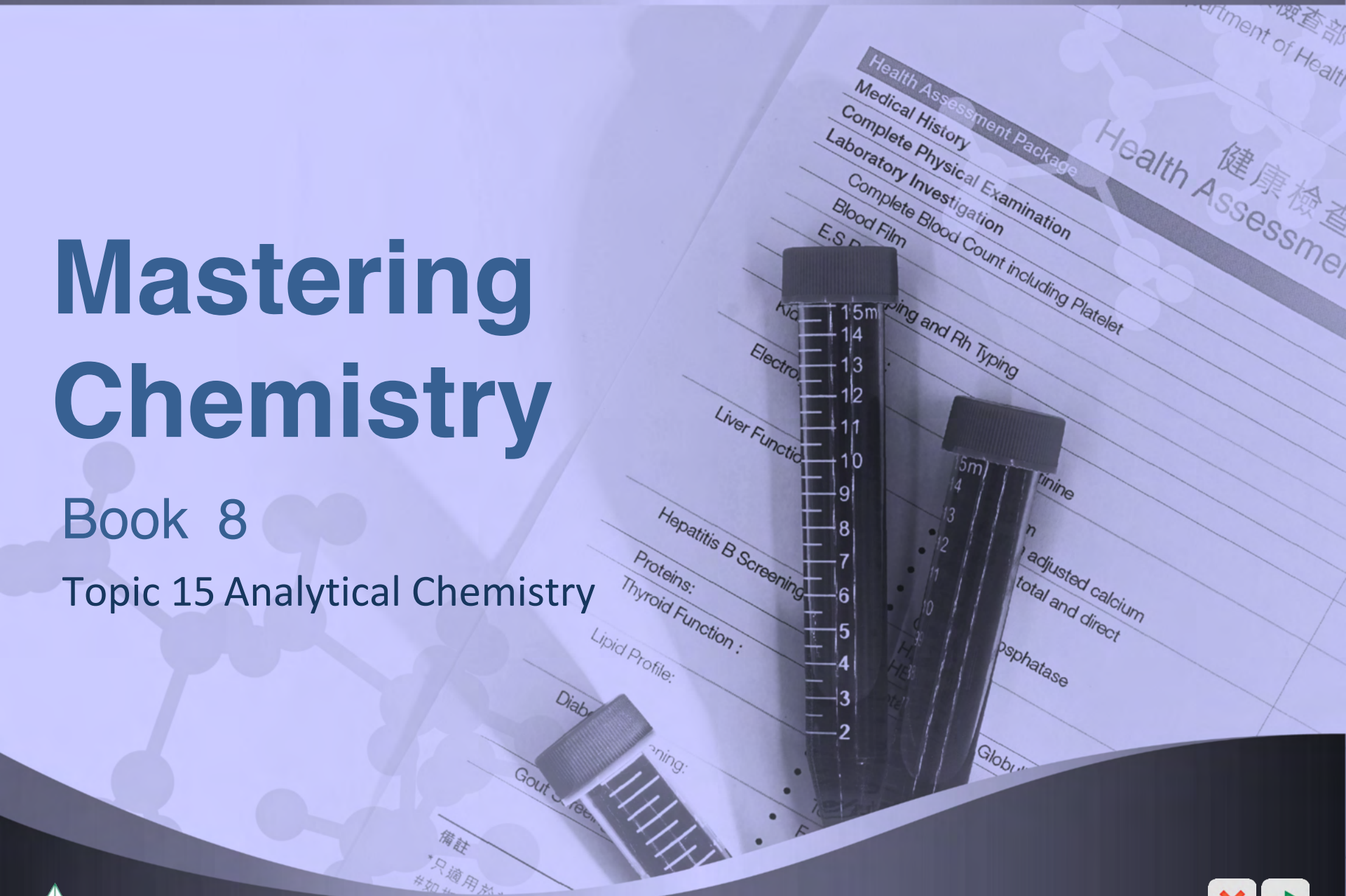
Mastering Chemistry

Book 8

Topic 15 Analytical Chemistry



Content

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Content

55.1 Introduction (p.180)

- Analytical chemistry is used in many fields.
  For example,
  - in the analysis of food and drugs;
  - in monitoring the levels of pollutants in air;
  - in forensic analysis;
  - in clinical laboratory tests.

Clinical laboratory tests

55.2 Analysis of food and drugs (p.180)

- Both traditional analytical methods (such as volumetric analysis) and modern instrumental analytical methods play an important role in the analysis of food and drugs.
- Samples of food are tested for their nutritional values, and the presence of pollutants, harmful pathogens or toxins.
- Food samples may also be analysed to ensure that legal levels of food additives are not exceeded and that they are free of pesticides.
- The structures of newly synthesised drugs are confirmed using a variety of spectroscopic and other techniques.

55.2 Analysis of food and drugs (p.180)

Analysing food by using volumetric analysis

- Volumetric analysis plays an important role in food analysis.
- The acidity of milk is an indication of its quality. This can be determined by titrating the milk sample with a standard aqueous solution of sodium hydroxide. Sulphur dioxide is used as a preservative in wine.
- The sulphur dioxide content in a sample of wine can be determined by titrating the sample with a standard aqueous solution of iodine.

Sulphur dioxide in wine can be determined by volumetric analysis

55.2 Analysis of food and drugs (p.180)

Q (Example 55.1)

An experiment is carried out to determine the amount of nitrogen in a milk powder sample.

Step 1 Heat a milk powder of 4.5 g with concentrated sulphuric acid so as to turn all the nitrogen in it into $(NH_4)_2SO_4(aq)$.

Step 2 Heat the reaction mixture obtained in *Step 1* with an excess of NaOH(aq) to liberate $NH_3(g)$. Use 100.0 cm^3 of 0.800 mol dm^{-3} HCl(aq) to absorb all the $NH_3(g)$ liberated.

Step 3 Dilute the solution formed to 250.0 cm^3 with deionised water.

Step 4 Titrate 25.00 cm^3 portions of the diluted solution with 0.100 mol dm^{-3} NaOH(aq), using phenolphthalein as an indicator. The mean titre is 20.50 cm^3.

a) Write chemical equations for the following reactions in *Step 2*:

i) the reaction between $(NH_4)_2SO_4(aq)$ and NaOH(aq);

ii) the reaction between $NH_3(g)$ and HCl(aq).

55.2 Analysis of food and drugs (p.180)

Q (Example 55.1) (continued)

b) State the colour change at the titration end point in *Step 4*.

c) Calculate the percentage by mass of nitrogen in the milk powder sample.
(Relative atomic mass: N = 14.0)

A

a) i) $(NH_4)_2SO_4(aq) + 2NaOH(aq) \rightarrow 2NH_3(g) + Na_2SO_4(aq) + 2H_2O(l)$

ii) $NH_3(g) + HCl(aq) \rightarrow NH_4Cl(aq)$

b) From colourless to pink

55.2 Analysis of food and drugs (p.180)

Q (Example 55.1) (continued)

A

c) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

$250.0\ cm^3$ — $0.100\ mol\ dm^{-3}$, $20.50\ cm^3$

↓

(used) $25.00\ cm^3$

Number of moles of NaOH in 20.50 cm^3 solution $= 0.100\ mol\ dm^{-3} \times \frac{20.5}{1\ 000}\ dm^3$

$= 2.05 \times 10^{-3}\ mol$

According to the equation, 1 mole of HCl reacts with 1 mole of NaOH.

i.e. number of moles of HCl in 25.00 cm^3 of diluted solution $= 2.05 \times 10^{-3}\ mol$

Number of moles of HCl in 250.0 cm^3 of diluted solution
$= 10 \times 2.05 \times 10^{-3}\ mol$
$= 0.0205\ mol$
= number of moles of HCl remain after *Step 2*

Number of moles of HCl used in *Step 2* $= 0.800\ mol\ dm^{-3} \times \frac{100.0}{1\ 000}\ dm^3$

$= 0.0800\ mol$

Number of moles of HCl used to absorb the NH_3 $= (0.0800 - 0.0205)\ mol$
$= 0.0595\ mol$
= number of moles of NH_3 liberated

Mass of N in sample $= 0.0595\ mol \times 14.0\ g\ mol^{-1}$
$= 0.833\ g$

Percentage by mass of N in sample $= \frac{0.833\ g}{4.50\ g} \times 100\%$
$= 18.5\%$

∴ the percentage by mass of nitrogen in the milk powder sample is 18.5%.

55.2 Analysis of food and drugs (p.180)

Identifying harmful food colourings by using thin layer chromatography

- Chemists carry out analyses to check whether there are harmful chemicals in food.

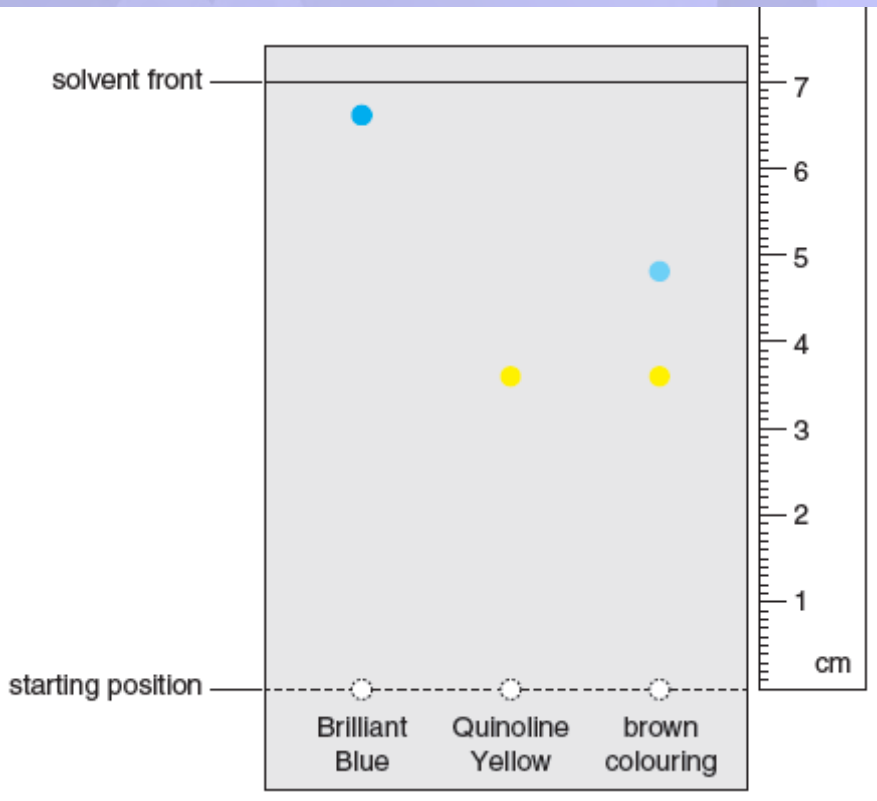
Chocolate beans contain artificial colourings, which can be analysed by using thin layer chromatography

55.2 Analysis of food and drugs (p.180)

Practice 55.1

A recent study reports that two artificial food colourings, Brilliant Blue and Quinoline Yellow, may be harmful to children's nervous systems.

A sweet manufacturer used thin layer chromatography to check if a brown colouring contained any harmful colourings. The result was shown below.



a) Suggest why it is important to be able to identify the colourings in food.

b) Calculate the R_f value for the yellow spot from the brown colouring.

c) What does the results tell you about the brown colouring and its suitability for use in sweets?

a) To check whether the colourings are safe to eat / permitted.

b) $R_f = \frac{3.6\text{ cm}}{7.0\text{ cm}}$

$= 0.51$

c)
- The brown colouring is made up of two colours.
- The brown colouring contains an unknown colouring.
- The brown colouring contains a harmful colouring (Quinoline Yellow).

55.2 Analysis of food and drugs (p.180)

Determining the amount of iron in vegetables by using colorimetry

- Iron is a vital element required by the human body. It is used in the manufacture of the oxygen-carrying proteins, haemoglobin and myoglobin.

55.2 Analysis of food and drugs (p.180)

Practice 55.2

A chemist used colorimetry to determine the amount of iron in a sample of spinach. $Fe^{3+}(aq)$ ion and $SCN^-(aq)$ ion react to give deep red $Fe(SCN)^{2+}(aq)$ ion. The chemist prepared four standard solutions of $Fe^{3+}(aq)$ ion. 1.00 cm^3 of each solution was treated with excess $SCN^-(aq)$ ion to give $Fe(SCN)^{2+}(aq)$ ion. The absorbance of each solution was measured by using a colorimeter installed with a blue filter. The following results were obtained:

	Standard solution			
	1	2	3	4
Concentration of Fe^{3+} ion (mg dm^{-3})	0.396	0.793	1.98	3.96
Absorbance	0.065	0.170	0.402	0.807

a) Suggest why a blue filter was used.

b) Prepare a calibration curve of the data.

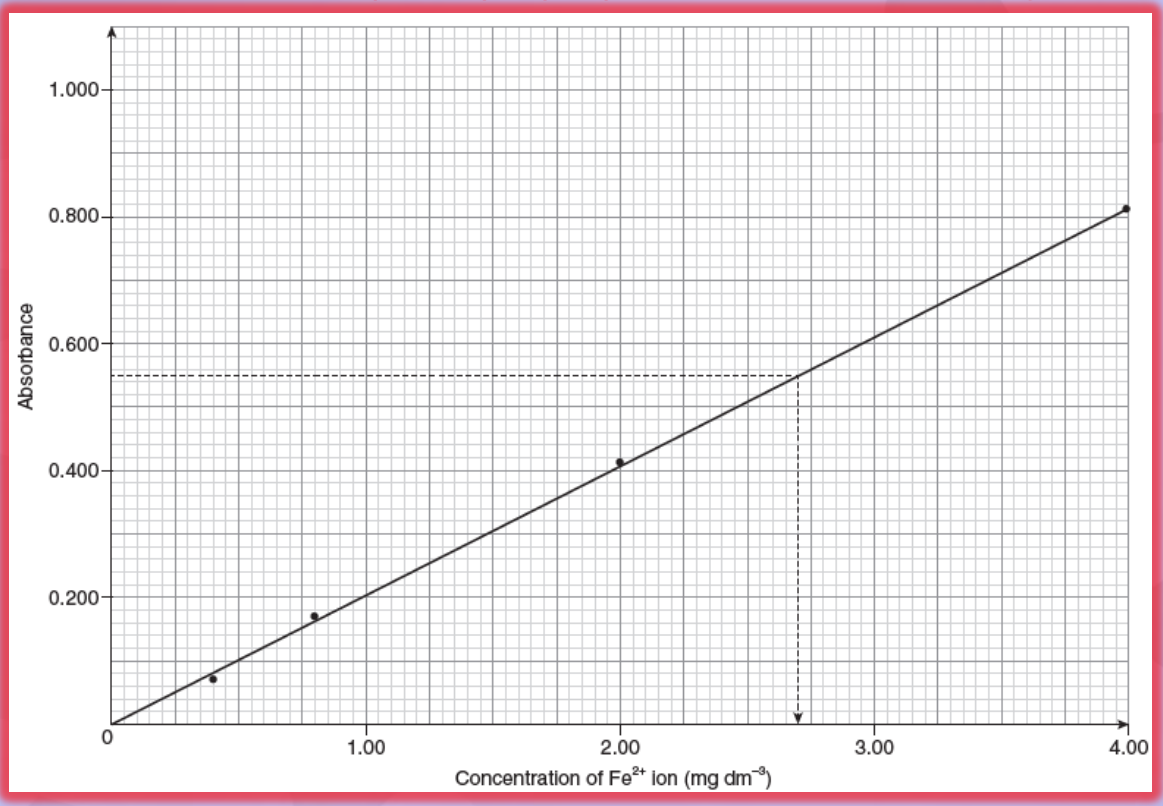
c) The chemist weighted 5.00 g of spinach and burnt the spinach to form ash. The ash was treated with dilute sulphuric acid and made up to 50.0 cm^3.
1.00 cm^3 of this solution was treated with excess $SCN^-(aq)$ ion. The absorbance of the mixture was found to be 0.550.
Determine the mass of iron in the sample of spinach.

