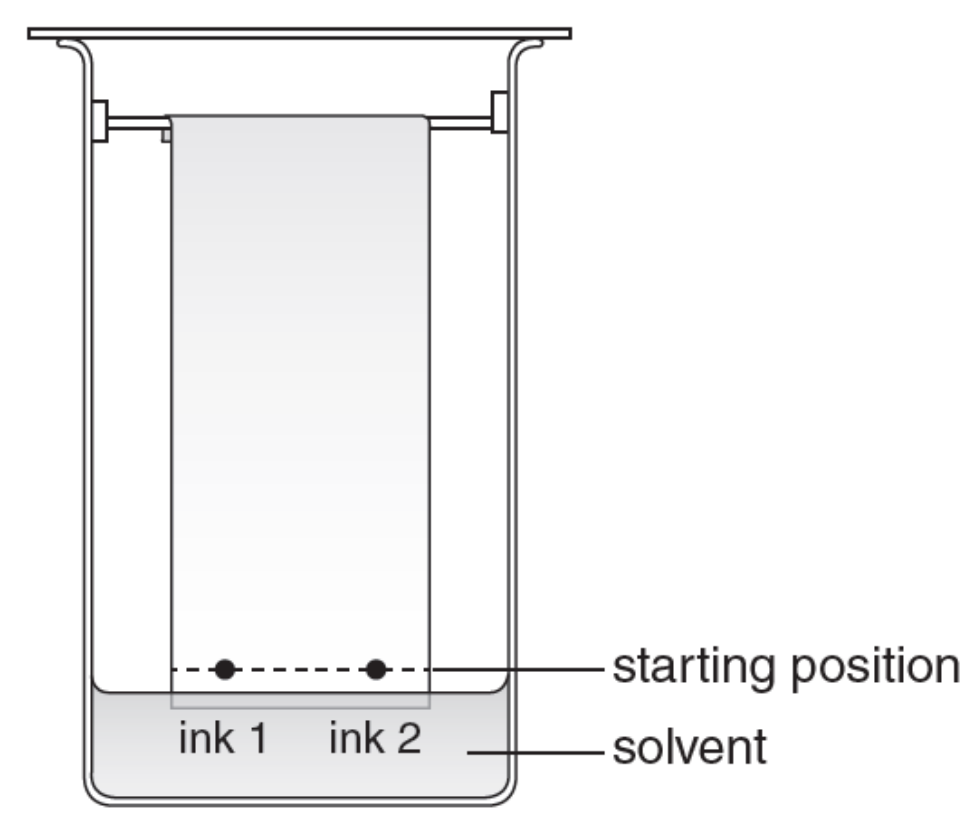
R_f for amino acid Y = $\frac{6.0}{8.0}$ = 0.75 (1)

Amino acid X is glycine.
Amino acid Y is tyrosine. } (1)

Unit Exercise (p.79)

25 Inks are mixtures of different dyes.

A student used paper chromatography to separate the dyes in two samples of inks. The experimental set-up the student used is shown below.



Unit Exercise (p.79)

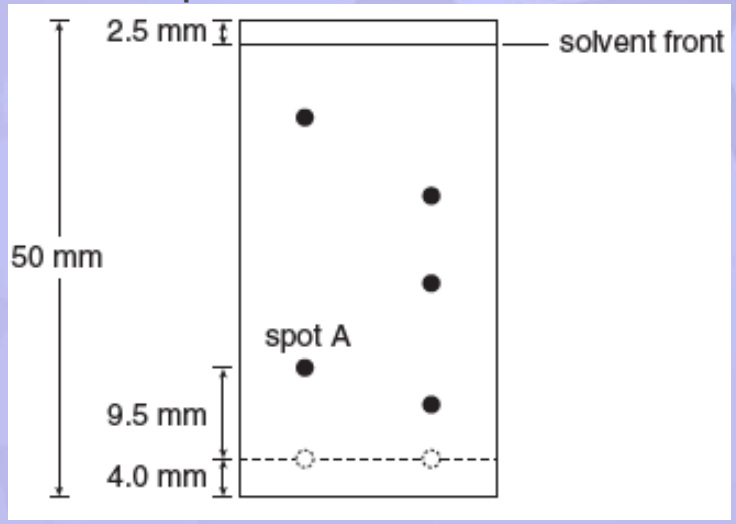
25 (continued)

a) Explain why the dotted line of starting position
   i) was drawn in pencil, NOT in ink;
   ii) was drawn above the solvent level.

b) Name the mobile phase and stationary phase in paper chromatography.

c) Explain how the components in ink are separated into two or more spots.

d) The result of the experiment is shown below.



i) Calculate the R_f value for spot A.
ii) Suggest why the two samples of inks are NOT the same.