55.2 Analysis of food and drugs (p.180)

Practice 55.2 (continued)

a) The deep red $Fe(SCN)^{2+}(aq)$ ion absorbs blue light to a large extent.

b)



c) Absorbance = 0.55, $[Fe^{2+}(aq)]$ found from the graph = 2.70 mg dm^{-3}

Mass of iron in the sample of spinach = 2.70 mg dm^{-3} x $\frac{50.0}{1\,000}$ dm^3 = 0.135 g

55.2 Analysis of food and drugs (p.180)

Analysis of drugs

- The World Health Organisation estimates that 25% of the drugs in developing countries are fake.
- In many cases, fake drugs are found to be without active ingredients or with the wrong ingredients.
- Chemists in the government laboratory analyse drugs sold in Hong Kong.
- Thin layer chromatography is usually used to conduct preliminary tests in the identification of fake drugs.

55.2 Analysis of food and drugs (p.180)

Analysing food and drugs by using gas chromatography-mass spectrometry

- Detailed analysis of food and drugs can be carried out by using gas chromatography in conjunction with mass spectrometry.
- This method is known as **gas chromatography-mass spectrometry (GC-MS) (氣相色層法-質譜法)**.

55.2 Analysis of food and drugs (p.180)

Gas chromatography

- Gas chromatography (GC) is a technique used to separate volatile components in a mixture.
- This type of chromatography not only separates the components in a mixture, but also gives a measure of how much of each component is present. The instrument used is called a gas chromatograph.

A gas chromatograph

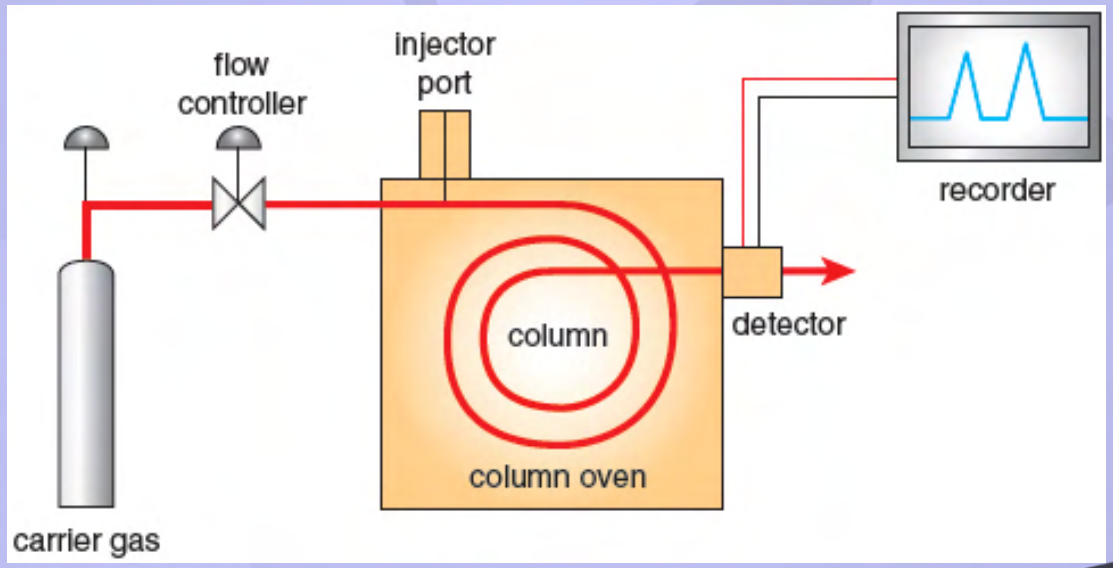
55.2 Analysis of food and drugs (p.180)

- The stationary phase is either a thin layer of a liquid or solid coated onto the inside of the chromatographic column. The mobile phase is a **carrier gas (載體氣)** which moves through the column.

55.2 Analysis of food and drugs (p.180)

How a gas chromatograph works

- A small sample mixture is injected into a chromatograph. The sample is vaporised and mixed with the carrier gas. The gases then pass through the column.



The main features of a gas chromatograph

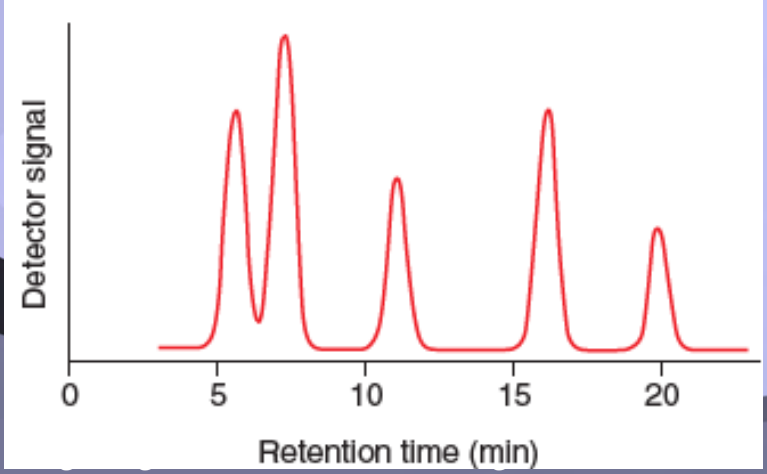
55.2 Analysis of food and drugs (p.180)

- After some time, the components emerge one by one. They pass into a detector, which sends a signal to a recorder as each component appears.
- A series of peaks, one for each component in the mixture, make up the chromatogram.

55.2 Analysis of food and drugs (p.180)

Interpreting a gas chromatogram

- The position of a peak is a record of how long it takes for a component to pass through the column. This is called the component's **retention time (保留時間)**.
- Identification can be made by comparing the retention time of an unknown component obtained from experiment with retention time of a known chemical species obtained from databook.



Each peak in the gas chromatogram represents each component in the mixture

55.2 Analysis of food and drugs (p.180)

- The area under each peak gives a measure of the relative amount of each component present in the sample mixture. This allows percentage composition of the mixture to be calculated.

- Applications of gas chromatography include:
  - tracking down the source of oil pollution from the pattern of peaks, which acts like a fingerprint for any batch of oil;
  - monitoring the presence of chemicals in industrial processes;
  - measuring the level of alcohol in blood samples from drivers;
  - detecting pesticides in river water.

55.2 Analysis of food and drugs (p.180)

Gas chromatography-mass spectrometry (GC-MS)

- GC-MS is an instrumental analytical technique comprised of a gas chromatograph and a mass spectrometer.
- In general, the gas chromatograph is used to separate complex chemical mixtures into individual components. Once separated, the components can be identified and quantified by the mass spectrometer.

Gas chromatograph-mass spectrometer

55.2 Analysis of food and drugs (p.180)

- Aromatic compounds such as fatty acids, esters, aldehydes and alcohols present in food and beverages can be easily analysed using GC-MS.
- The technique can also be used to detect spoilage or contamination of food, and pesticide residues in fruits and vegetables.
- In the pharmaceutical industry, GC-MS is used in research and development, production, and quality control. It is used in identification of impurities in active pharmaceutical ingredients.

55.2 Analysis of food and drugs (p.180)

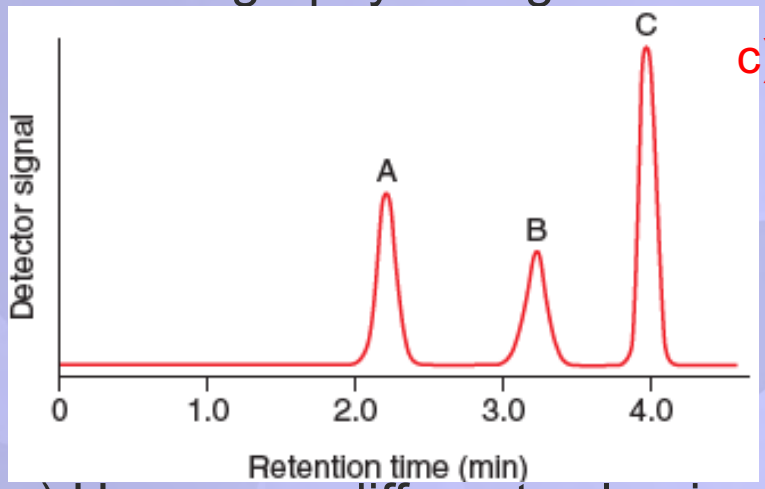
- Examples of analytical methods used in the analysis of food and drugs.

Method	Substance(s) to be analysed
Volumetric analysis	• food additives (e.g. sulphur dioxide content in white wine) • amount of nitrogen in milk powder sample
Thin layer chromatography (usually as preliminary tests)	• food additives (e.g. colourings for chocolate beans) • drugs
Colorimetry	• amount of iron in vegetables
Gas chromatography-mass spectrometry	• compounds in food and beverages • drugs

55.2 Analysis of food and drugs (p.180)

Practice 55.3

A food scientist analysed the food colourings from one type of sweet using gas chromatography. The gas chromatogram obtained is shown below.



a) How many different colourings were used in the sweet? 3

b) The food scientist wanted to identify colouring A. How could this be carried out? Match the retention time of colouring A with those of known colourings.

c) The food scientist suggested that the chromatogram gave both qualitative and quantitative information about the colourings used in the sweet. Explain why this is true.

c) The chromatogram gives qualitative information because it can show which colourings are used. The chromatogram gives quantitative information because it can show how much of each colouring is used. The area under each peak gives a measure of the relative amount of each colouring present.

55.3 Environmental protection (p.190)

- The Environmental Protection Department (EPD) aims to improve the quality of the air.
- The department closely monitors the level of air pollutants such as carbon monoxide and **dioxins (二噁英)**, as well as indoor air pollutants like **formaldehyde (甲醛)** (methanal).

55.3 Environmental protection (p.190)

Carbon monoxide

- Carbon monoxide is a colourless, odourless, tasteless gas produced by the incomplete combustion of hydrocarbons.
- Car emissions are the largest source of carbon monoxide.
- Carbon monoxide is also present in the emissions from industrial processes, such as coke plants and power plants.

Car emissions are the largest source of carbon monoxide

55.3 Environmental protection (p.190)

- Carbon monoxide is a highly poisonous gas. It can affect the oxygen carrying capacity of the blood, putting a strain on tissues with high oxygen demand, such as the heart and the brain.
- Exposure effects can include headache, dizziness, nausea, and even death at high levels. Hence the level of carbon monoxide in the air is monitored for personal safety reasons.

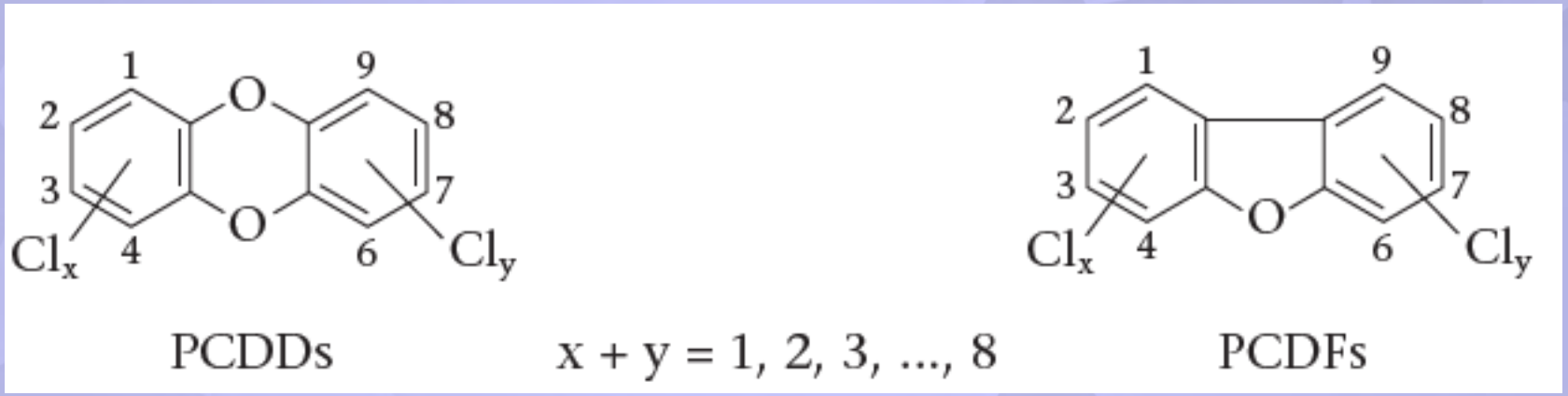
55.3 Environmental protection (p.190)

Dioxins

- Dioxins are environmentally persistent organic pollutants comprising **polychlorinated dibenzo-para-dioxins (PCDDs) (多氯二聯苯二噁英)** and **polychlorinated dibenzofurans (PCDFs) (多氯二苯呋喃)**.
- Dioxins are produced as byproducts in the manufacture of some chlorinated organic compounds. They are also formed if the temperature is not high enough when waste materials containing chlorine (e.g. PVC) are burnt.

55.3 Environmental protection (p.190)

- Dioxins can also be released into the air during natural processes, such as forest fires.



Structural formulae of PCDDs and PCDFs

- Dioxins are highly toxic and can cause reproductive and developmental problems, damage the immune system, interfere with hormones and also cause cancer.

55.3 Environmental protection (p.190)

Measuring the level of dioxins in air

- The level of dioxins in air can be measured by gas chromatographymass spectrometry. This method can detect chemicals in amounts as small as a picogram (10^{-12} g).
- It can measure more accurately the low level of dioxin than using methods based on volumetric analysis.

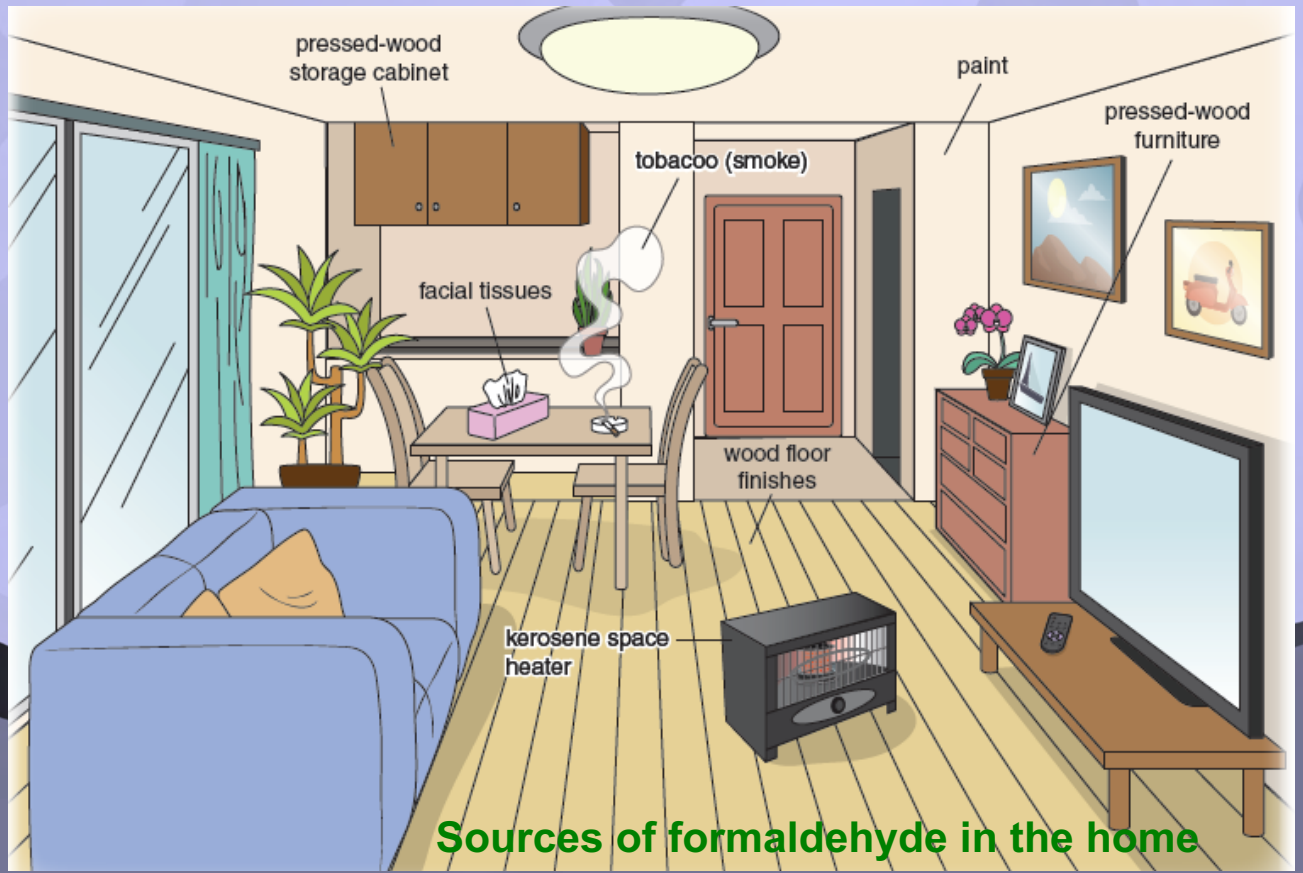
55.3 Environmental protection (p.190)

Formaldehyde – a common indoor air pollutant

- Formaldehyde (methanal, HCHO) is a common indoor air pollutant. It is a colourless gas with a pungent odour at high concentration.
- Formaldehyde is found in pressed-wood products (e.g. particle board and plywood), carpet adhesives, permanent-press fabrics and paper product coatings.

55.3 Environmental protection (p.190)

- Sources of formaldehyde in the home include building materials, smoking, paper products, pressed-wood products, and the use of un-vented, fuel-burning appliances, like gas stoves or kerosene space heaters.



Sources of formaldehyde in the home

55.3 Environmental protection (p.190)

- Formaldehyde can make you feel sick if you breathe a lot of it. People can have symptoms such as:
  - sore throat;
  - cough;
  - scratchy eyes;
  - nosebleeds.
- Formaldehyde is also a suspected human carcinogen.

55.3 Environmental protection (p.190)

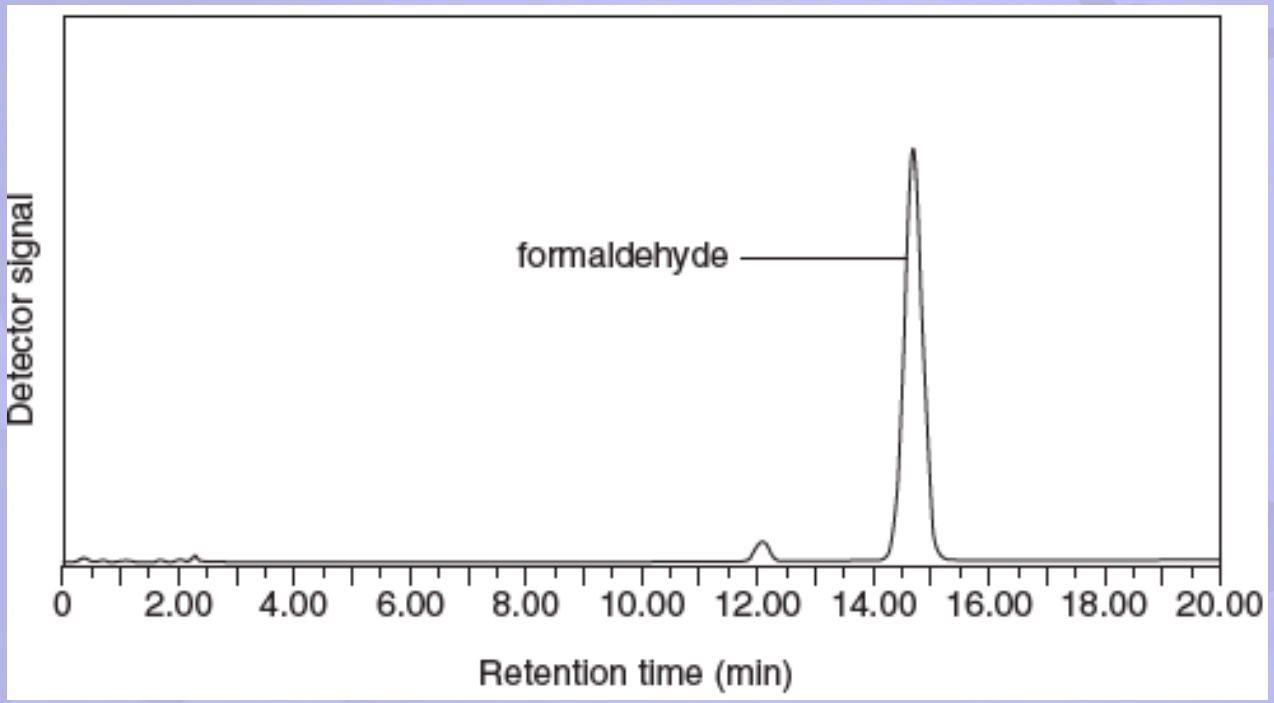
Measuring the level of formaldehyde in indoor air

- The level of formaldehyde in indoor air can be measured by using high performance liquid chromatography (HPLC) (高效能液相色層法).
- In a high performance liquid chromatograph, the mixture is forced through a column containing the stationary phase by a solvent driven by a high pressure pump.
  It is similar to column chromatography except that the pump drives the solvent rather than gravity.

A scientist used a high performance liquid chromatography (HPLC) to measure the level of a chemical species

55.3 Environmental protection (p.190)

- The concentration of formaldehyde can be obtained based on the peak area of the corresponding signal.



A high performance liquid chromatogram of formaldehyde

55.3 Environmental protection (p.190)

- Examples of analytical methods used for measuring levels of air pollutants.

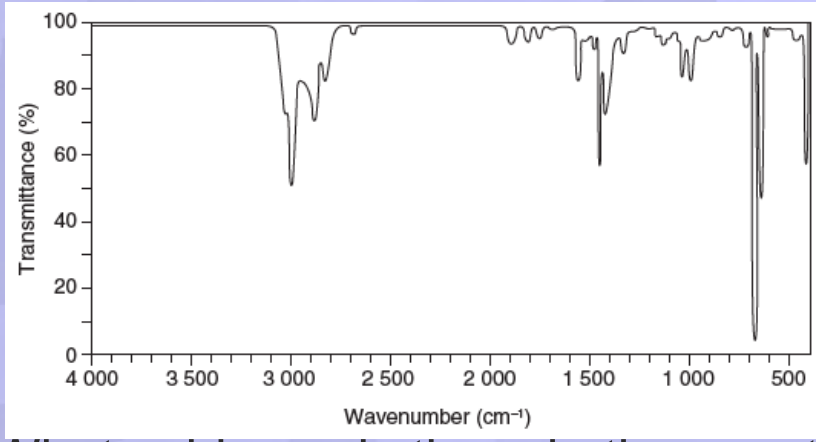
Method	Substance to be analysed
Infrared spectroscopy	• carbon monoxide
Gas chromatography-mass spectrometry	• dioxins
High performance liquid chromatography	• formaldehyde

55.3 Environmental protection (p.190)

Practice 55.4

1 Forest fires release a large number of organic compounds into the atmosphere, many in very small quantities.
Compounds in the smoke from forest fires can be analysed using GC-MS.
Explain how GC-MS enables the compounds to be identified.

2 An environmental chemist used infrared spectroscopy to monitor air pollution outside a petrol station. The infrared spectrum below was obtained from one of these pollutants.



What evidence is there in the spectrum that the pollutant may be a hydrocarbon rather than an alcohol or a carbonyl compound?
(Refer to the information given in Table 54.1.)

1 GC separates the compounds.
MS identifies the compounds by comparing with standard mass spectra.

2 No strong absorption peak at about 3 230–3 670 cm^{-1}, i.e. not an alcohol.
No strong absorption peak at about 1 680–1 800 cm^{-1}, i.e. not a carbonyl compound.

55.4 Chemistry aspect of forensic science (p.196)

- Forensic science refers to application of various fields of science and technology to establish facts about a crime and find evidence that can be used in both civil and criminal laws.
- Samples collected from a crime scene are sent to a laboratory and analysed by specialists. Samples can include things like fingerprints, hair and gunshot residue.

Crime scene

55.4 Chemistry aspect of forensic science (p.196)

- The laboratory work is mainly an application of the techniques of analytical science.
- In the chemistry branch, the main analytical techniques are various forms of chromatography, mass spectrometry and infrared spectroscopy.

55.4 Chemistry aspect of forensic science (p.196)

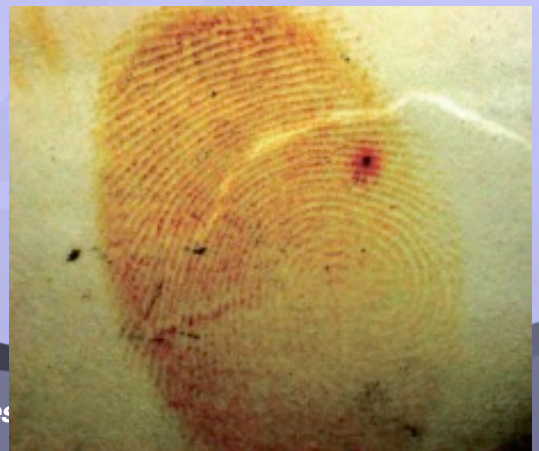
Fingerprints

- No two people have exactly the same fingerprints.
- Investigators and analysts can compare unknown fingerprints collected from a crime scene to the known prints of victims, witnesses and potential suspects to assist in criminal cases.
- Visible fingerprints can be photographed but an important scientific problem is how to make latent fingerprints which are not visible to the naked eye available for examination.

55.4 Chemistry aspect of forensic science (p.196)

Developing latent fingerprints by iodine sublimation

- Iodine sublimation is a process used to develop latent fingerprints on porous surfaces such as paper, cardboard and raw wood.
- When iodine crystals are warmed, they produce a purple vapour by sublimation.
- The iodine vapour gets adsorbed onto the oily substances present in the fingerprint deposit, giving a yellow-brown colouration.



Iodine sublimation is used to develop latent fingerprints

55.4 Chemistry aspect of forensic science (p.196)

Drink driving

- After a person has taken an alcoholic drink, the alcohol passes quickly through the walls of the stomach and intestines into the blood vessels. It is then carried to all parts of the body.
- Alcohol reduces the important skills a driver need to drive safely, including:
  - judgment;
  - vision;
  - colour distinction; and
  - reaction time.
- In Hong Kong, if the alcohol content in a driver exceeds:
  - 22 mg of alcohol per 100 cm^3 of breath; or
  - 50 mg of alcohol per 100 cm^3 of blood; or
  - 67 mg of alcohol per 100 cm^3 of urine,

  the driver may be prosecuted.

55.4 Chemistry aspect of forensic science (p.196)

The working principle of a breathalyser

- Ethanol in alcoholic drink reacts with dichromate ion in acidic solution according to the equation below.

$$2Cr_2O_7^{2-}(aq) + 3C_2H_5OH(aq) + 16H^+(aq) \longrightarrow 4Cr^{3+}(aq) + 3CH_3COOH(aq) + 11H_2O(l)$$

Orange dichromate ion is converted to green chromium(III) ion in the reaction.

- This reaction and its associated colour change were the basis for the breathalyser formerly used by many police forces in countries or regions to detect and measure alcohol levels in the breath of drivers.

55.4 Chemistry aspect of forensic science (p.196)

- In the breathalyser test, the breath sample is bubbled into a vial which contains a solution of dichromate ion.
- Any ethanol in the breath sample reacts with the dichromate ion according to the reaction above, and the solution changes colour as a result of the reaction.
- The reacted mixture in this vial is compared to another vial which contains dichromate ion but no ethanol (so it will be bright orange). The difference in colour between the two vials gives an indication of the amount of ethanol in the suspect's breath.

Designing and making a portable alcohol breathalyser
Ref.

55.4 Chemistry aspect of forensic science (p.196)

Drug testing

- Drug testing beyond the health care and criminal justice systems has increased throughout the past years.
- Common areas for drug testing include the workplace (e.g. preemployment testing), athletics, legal and criminal situations (e.g. postaccident testing, rehabilitation testing of ex-convicts), and health care (e.g. treatment, cause of death).

55.4 Chemistry aspect of forensic science (p.196)

- Urine, blood, hair, saliva, sweat, and nails are some biological specimens used to perform laboratory drug testing. Urine is most often the preferred test substance because of ease of collection.

Urine samples used to perform drug testing

55.4 Chemistry aspect of forensic science (p.196)

- Drug testing usually involves an initial screening test followed by a second test that identifies and / or confirms the presence of a drug or drugs.
- Thin layer chromatography can be used for initial screening. The R_f value and the colour are characteristics of a drug.
- Thin layer chromatography can demonstrate the presence of a drug, but it cannot specify the quantity of the drug present.