Unit Exercise (p.79)

25 (continued)

a) i) Ink is soluble in the solvent while graphite is not. (1)
ii) So the dots would not run into the solvent. (1)

b) Mobile phase: solvent (1)
Stationary phase: water trapped in the fibres of the chromatography paper (1)

c) The components in ink have different relative solubilities in the mobile phase and in the stationary phase. (1)
Components that are more soluble in the mobile phase than in the stationary phase move rapidly up the paper, while those that are more soluble in the stationary phase are not carried as far up the paper. (1)

d) i) R_f for spot A $= \dfrac{9.5 \text{ mm}}{(50 - 2.5 - 4.0) \text{ mm}}$
$= 0.22$ (1)
ii) They contain different dyes. (1)

Unit Exercise (p.79)

26 Describe how impurities affect the melting temperature of an impure solid.

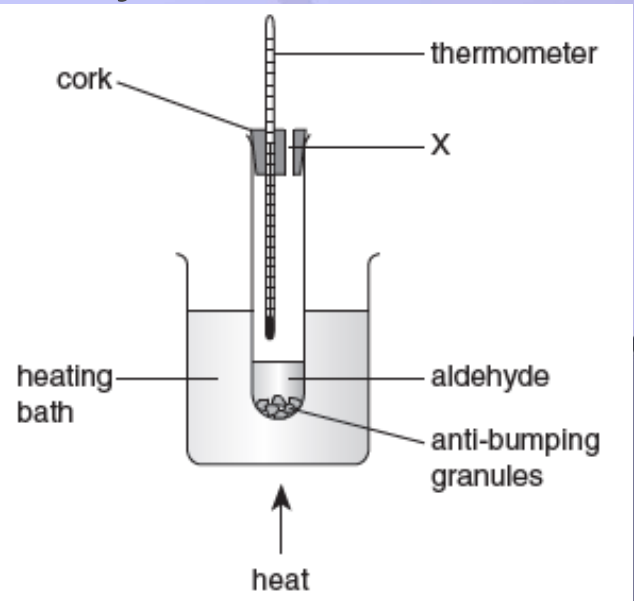
The melting temperature is NOT sharp. (1)
The melting temperature is less than that of the pure solid. (1)

Unit Exercise (p.79)

27 At a given pressure, a pure liquid boils at a constant temperature. This boiling point can be used to help identify the liquid. One procedure for measuring the boiling point of an aldehyde is shown in the diagram.

Procedure

- Set up the apparatus as shown in the diagram. Make sure that the bulb of the thermometer is about 3 cm above the level of the aldehyde.



Unit Exercise (p.79)

27 (continued)

- Add a few anti-bumping granules to the aldehyde.
- Heat the liquid in the beaker gently until the aldehyde begins to boil. The boiling point of the aldehyde is greater than 150 °C.
- Adjust the heat source so that the aldehyde boils gently.
- Record the temperature when it becomes steady.
- Record the atmospheric pressure.

a) State the purpose of the anti-bumping granules.

b) Give ONE reason why it is essential for the cork to have the hole, labelled X, in it.

c) State TWO properties that a liquid must have to make it suitable for use in the heating bath in this boiling point determination.

d) State why the atmospheric pressure was recorded.

e) State why the boiling point of a compound may be insufficient on its own to identify the compound.

(AQA Advanced GCE, Unit 6T, P13, May 2013, 8)

Unit Exercise (p.79)

27 (continued)

a) To prevent uneven boiling. (1)

b) Allow vapour to escape. (1)

c) Property 1: The boiling point of the liquid is above that of the sample. (1)
Property 2: The liquid does not ignite easily. (1)

d) Boiling point varies with pressure. (1)

e) Many compounds may have the same boiling point. (1)

Unit Exercise (p.79)

28 A pale yellow waxy solid was obtained in an experiment. The melting point of the solid was believed to be about 38 °C.

Devise a simple experiment that can be used to find the melting point of the solid.

Insert some of the solid into a capillary tube and then attach the tube open end upwards to a thermometer with a rubber band. (1)

Place the thermometer into a bath of water. (1)

Slowly heat the water bath with constant stirring. Notice the temperature at which the solid starts and finishes melting. (1)