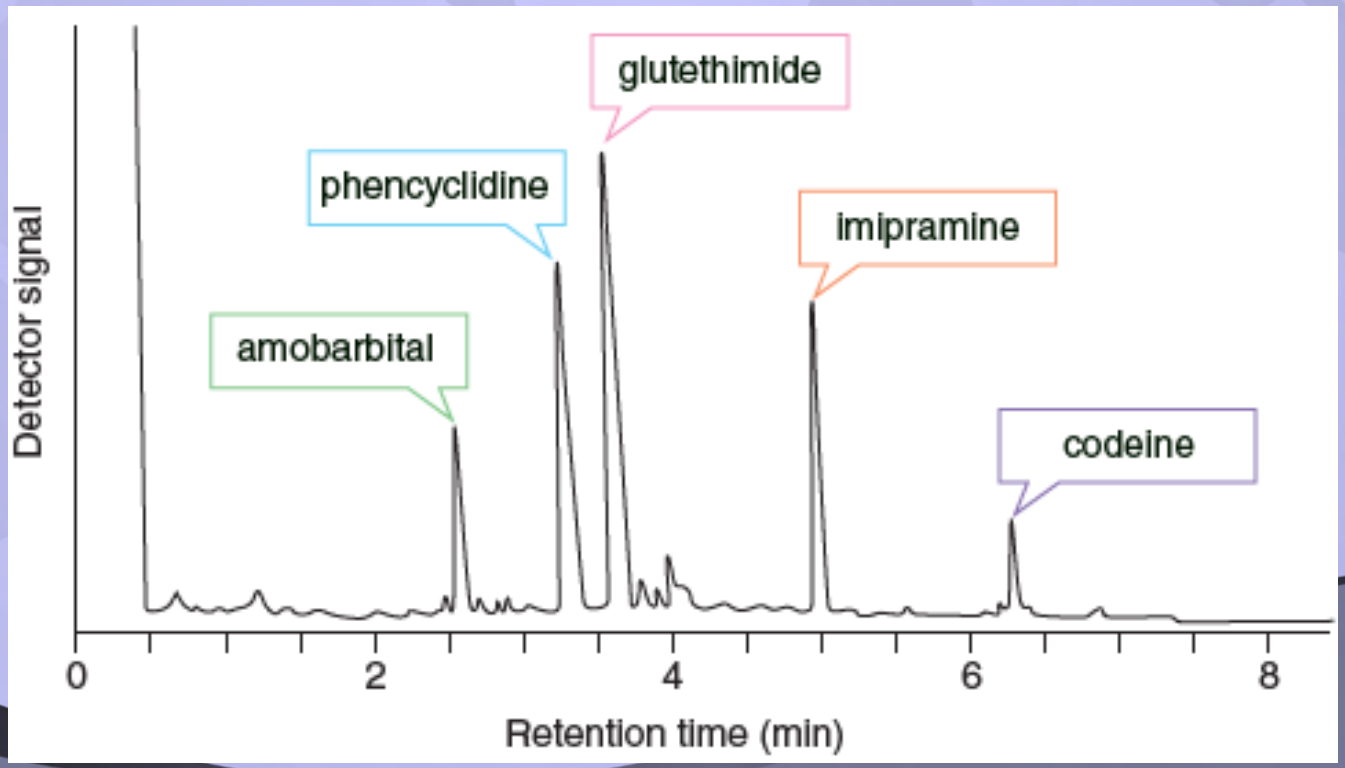
55.4 Chemistry aspect of forensic science (p.196)

- Confirmatory drug tests for the non-negative specimens are performed with gas chromatography-mass spectrometry (GC-MS) or liquid chromatography-mass spectrometry (LC-MS) methodology.

- These instruments are capable of identifying and distinguishing the drug from other compounds that might be present in the specimen. At the same time, they can accurately measure the concentration of the target compound.

55.4 Chemistry aspect of forensic science (p.196)

- A gas chromatogram run to investigate the presence of drugs in a urine sample. The analysis results show that five drugs were present in the sample, identified from their retention times.



55.4 Chemistry aspect of forensic science (p.196)

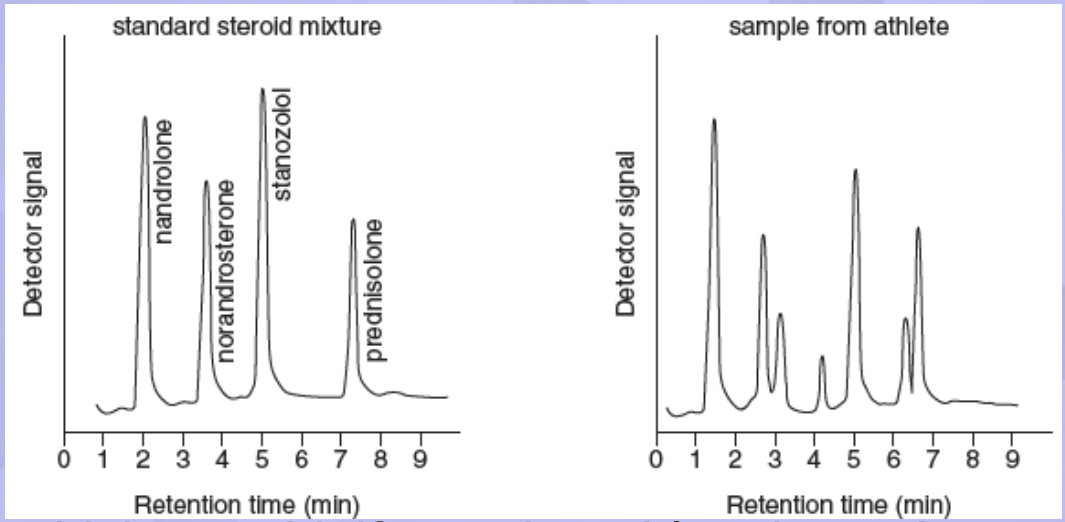
- Examples of analytical methods used in the chemistry aspect of forensic science.

Method	Substance(s) to be analysed
Iodine sublimation	• latent fingerprints
Dichromate ion in breathalyser	• ethanol content in breath
Gas chromatography	• ethanol content in blood
Thin layer chromatography	• drugs (usually as preliminary tests)
Gas chromatography-mass spectrometry	• confirmatory test for drugs

55.4 Chemistry aspect of forensic science (p.196)

Practice 55.5

1 An athlete provided a sample of urine to be tested for steroids. The sample and the steroid standards were treated and then analysed by gas chromatography. Below were chromatograms of a standard mixture containing four different steroids, and the sample from the athlete.



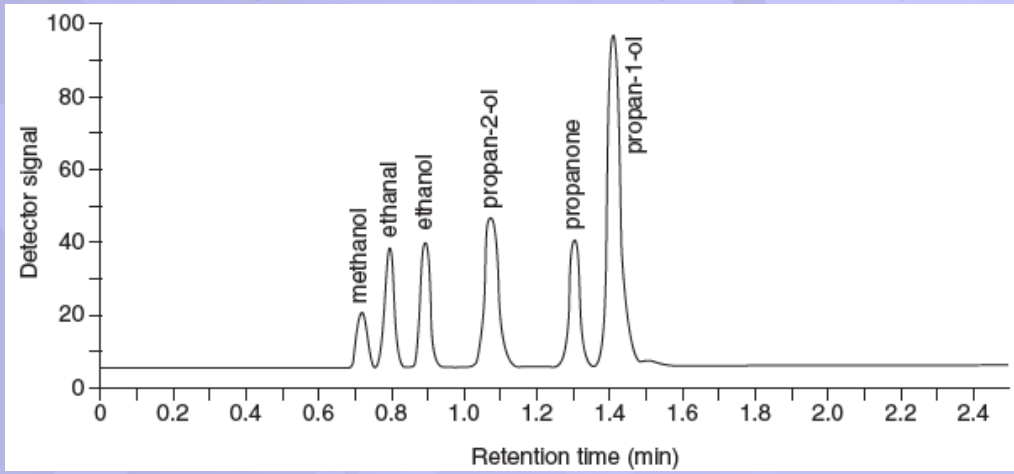
Identify which steroid, if any, the athlete has taken.

Stanozolol

55.4 Chemistry aspect of forensic science (p.196)

Practice 55.5 (continued)

2 A blood sample may contain a number of volatile chemicals that can interfere with the identification and measurement of ethanol in the blood. A sample containing a mixture of ethanol and several other volatile chemicals was injected into the gas chromatograph. The following chromatogram was obtained.



Ethanol has a unique retention time.
Each chemical produces a distinct peak on the chromatogram.

A forensic chemist claims that the presence of these volatile chemicals would not affect the qualitative analysis of ethanol.
What evidence is presented in the chromatogram to support this claim?

55.5 The role of analytical chemistry in clinical diagnoses (p.202)

Amino acid disorder screening

- Amino acid disorder screening is done in newborns to detect inborn errors in metabolism of amino acids.
- Some congenital amino acid metabolic defects cause mental retardation that can be prevented with prompt treatment of the newborn.

Some tests are done in a newborn to make sure it is in a good condition

55.5 The role of analytical chemistry in clinical diagnoses (p.202)

- Both the blood and urine tests use thin layer chromatography to separate the amino acids present.
- Using this technique, the amino acids form a characteristic pattern on a TLC plate. This pattern is then compared to the normal pattern to determine if there are abnormalities.

55.5 The role of analytical chemistry in clinical diagnoses (p.202)

Mass spectrometry for the discovery of novel cancer biomarkers

- Mass spectrometry is a central analytical technique used for cancer marker discovery and monitoring.
- A ‘biomarker’ is defined as a measurable analyte that correlates with a specific state of a living body, such as a normal biological condition, a pathological process, or a pharmacological response to a therapeutic intervention.
- A biomarker can distinguish and discriminate between comparative biological conditions such as cancer and noncancer.

55.5 The role of analytical chemistry in clinical diagnoses (p.202)

- There are 20 000 to over 100 000 unique types of protein within a typical human cell. Each protein has its own unique amino acid sequence and structure.
- Protein biomarkers in blood or tissues play an important role in cancer detection, monitoring and treatment.
- Body fluids taken from cancer patients can be analysed by using mass spectrometry in order to detect and identify biomarkers.
- Spectral peaks are identified and compared with those obtained from a normal body. This may indicate either normal or diseased state in the body.

55.5 The role of analytical chemistry in clinical diagnoses (p.202)

- Examples of analytical methods used in clinical diagnosis.

Method	Substance to be analysed
Thin layer chromatography	• amino acid
Mass spectrometry	• protein profile of patients

Key terms (p.204)

gas chromatography-mass spectrometry (GC-MS)	氣相色層法-質譜法	formaldehyde	甲醛
carrier gas	載體氣	polychlorinated dibenzo-para-dioxins (PCDDs)	多氯二聯苯二噁英
retention time	保留時間	polychlorinated dibenzofurans (PCDFs)	多氯二苯呋喃
dioxin	二噁英	high performance liquid (HPLC)	高效能液相色層法

Summary (p.205)

1 The table below summarises examples of analytical methods used in the analysis of food and drugs.

Method	Substance(s) to be analysed
Volumetric analysis	• food additives (e.g. sulphur dioxide content in white wine) • amount of nitrogen in milk powder sample
Thin layer chromatography (usually as preliminary tests)	• food additives (e.g. colourings for chocolate beans) • drugs
Colorimetry	• amount of iron in vegetables
Gas chromatography-mass spectrometry	• compounds in food and beverages • drugs

2 The table below summarises examples of analytical methods used for measuring levels of air pollutants.

Method	Substance to be analysed
Infrared spectroscopy	• carbon monoxide
Gas chromatography-mass spectrometry	• dioxins
High performance liquid chromatography	• formaldehyde

Summary (p.205)

3 The table below summarises examples of analytical methods used in the chemistry aspect of forensic science.

Method	Substance(s) to be analysed
Iodine sublimation	• latent fingerprints
Dichromate ion in breathalyser	• ethanol content in breath
Gas chromatography	• ethanol content in blood
Thin layer chromatography	• drugs (usually as preliminary tests)
Gas chromatography-mass spectrometry	• confirmatory test for drugs

4 The table below summarises examples of analytical methods used in clinical diagnosis.

Method	Substance to be analysed
Thin layer chromatography	• amino acid
Mass spectrometry	• protein profile of patients

Unit Exercise (p.206)

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

 question targeted at level 3 and above;

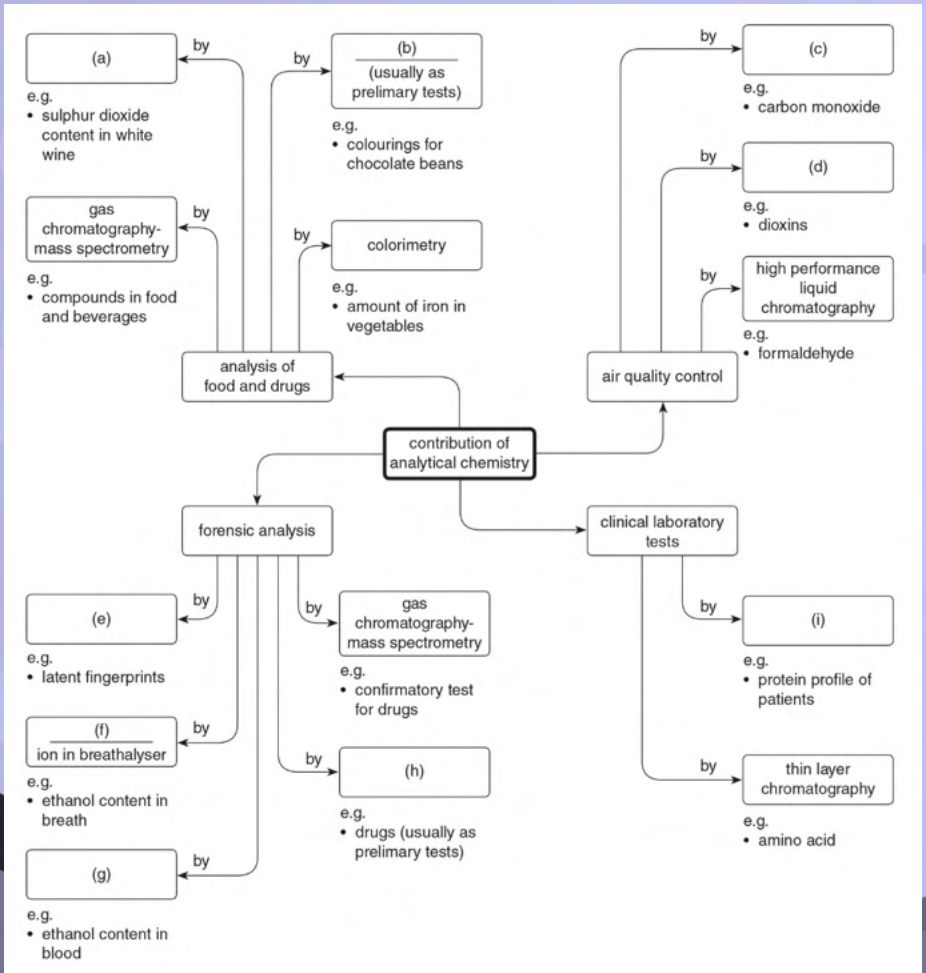
 question targeted at level 4 and above;

 question targeted at level 5.

Unit Exercise (p.206)

PART I KNOWLEDGE AND UNDERSTANDING

1 Complete the following concept maps.

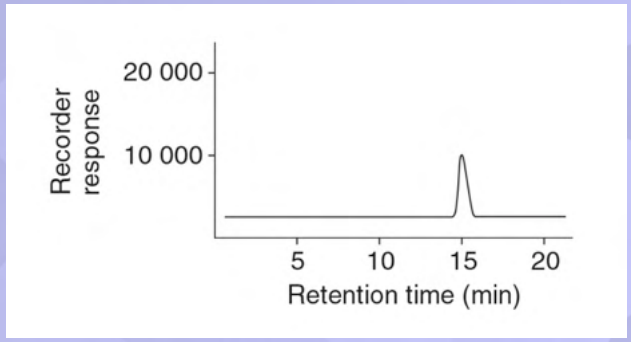


a) volumetric analysis
b) thin layer chromatography
c) infrared spectroscopy
d) gas chromatography-mass spectrometry
e) iodine sublimation
f) dichromate
g) gas chromatography
h) thin layer chromatography
i) mass spectrometry

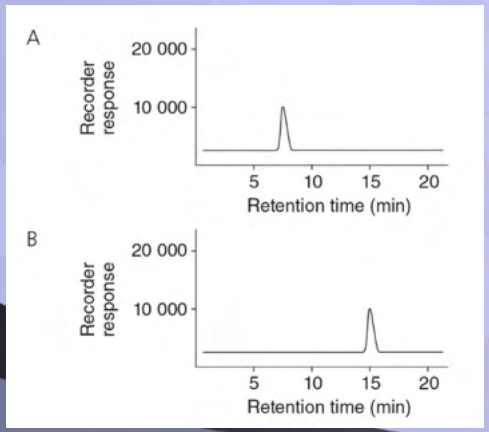
Unit Exercise (p.206)

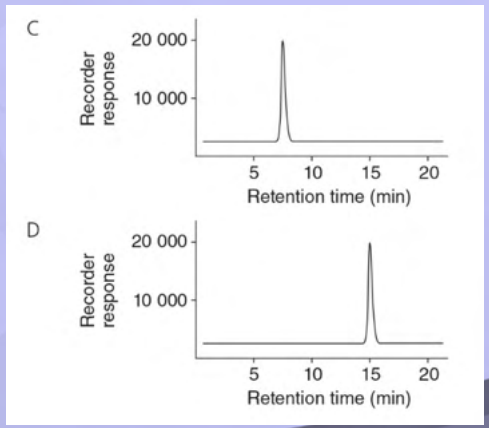
PART II MULTIPLE CHOICE QUESTIONS

2 The following chromatogram was produced when 0.1 mg of pentan-2-one was passed through a gas chromatographic column.



Which of the following chromatograms is produced when 0.2 mg of pentan-2-one is passed through the same column under identical conditions?





Answer: D

Unit Exercise (p.206)

3 Select the correct states for the stationary and mobile phases in HPLC.

	Stationary phase	Mobile phase
A	liquid	gas
B	gas	liquid
C	solid	liquid
D	solid	gas

(Edexcel IAL, Advanced, Unit 4, WCH04/01, Jan. 2014,1)

Answer: C

Unit Exercise (p.206)

4 An aqueous mixture of two substances (X and Y) is subjected to analysis by both paper chromatography and high performance liquid chromatography (HPLC). In both forms of chromatography, component Y of the mixture is bonded more strongly to the stationary phase than component X.

In term of R_f and R_t, where R_t is the retention time in HPLC, component Y has the

A higher R_f and higher R_t.
B higher R_f and lower R_t.
C lower R_f and higher R_t.
D lower R_f and lower R_t.

Answer: C

Explanation:
In paper chromatography, component Y that bonded more strongly to the stationary phase travels slowly up the paper, i.e. lower R_f.

In HPLC, the retention time measures how long it takes for a component to pass through the chromatographic column. Component Y that bonded more strongly to the stationary phase takes a long time to pass through the chromatographic column, i.e. higher R_t.

Unit Exercise (p.206)

5 Which gas is the least suitable as a carrier gas in gas chromatography?

A Argon
B Carbon dioxide
C Oxygen
D Nitrogen

(Edexcel Advanced GCE, Unit 4, 6CH04/01, Jun. 2015, 4)

Answer: C

Unit Exercise (p.206)

6 In one type of high performance liquid chromatography (HPLC), the stationary phase is non-polar and a polar solvent is used as the eluent. Which of the following would travel through the chromatography column most quickly?

A Tetrachloromethane
B Chloromethane
C Iodomethane
D Hexane

Answer: B

Explanation:
Compared with the other chemical species, chloromethane is most soluble in the polar eluent. Hence it would travel through the chromatography column most quickly.

(Edexcel Advanced GCE, Unit 4, 6CH04/01R, Jun. 2013, 10)

Unit Exercise (p.206)

7 Which of the following statements about formaldehyde are correct?

(1) It is a common indoor air pollutant.
(2) It is irritating to eyes and respiratory tract.
(3) Its level in the air is determined by infrared spectroscopy.

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

Explanation:
(3) The level of formaldehyde in the air is determined by high performance liquid chromatography.

Answer: A

Unit Exercise (p.206)

8 Which of the following instrumental analytical methods is / are commonly used to determine the level of dioxins in the air?

(1) Gas chromatography-mass spectrometry
(2) Colorimetry
(3) Thin layer chromatography

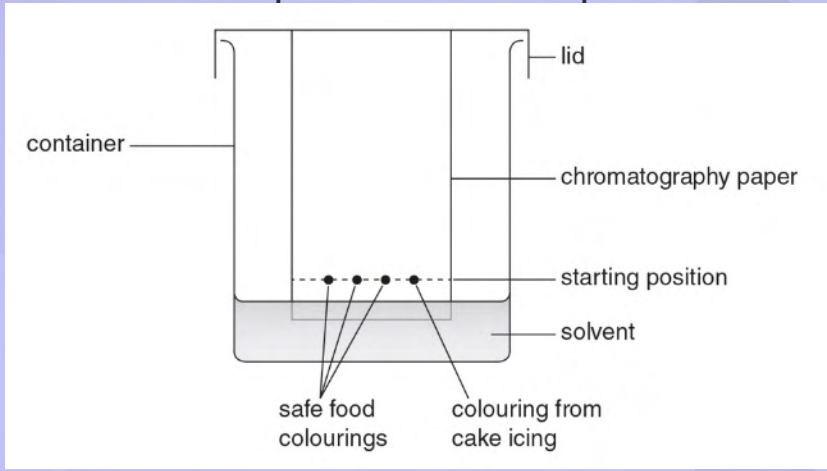
A (1) only
B (2) only
C (1) and (3) only
D (2) and (3) only

Answer: A

Unit Exercise (p.206)

PART III STRUCTURED QUESTIONS

9 Icing on cakes was tested to check that safe colourings were used when they were made. Paper chromatography is one method of testing.
The diagram below showed an experimental set-up a student used.



a) Suggest why there was a lid on the container.
To prevent the evaporation of the solvent. (1)

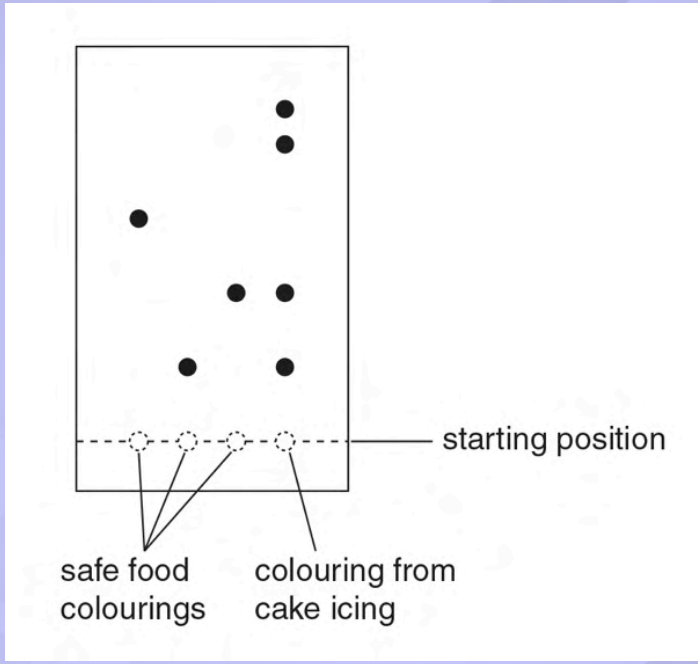
b) The dotted line of starting position was drawn in pencil, NOT in ink. Suggest why.
Ink is soluble in the solvent while graphite is not. (1)

c) Name the mobile phase and stationary phase in paper chromatography.
Mobile phase: solvent (1)
Stationary phase: water trapped in the fibres of the chromatography paper (1)

Unit Exercise (p.206)

9 (continued)

d) The diagram below showed the paper chromatogram obtained.



i) How many different colourings were used in the colouring from the cake icing?

4 (1)

ii) Discuss if the cake icing is safe to eat.

Cannot tell whether the cake icing is safe to eat because some colours could be unsafe. (1)

Unit Exercise (p.206)

10 Some orange drinks contain the artificial food colourings Tartrazine and Sunset Yellow. These colourings are thought to cause hyperactivity in children.

a) Suggest TWO reasons why a manufacturer uses these additives.
Improve the colour / appearance of the drink. (1)
Maintain the low cost of the drink. / Using natural colours would make the drink cost more. (1)

b) A scientist working for a company making orange drink wants to show that the orange drink produced does not contain these two colourings. Samples of Tartrazine, Sunset Yellow and the orange drink are available.

i) Describe how the scientist can show that the orange drink does NOT contain the two colourings by using thin layer chromatography. (You may include a diagram of the chromatogram obtained.)
Compare the spots from the orange drink with those of the two additives.
There should be no matching spots. (1)

ii) The scientist uses thin layer chromatography rather than paper chromatography. Explain the advantages of using thin layer chromatography.
- Quicker (1)
- Smaller samples (1)
- Clearer separation (1)

Unit Exercise (p.206)

11 The concentration of NO_2 in air can be determined by passing the sample through a solution of H_2O_2, which oxidises NO_2 to HNO_3, and titrating the HNO_3 with an alkali.

A technician passed 25.0 dm^3 of a sample of air through $H_2O_2(aq)$. The resulting mixture required 9.15 cm^3 of 1.00×10^{-2} mol dm^{-3} NaOH(aq) for complete neutralisation.

What is the concentration of NO_2, in mg dm^{-3}, in the sample of air?

(Relative atomic masses: N = 14.0, O = 16.0)

$HNO_3(aq) + NaOH(aq) \longrightarrow NaNO_3(aq) + H_2O(l)$

1.00×10^{-2} mol dm^{-3}

9.15 cm^3

Number of moles of NaOH in 9.15 cm^3 solution = 1.00×10^{-2} mol $dm^{-3} \times \frac{9.15}{1\,000}$ dm^3

$= 9.15 \times 10^{-5}$ mol (1)

According to the equation, 1 mole of HNO_3 reacts with 1 mole of NaOH.

i.e. number of moles of $HNO_3 = 9.15 \times 10^{-5}$ mol (1)

Mass of NO_2 in the sample of air = 9.15×10^{-5} mol $\times$ 46.0 g $mol^{-1} = 4.21 \times 10^{-3}$ g = 4.21 mg

Concentration of NO in the sample of air = $\frac{4.21 \text{ mg}}{25.0 \text{ dm}^3}$

$= 0.168$ mg dm^{-3} (1)

∴ the concentration of NO_2 in the sample of air is 0.168 mg dm^{-3}.

Unit Exercise (p.206)

12 Hydrogen peroxide is used in hair bleach.
10.00 cm^3 of a sample of hair bleach were placed in a volumetric flask and the volume was made up to 250.0 cm^3. 25.00 cm^3 portions of this solution were acidified and titrated with 0.0269 mol dm^{-3} $KMnO_4(aq)$.
The mean titre was 17.40 cm^3.

a) The equation below represents the reaction between KMnO4(aq) and $H_2O_2(aq)$ in acidic solution.

$$\underline{2}\ MnO_4^-(aq) + \underline{5}\ H_2O_2(aq) + \underline{6}\ H^+(aq) \longrightarrow \underline{2}\ Mn^{2+}(aq) + \underline{8}\ H_2O(l) + \underline{5}\ O_2(g)$$

(1)

Balance this equation by putting the appropriate numbers.

b) State the colour change at the end point of the titration.
From colourless to pale pink (1)

Unit Exercise (p.206)

12 (continued)

c) Calculate the concentration, in mol dm^{-3}, of hydrogen peroxide in the hair bleach.

$2MnO_4^-(aq)$ + $5H_2O_2(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$

0.0269 mol dm^{-3}

17.40 cm^3

10.00 cm^3

↓

250.0 cm^3

↓

(used) 25.00 cm^3

Number of moles of MnO_4^- ion in 17.40 cm^3 solution = 0.0269 mol dm^{-3} x $\frac{17.40}{1\,000}$ dm^3

$= 4.68 \times 10^{-4}$ mol (1)

According to the equation, 2 moles of MnO_4^- ion react with 5 moles of H_2O_2.

i.e. number of moles of H_2O_2 in 25.00 cm^3 solution = $\frac{5}{2}$ x 4.68×10^{-4} mol

$= 1.17 \times 10^{-3}$ mol (1)

Number of moles of H_2O_2 in 250.0 cm^3 solution = $10 \times 1.17 \times 10^{-3}$ mol $= 1.17 \times 10^{-2}$ mol

= number of moles of H_2O_2 in 10.00 cm^3 hair bleach

Concentration of H_2O_2 in hair bleach = $\frac{1.17 \times 10^{-2}\ \text{mol}}{\frac{10.00}{1\,000}\ dm^3}$

$= 1.17$ mol dm^{-3} (1)

∴ the concentration of hydrogen peroxide in the hair bleach is 1.17 mol dm^{-3}.

Unit Exercise (p.206)

13 The nitrogen content of bread was determined using the procedure below.

Step 1 The nitrogen in 3.00 g of bread was converted into ammonia.

Step 2 The ammonia was passed into 50.0 cm^3 of 0.130 mol dm^{-3} hydrochloric acid.

Step 3 The excess hydrochloric acid was titrated with 0.106 mol dm^{-3} sodium hydroxide solution. 23.30 cm^3 of the alkali were required to reach the end point.

a) Calculate the number of moles of excess hydrochloric acid.

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

0.106 mol dm^{-3}

23.30 cm^3

Number of moles of NaOH in 23.30 cm^3 solution = 0.106 mol dm^{-3} x $\frac{23.30}{1\,000}$ dm^3

$= 2.47 \times 10^{-3}$ mol (1)

According to the equation, 1 mole of HCl reacts with 1 mole of NaOH.

i.e. number of moles of excess hydrochloric acid = 2.47×10^{-3} mol (1)

Unit Exercise (p.206)

13 (continued)

b) Calculate the percentage by mass of nitrogen in the bread.
(Relative atomic mass: N = 14.0)

Number of moles of HCl at start = $0.130 \text{ mol dm}^{-3} \times \frac{50.0}{1\,000} \text{ dm}^3$
$= 6.50 \times 10^{-3} \text{ mol}$

Number of moles of HCl reacted with NH_3 = $(6.50 \times 10^{-3} - 2.47 \times 10^{-3})$ mol
$= 4.03 \times 10^{-3}$ mol (1)

Ammonia reacts with hydrochloric acid according to the equation:

$NH_3(g) + HCl(aq) \longrightarrow NH_4Cl(aq)$

According to the equation, 1 mole of NH_3 reacts with 1 mole of HCl.
i.e. number of moles of $NH_3 = 4.03 \times 10^{-3}$ mol (1)

Mass of nitrogen in bread = $4.03 \times 10^{-3} \text{ mol} \times 14.0 \text{ g mol}^{-1}$
$= 5.64 \times 10^{-2}$ g

Percentage by mass of nitrogen in bread = $\frac{5.64 \times 10^{-2} \text{ g}}{3.00 \text{ g}} \times 100\%$

$= 1.88\%$ (1)

∴ the percentage by mass of nitrogen in the bread is 1.88%.

Unit Exercise (p.206)

14 A technician analysed a mixture of hydrocarbons using gas chromatography. He first calibrated the equipment using standard hydrocarbons.

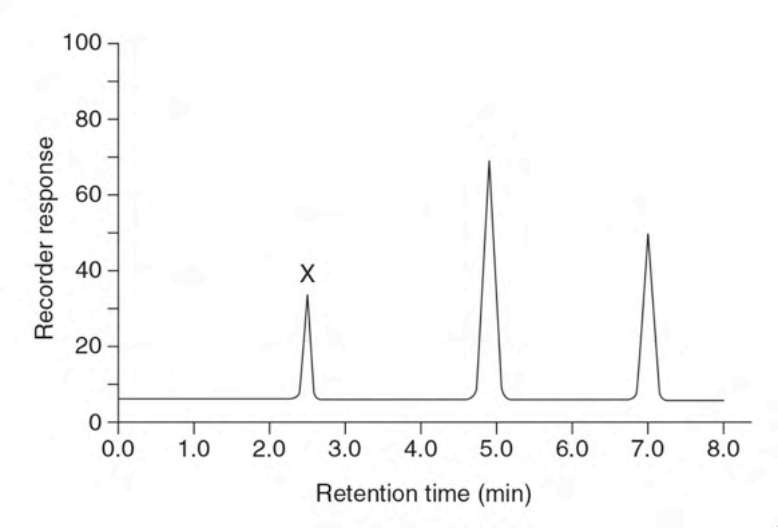
The retention times of these hydrocarbon are shown in the table.

Hydrocarbon	Retention time (min)
Methane	1.7
Ethane	2.5
Propane	3.8
Butane	4.9
Pentane	7.0

Unit Exercise (p.206)

14 (continued)

The technician then analysed the mixture of hydrocarbons. The gas chromatogram obtained is shown below.



a) Identify the mobile and stationary phases in gas chromatography.

Mobile phase: carrier gas (1)

Stationary phase: a thin layer of a liquid or solid coated onto the inside of the chromatographic column (1)

b) State what is meant by 'retention time'.

The time (from the injection of the sample) for the component to leave the chromatographic column (1)

Unit Exercise (p.206)

14 (continued)

c) What is the hydrocarbon corresponds to peak X?

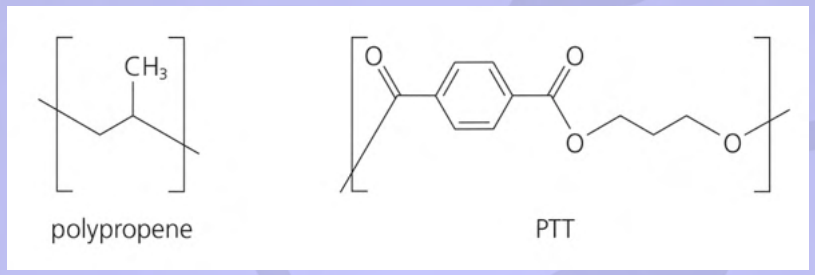
Ethane (1)

d) How does the gas chromatogram show that butane has the highest concentration?

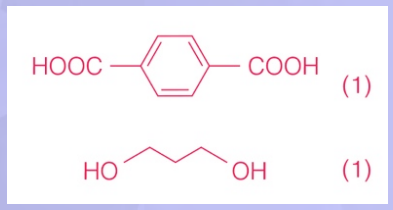
The peak at retention time 4.9 min is the highest. (1)

Unit Exercise (p.206)

15 Polypropene and PTT are two polymers used in the manufacture of carpets. The repeating units of these two polymers are shown below.



a) Draw the structures of two monomers that could be combined to give PTT.



b) Forensic scientists can use infrared spectroscopy to identify small amounts of carpet fibres left on the shoes of people at the scene of a crime.
Give the wavenumber range of ONE absorption you could use to distinguish between the infrared spectra of polypropene and PTT.

(Refer to the information given in Table 54.1.)

The infrared spectrum of PTT has an absorption peak at about 1 680–1 800 cm^{-1} while the infrared spectrum of polypropene does not. (1)

Unit Exercise (p.206)

16 E300 is an antioxidant used in white wines. It prevents dissolved oxygen reacting with the ethanol to form an acid, X, which would produce a sour-tasting wine.

a) Draw the structural formula of the acid, X, responsible for the wine's sour taste.

Any two of the following:
- Quicker (1)
- More accurate (1)
- Can detect very small quantities / more sensitive (1)

b) Explain how GC-MS enables the substances to be identified.

The gas chromatograph is used to separate complex chemical mixtures into individual components. (1)
Once separated, the components can be identified and quantified by the mass spectrometer. (1)

Unit Exercise (p.206)

17 The dioxin levels in air are generally measured through instrumental analysis but not gravimetric analysis or volumetric analysis.

a) Suggest a source of dioxins in air.

b) Explain why there is a need to measure the dioxin levels in air.

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

c) Suggest an instrumental analytical method for measuring the dioxin levels in air, and state why this method, rather than methods based on gravimetric analysis or volumetric analysis, is to be used.

(HKDSE, Paper 2, 2012, 3(b))

Unit Exercise (p.206)

18 Formaldehyde (methanal) is a common indoor air pollutant.

a) Suggest an indoor source of the pollutant.

Any one of the following:

- Building materials (1)
- Smoking (1)
- Paper products (1)
- Pressed-wood products (1)
- Gas stoves (1)
- Kerosene space heaters (1)

b) State ONE health hazard associated with formaldehyde.

Any one of the following:

- Sore throat (1)
- Cough (1)
- Scratchy eyes (1)
- Nosebleeds (1)

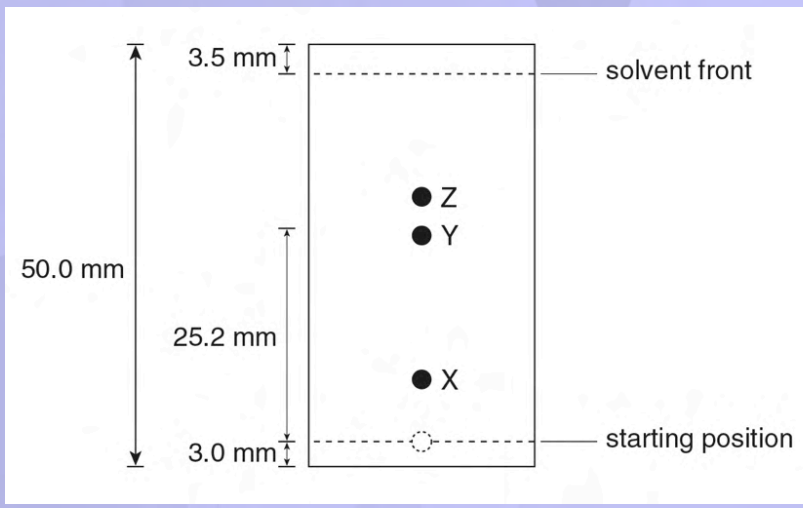
c) Suggest an instrumental analytical method that can be used to determine the level of formaldehyde in indoor air.

High performance liquid chromatography (1)

Unit Exercise (p.206)

19 Silk is a natural fibre. It is made up of two main proteins, fibroin and sericin.

A section of sericin was hydrolysed and the amino acids formed analysed by thin layer chromatography (TLC). The chromatogram obtained and a table of R_f values for amino acids are shown below.



Amino acid	R_f
Alanine	0.38
Aspartic acid	0.15
Leucine	0.75
Methionine	0.58
Threonine	0.35

a) Estimate the R_f value for the amino acid found at Y. Hence identify the amino acid found at Y.

R_f of amino acid found at Y = $\dfrac{25.2 \text{ mm}}{(50.0 - 3.0 - 3.5) \text{ mm}}$

= 0.58 (1)

Thus, the amino acid found at Y is methionine. (1)

Unit Exercise (p.206)

19 (continued)

b) Which of the amino acids (at X, Y or Z) had the longest retention time if this separation was conducted using high performance liquid chromatography with the same stationary phase and mobile phase? Explain your choice.

The amino acid found at X.
This amino acid is adsorbed by the stationary phase most strongly. (1)

Unit Exercise (p.206)

20 Ethanol is the main alcohol found in alcoholic drinks. It is produced by the fermentation of sugars.

a) State ONE effect of alcohol on an individual's ability to drive.

Any one of the following:

- Slow reaction time (1)
- Lack of coordination (1)
- Reduce concentration (1)
- Decrease vision (1)
- Decrease colour distinction (1)
- Inhibit judgement (1)

b) State ONE effect of alcohol on an individual's ability to drive.

Early breathalysers involved the motorist blowing into a tube containing crystals of potassium dichromate mixed with concentrated sulphuric acid.

i) What colour change occurs when acidified potassium dichromate reacts with ethanol? Orange to green (1)

Unit Exercise (p.206)

20 (continued)

b) ii) Write an equation for the oxidation of ethanol using [O] to represent the acidified potassium dichromate

$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$ (1)

or

$CH_3CH_2OH + 2[O] \longrightarrow CH_3COOH + H_2O$ (1)

c) In the case of a positive breathalyser test the motorist is tested a second time using infrared spectroscopy.

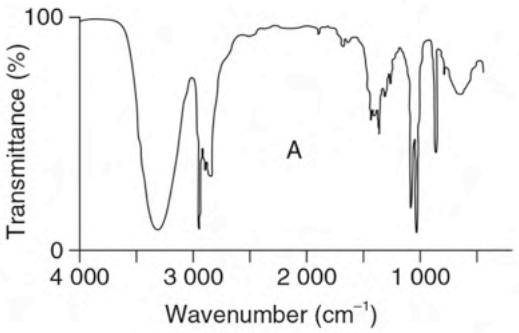
i) State and explain the effect of infrared radiation on molecules.

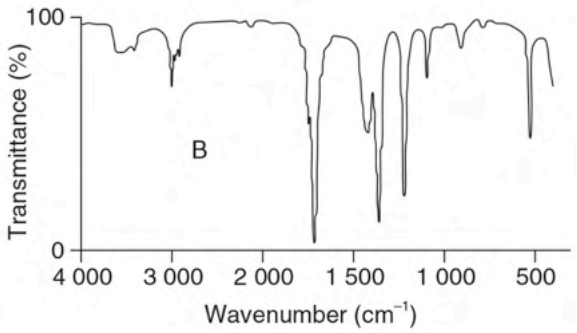
Bonds in a molecule absorb infrared radiation of specific frequencies and vibrate more. (1)

Unit Exercise (p.206)

20 (continued)

c) ii) The infrared spectrum must be carefully read to distinguish between ethanol and propanone, which is found in the breath of diabetics. Use the data in Table 54.1 to determine which spectrum, A or B, is for ethanol. Explain your choice and refer to both spectra in your answer.





(CEA Advanced Subsidiary GCE, Unit AS 2, Module 2, Jan. 2014, 14(b)–(d))

Spectrum A for ethanol

The broad and strong absorption peak at about 3 230–3 670 cm^{-1} corresponds to a O–H bond (alcohol). (1)

Spectrum B for propanone

The strong absorption peak at about 1 680–1 800 cm^{-1} corresponds to a C=O bond. (1)

Unit Exercise (p.206)

21 Fingerprints on porous surfaces like cloth are detected using chemical treatments.

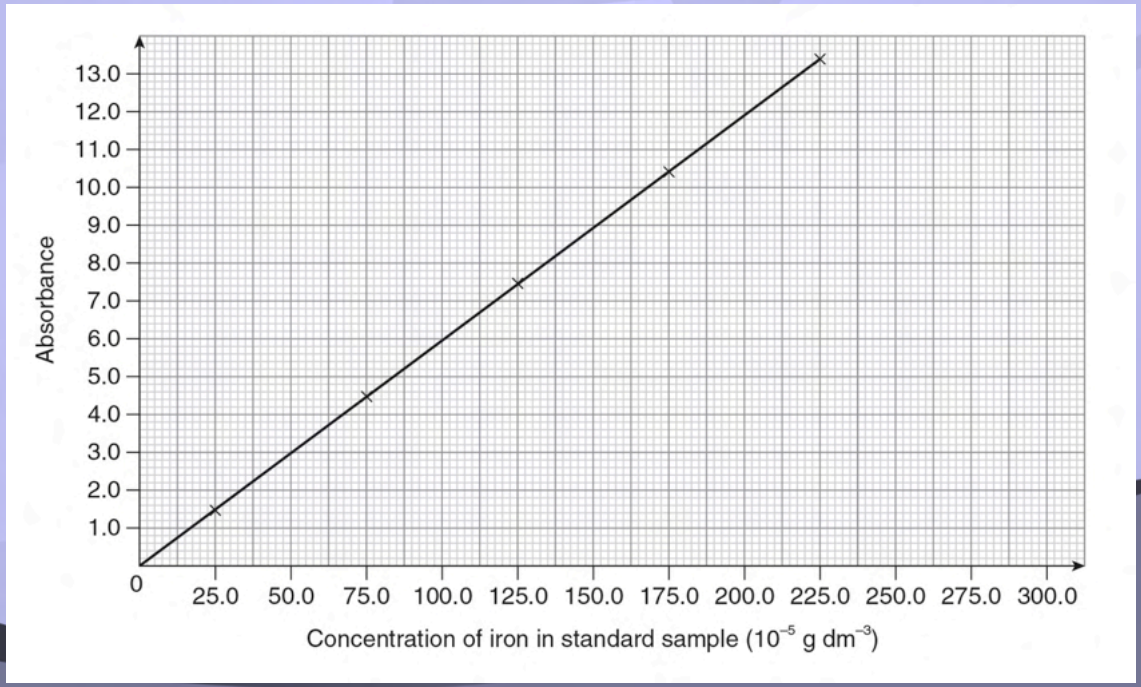
a) Name a suitable chemical used to obtain fingerprints on a woollen coat.
Iodine vapour (1)

b) Give ONE advantage and ONE disadvantage of having a database of fingerprints of all people in Hong Kong.
Advantage: help to fight crime (1)
Disadvantage: human rights / cost / information may be lost (1)

Unit Exercise (p.206)

22 A medical technician analysed iron in blood. She added several reagents to blood serum, one of which reduced iron(III) to iron(II), and another which complexed the iron(II) ion to form a chemical species of red colour. She prepared samples of blood serum with known iron concentration and then measured the absorbance of each sample with a LED based colorimeter having a green LED as the light source.

The calibration curve below shows the absorbance of the standard samples.



Unit Exercise (p.206)

22 (continued)

a) Suggest why a green LED was used as the light.

The chemical species of red colour absorbs green light to a large extent. (1)

b) With reference to the above calibration curve, state the relationship between absorbance and concentration of iron in blood serum.

The absorbance is directly proportional to the concentration of iron. (1)

c) The absorbance of the sample from a patient was 11.7. Find the concentration of iron in the patient's blood serum.

Concentration of iron in patient's blood serum = 196×10^{-5} g dm^{-3} (1)

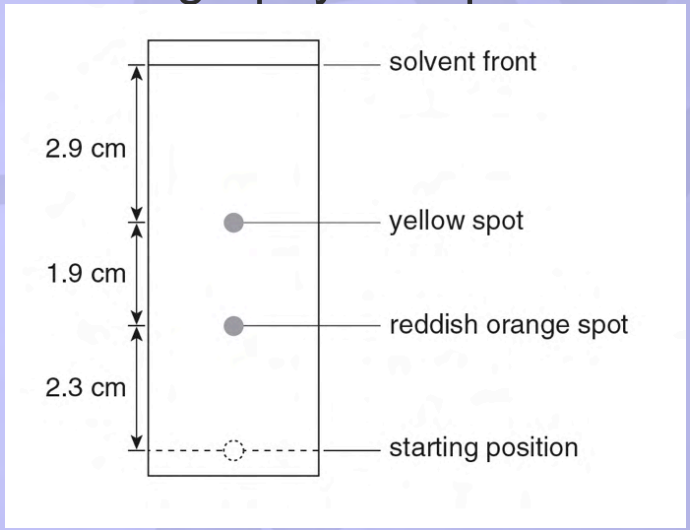
d) If the concentration of iron in normal serum is from 40×10^{-5} g dm^{-3} to 155×10^{-5} g dm^{-3}, what do you expect the doctor to tell the patient?

The concentration of iron in blood serum exceeds the normal level. (1)

Unit Exercise (p.206)

23 The main pigments in a certain brand of tomato paste are lycopene (reddish orange) and β-carotene (yellow). In order to isolate lycopene from the tomato paste, an experiment involving solvent extraction, thin layer chromatography (TLC) and column chromatography was performed.

a) The result of TLC is shown below:



Calculate the R_f value for the lycopene spot.

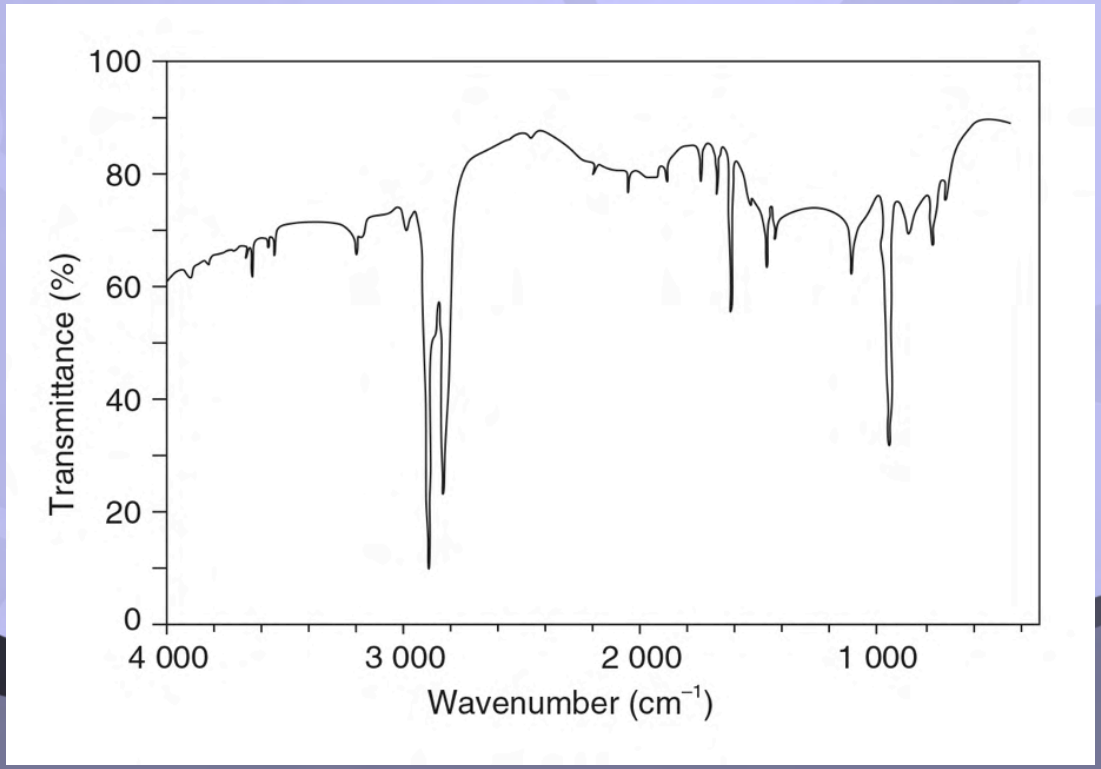
b) With reference to the result of TLC, explain whether the first-collected coloured fraction in the column chromatography is lycopene or β-carotene, if the same stationary phase and mobile phase are used.

Unit Exercise (p.206)

23 (continued)

c) Suggest an instrumental method that can be used to determine the concentration of lycopene in the collected lycopene fraction. State the physical property of the lycopene fraction that needs to be measured.

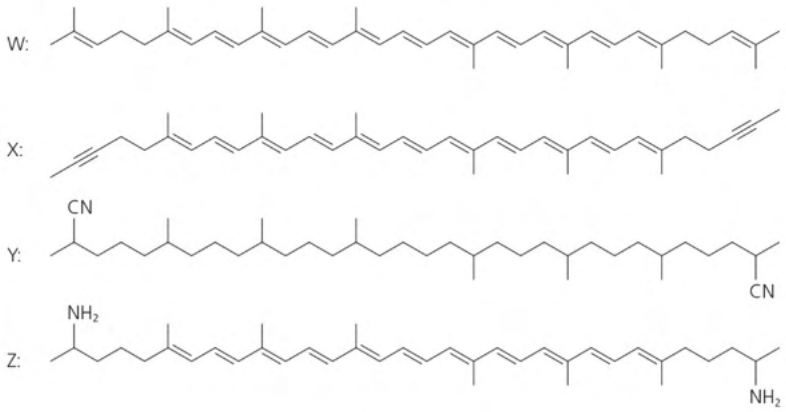
d) The infrared spectrum of lycopene is shown below:



Unit Exercise (p.206)

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

By referring to the characteristic infrared absorption wavenumber ranges (stretching modes) given in the table below, suggest which of the following structures (W, X, Y or Z) may be the structure of lycopene. Explain your answer.



Characteristic infrared absorption wavenumber ranges (stretching modes)

Bond	Compound type	Wavenumber range (cm^{-1})
C=C	alkenes	1 610–1 680
C=O	aldehydes, ketones, carboxylic acids and derivatives	1 680–1 800
C≡C	alkynes	2 070–2 250
C≡N	nitriles	2 200–2 280
O–H	acids (hydrogen-bonded)	2 500–3 300
C–H	alkanes, alkenes, arenes	2 840–3 095
O–H	alcohols, phenols (hydrogen-bonded)	3 230–3 670
N–H	amines	3 350–3 500

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

Topic Exercise (p.216)

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.

Topic Exercise (p.216)

PART I MULTIPLE CHOICE QUESTIONS

1 Which pair would give a bright yellow precipitate when mixed?

A Hydrochloric acid and copper(II) sulphate solution
B Sodium hydroxide solution and iron(III) sulphate solution
C Sodium iodide solution and lead(II) nitrate solution
D Sodium sulphate solution and barium nitrate solution

(OCR Advanced Subsidiary, Chem. B (Salters), H033/01, Jun. 2016, 3)

Explanation:
Sodium iodide solution and lead(II) nitrate solution give a yellow precipitate (PbI_2) when mixed.

$Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$

Answer: C

Topic Exercise (p.216)

2 When chlorine gas is bubbled into an aqueous solution of compound X, a colour change is observed. When the resulting solution is shaken with heptane, the organic layer remains colourless. What may compound X be?

A Sodium iodide
B Sodium bromide
C Iron(II) sulphate
D Copper(II) nitrate

Explanation:
Chlorine can oxidise iron(II) ion to iron(III) ion. When the resulting solution is shaken with heptane, the organic layer remains colourless.

Answer: C

Topic Exercise (p.216)

3 Compound X can decolourise a warm acidified aqueous solution of potassium permanganate and form an orange precipitate when treated with 2,4-dinitrophenylhydrazine.

What could X be?

A $CH_3CH=CHCH_2OH$
B $CH_3COCH_2CH_3$
C $CH_3CH_2CH_2CHO$
D $CH_3CH(OH)CH_2COOH$

Answer: C

Explanation:
Carbonyl compounds (i.e. $CH_3COCH_2CH_3$ and $CH_3CH_2CH_2CHO$) give a precipitate with 2,4-dinitrophenylhydrazine.
$CH_3CH_2CH_2CHO$ can decolourise a warm acidified $KMnO_4(aq)$ while $CH_3COCH_2CH_3$ cannot.

Topic Exercise (p.216)

4 Thallium(III) ions oxidise iodide ions to iodine.

$2I^- \longrightarrow I_2 + 2e^-$

0.0012 mol of Tl^{3+} ions oxidised 0.0024 mol iodide ions.

What is the oxidation number of the thallium ions produced in this reaction?

A +1
B +2
C +4
D +5

Explanation:
1 mole of Tl^{3+} ion oxidises 2 moles of I^- ion, i.e. 1 mole of Tl^{3+} ion accepts 2 moles of electrons in the process.
Thus, Tl^+ ions are produced.

Answer: A

(Edexcel IAL, Advanced, Unit 5, WCH05/01, Jun. 2017, 2)

Topic Exercise (p.216)

5 25.0 cm^3 of a 0.0100 mol dm^{-3} solution of vanadium(II) ions is titrated with an acidified solution containing 0.0200 mol dm^{-3} permanganate ions, MnO_4^-.

$$3MnO_4^- + 5V^{2+} + 4H^+ \longrightarrow 3Mn^{2+} + 5VO_2^+ + 2H_2O$$

What volume, in cm^3, of this solution of permanganate ions is needed for the reaction?

A 7.5
B 15.0
C 20.8
D 41.7

Explanation:

Number of moles of V^{2+} ion in 25.0 cm^3 solution
$= 0.0100 \text{ mol dm}^{-3} \times \frac{25.0}{1\,000} \text{ dm}^3$
$= 2.50 \times 10^{-4}$ mol

According to the equation, 3 moles of MnO_4^- ion react with 5 moles of V^{2+} ion.

i.e. number of moles of MnO_4^- ion $= \frac{3}{5} \times 2.50 \times 10^{-4}$ mol
$= 1.50 \times 10^{-4}$ mol

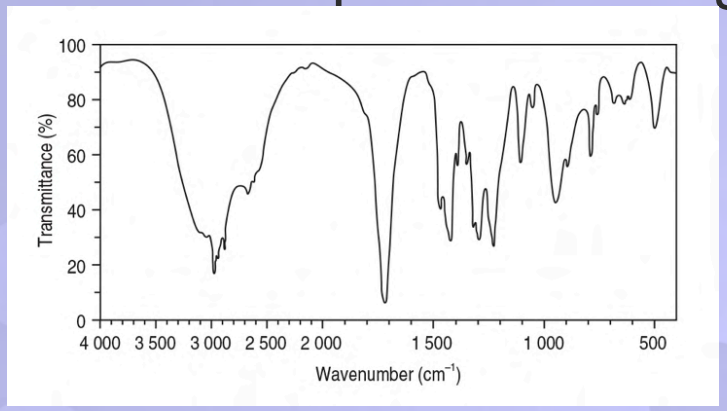
Volume of solution of permanganate ion
$= \frac{1.50 \times 10^{-4} \text{ mol}}{0.0200 \text{ mol dm}^{-3}}$
$= 7.50 \times 10^{-3} \text{ dm}^3$
$= 7.5 \text{ cm}^3$

Answer: A

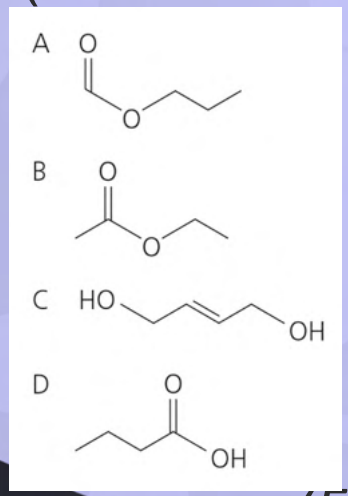
(Edexcel IAL, Advanced, Unit 5, WCH05/01, Jun. 2017, 5)

Topic Exercise (p.216)

6 Which compound would give the infrared spectrum shown?



(Refer to the information given in Table 54.1)



Explanation:
The broad absorption peak at about 2 500–3 300 cm^{-1} shows the presence of a O–H bond (acid).

Answer: D

(Edexcel IAL, Advanced, Unit 5, WCH05/01, Jun. 2017, 16)

Topic Exercise (p.216)

7 How many structural isomers with the molecular formula $C_4H_{10}O$ give infrared absorptions both at appropriately 1 200 cm^{-1} and at approximately 3 400 cm^{-1}?

(Refer to the information given in Table 54.1.)

A 2
B 4
C 6
D 7

Explanation:
The infrared spectra of alcohols have an absorption peak at about 3 230–3 670 cm^{-1}.
The following alcohols have the molecular formula $C_4H_{10}O$:

Answer: B

(Cambridge Advanced Subsidiary and Advanced Level, 9701/12, Paper 1, Mar. 2018, 30)

Topic Exercise (p.216)

8 In a mass spectrometer, positive ions are accelerated by

A bombarding them with fast-moving electrons.
B bombarding them with fast-moving protons.
C passing them between charged plates.
D passing them through a magnetic field.

(Edexcel IAL, Advanced Subsidiary, Unit 1, WCH01/01, Jan. 2014, 3)

Answer: C

Topic Exercise (p.216)

9 For which of the following mixtures of reagents are the colour changes described correctly?

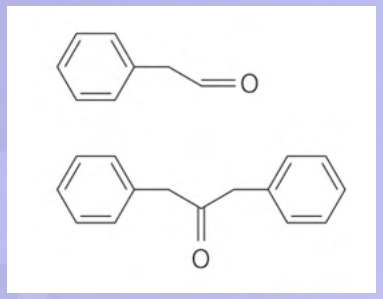
	Reagents	Colour change
(1)	propanal + warm acidified $K_2Cr_2O_7(aq)$	orange to green
(2)	propanone + warm Tollens' reagent	no observable change
(3)	cyclohexene + cold acidified $KMnO_4(aq)$	purple to colourless

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

Answer: D

Topic Exercise (p.216)

10 Many of the flavour and aroma molecules found in chocolate are aldehydes and ketones. Two examples are shown below.

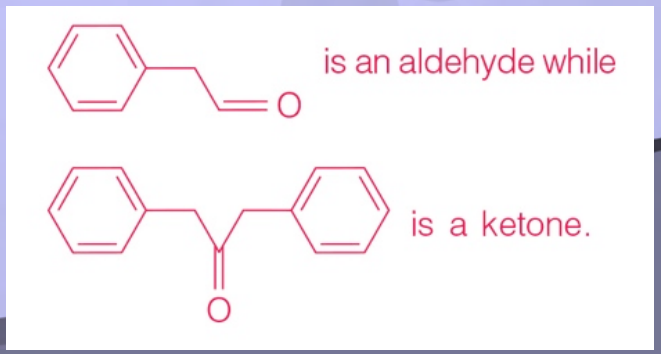


Which of the following reagents can be used to distinguish between the above two compounds?

(1) Acidified aqueous solution of potassium dichromate
(2) Tollens' reagent
(3) 2,4-dinitrophenylhydrazine

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

Explanation:



Answer: A

Topic Exercise (p.216)

Directions:
Each question (Questions 11–12) consists of two separate statements. Decide whether each of the two statements is true or false; if both are true, then decide whether or not the second statement is a correct explanation of the first statement. Then select one option from A to D according to the following table :

A	Both statements are true and the 2nd statement is a correct explanation of the 1st statement.
B	Both statements are true but the 2nd statement is NOT a correct explanation of the 1st statement.
C	The 1st statement is false but the 2nd statement is true.
D	Both statements are false.

Topic Exercise (p.216)

11 1st statement

Thin layer chromatography can be used to check the purity of a product obtained.

2nd statement

A pure compound produces only one spot on the chromatogram.

Answer: A

Topic Exercise (p.216)

12 1st statement

Volumetric analysis is commonly used to show the presence of a prohibited drug in a sample of urine.

2nd statement

Volumetric analysis involves measuring the volume of a solution containing sufficientreagent to react completely with the chemical species being analysed.

Explanation:

Instrumental analytical methods are sensitive and reliable. They are commonly used to show the presence of prohibited drugs in urine samples.

Answer: C

Topic Exercise (p.216)

PART II STRUCTURED QUESTIONS

13 Outline how you would separate $CaSO_4(s)$, $Na_2CO_3(s)$ and $NH_4Cl(s)$ from a mixture of the three compounds.

Heat the mixture. Only $NH_4Cl(s)$ sublimes.
It can be collected on a cold surface. (1)
Add water to the remaining solid mixture. (1)
$CaSO_4(s)$ is insoluble. It can be collected by filtration.
$Na_2CO_3(s)$ can be obtained from its solution by crystallisation. (1)

Topic Exercise (p.216)

14 Suppose you are given four different solutions.
Each solution contains one of the following compounds:

- ammonium sulphate;
- potassium sulphate;
- potassium chloride;
- sodium iodide.

Suggest how you can identify each solution.

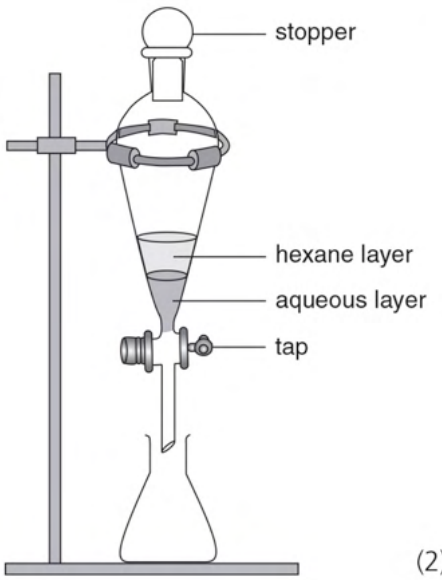
Test with dilute aqueous solution of sodium hydroxide
Warm each solution with dilute NaOH(aq) separately. (1)
Solution of ammonium sulphate gives a gas (ammonia) that turns moist red litmus paper blue. (1)
Solutions of other compounds give no observable change.
Test with aqueous solution of barium nitrate
Add $Ba(NO_3)_2(aq)$ to each of the three other solutions. (1)
Solution of potassium sulphate gives a white precipitate ($BaSO_4$). (1)
The other solutions give no observable change.
Test with aqueous solution of silver nitrate
Add dilute $HNO_3(aq)$ followed by $AgNO_3(aq)$ to each of the two remaining solutions (i.e. KCl(aq) and NaI(aq)). (1)
KCl(aq) gives a white precipitate (AgCl(s)) while NaI(aq) gives a yellow precipitate (AgI(s)). (1)
Add dilute $NH_3(aq)$ to each precipitate. (1)
AgCl(s) dissolves but AgI(s) does not. (1)

Topic Exercise (p.216)

15 A sample of solid carboxylic acid contains some non-polar organic impurities. The acid is extracted from the sample using the steps below.

Step 1 Dissolve the sample in excess NaOH(aq).
Step 2 Shake the solution from *Step 1* with hexane. Collect the aqueous layer.
Step 3 Add HCl(aq) to the aqueous layer until no more precipitate forms.
Step 4 Collect the precipitate by filtration.

a) i) The density of hexane is 0.66 g cm^{-3}. Draw a diagram of the apparatus used in *Step 2*, labelling the organic and aqueous layers.



(2)

Topic Exercise (p.216)

15 (continued)

a) ii) Suggest the necessary safety precaution in *Step 2*.

Open the tap of the separating funnel regularly to release the pressure built up inside the funnel. (1)

b) Briefly explain the purpose of carrying out *Steps 1*, *2* and *3* respectively.

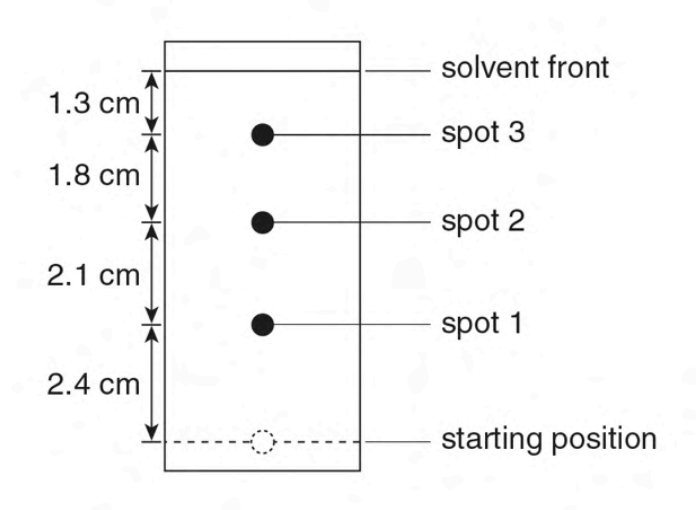
Step 1 To give a salt. (1)

Step 2 Allow the non-polar impurities to dissolve in hexane while the salt to stay in the aqueous solution. (1)

Step 3 Add HCl(aq) to regenerate the carboxylic acid. (1)

Topic Exercise (p.216)

16 A mixture of three compounds (X, Y and Z) was analysed by paper chromatography using a non-polar solvent. The chromatogram obtained was shown below.



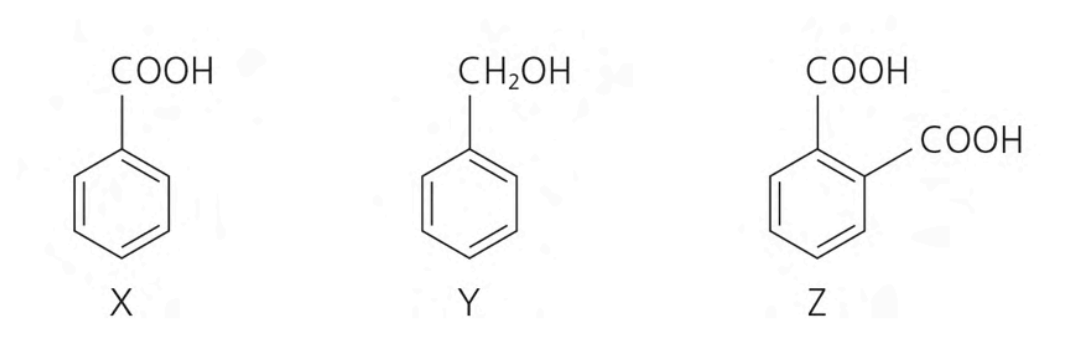
a) Calculate the R_f value for spot 2.

$$R_f \text{ for spot 2} = \frac{(2.4 + 2.1)\text{ cm}}{(2.4 + 2.1 + 1.8 + 1.3)\text{ cm}} = 0.59 \quad (1)$$

Topic Exercise (p.216)

16 (continued)

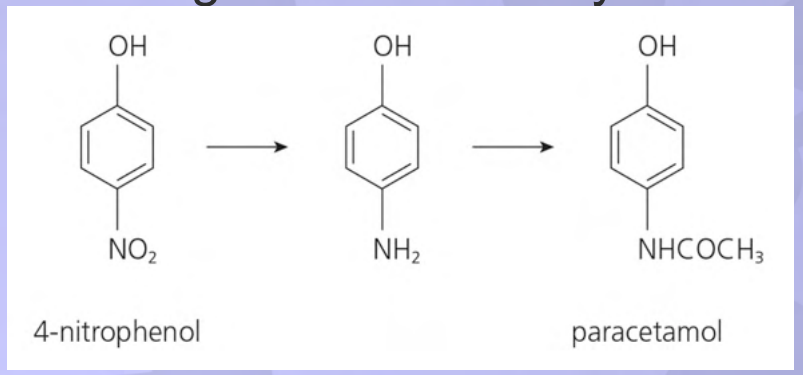
b) Which of the following compounds corresponds to spot 1? Explain your answer.



Compound Z corresponds to spot 1.
The compounds separate because of their different relative solubilities
in the non-polar solvent and in the water in fibres of the paper. (1)
Compound Z is the most soluble in the water / least soluble in the non-polar solvent. (1)
Thus, compound Z travels up the paper most slowly. (1)

Topic Exercise (p.216)

17 Paracetamol is an over-the-counter analgesic. It can be synthesised from 4-nitrophenol as shown below:



A student used thin layer chromatography (TLC) to analyse the products of this synthesis.

The R_f value of paracetamol was found to be 0.40.

a) 4-nitrophenol adsorbs less strongly than paracetamol onto the stationary phase of this TLC plate. Predict whether the R_f value of 4-nitrophenol in this analysis is greater or smaller than that of paracetamol. Explain your answer.

The R_f value of 4-nitrophenol is greater than that of paracetamol. The substance that adsorbs less strongly onto the stationary phase would travel up further from the starting point. (1)

Topic Exercise (p.216)

17 (continued)

b) In another experiment, a mixture of 4-nitrophenol and paracetamol was separated by using column chromatography. The same stationary phase and mobile phase were used.

Explain whether the first-collected fraction was 4-nitrophenol or paracetamol.

4-nitrophenol

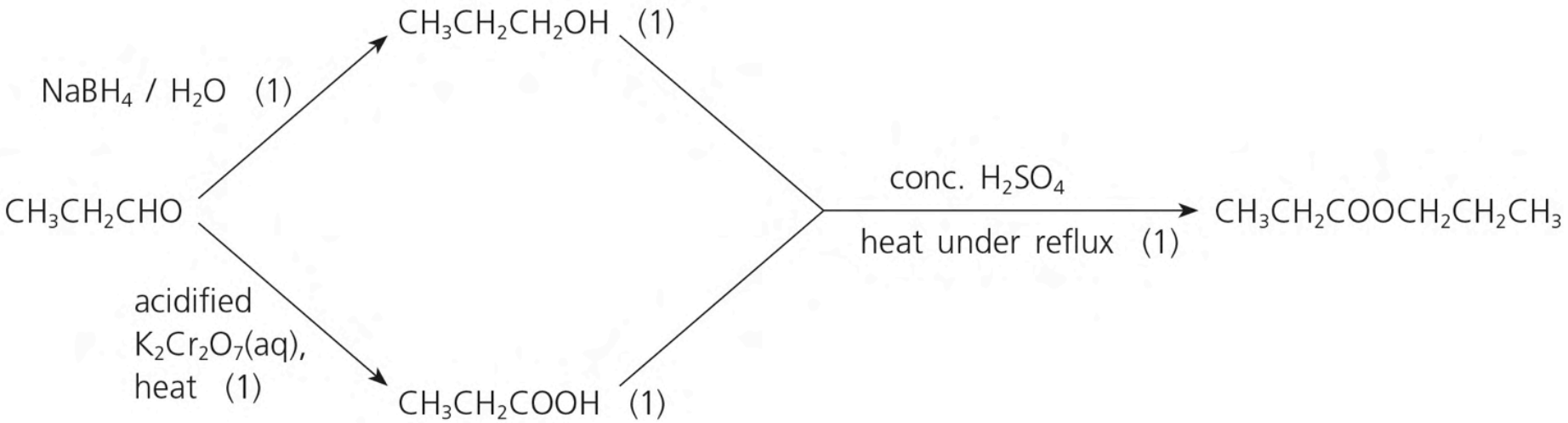
The substance that adsorbs less strongly onto the stationary phase takes a shorter time to reach the bottom of the column. (1)

Topic Exercise (p.216)

18 a) You are provided with propanal, inorganic reagents and organic solvents.

Outline a synthetic route, with NO MORE THAN THREE STEPS, to obtain 1-propyl propanoate.

For each step, give the reagent(s), reaction conditions (as appropriate) and structure of the organic product.



Topic Exercise (p.216)

18 (continued)

b) Identify ONE method that could be used to verify that the substance produced is pure 1-propyl propanoate. Explain how this method would indicate that the product is pure 1-propyl propanoate.

Any one of the following:

- Infrared spectroscopy
  Run an infrared spectrum of the organic product and compare it with the infrared spectrum of pure 1-propyl propanoate. (1)
  OR
  Pure 1-propyl propanoate will not produce broad absorption peak at 2 500–3 300 cm^{-1} (O–H, acid) or 3 230–3 670 cm^{-1} (O–H, alcohol). (1)

- Boiling point
  Determine the boiling point of the organic product.
  Compare the boiling point of the product with the boiling point of pure 1-propyl propanoate from databooks. (1)

- Thin layer chromatography
  Run a thin layer chromatogram of the organic product.
  A single spot suggests that the product is pure. (1)

Topic Exercise (p.216)

19 A sample of mass 0.315 g contained only KCl and KBr. The sample was dissolved in 50 cm^3 of deionised water and titrated with 0.120 mol dm^{-3} $AgNO_3(aq)$, using a chromate indicator. 31.25 cm^3 of $AgNO_3(aq)$ were required to reach the titration end point.

a) State and explain the colour change at the end point.

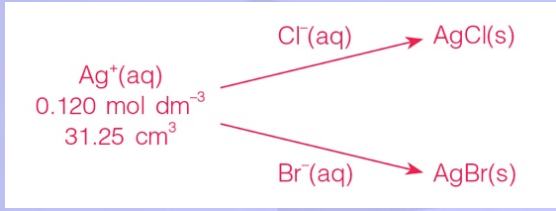
The first appearance of a reddish brown colour indicates the end point. (1)
After all the halide ion has been precipitated as silver halides, one drop of excess silver nitrate solution results in the formation of a reddish brown precipitate of silver chromate.
This signals the end point of the titration. (1)

Topic Exercise (p.216)

19 (continued)

b) Calculate the percentage by mass of KCl in the sample.
(Formula masses: KCl = 74.6; KBr = 119.0)

Let x g be the mass of KCl in the sample, and $(0.315 - x)$ g be the mass of KBr in the sample.



Number of moles of Ag^+ ion in 31.25 cm^3 solution = 0.120 mol dm^{-3} x $\frac{31.25}{1\,000}$ dm^3 = 3.75×10^{-3} mol (1)

1 mole of Ag^+ ion reacts with 1 mole of Cl^- / Br^- ion to give 1 mole of AgCl / AgBr.
i.e. number of moles of Cl^- ion and Br^- ion in the sample = 3.75×10^{-3} mol (1)

Number of moles of KCl = $\frac{x}{74.6}$ mol

Number of moles of KBr = $\frac{0.315 - x}{119.0}$ mol

i.e. $3.75 \times 10^{-3} = \frac{x}{74.6} + \frac{0.315 - x}{119.0}$

$x = 0.220$ (1)

Percentage by mass of KCl in the sample = $\frac{0.220\text{ g}}{0.315\text{ g}} \times 100\% = 69.8\%$ (1)

∴ the percentage by mass of KCl in the sample is 69.8%.

Topic Exercise (p.216)

20 The amount of nitrogen in a sample of cheese was determined using the steps listed below.

Step 1 The nitrogen in 8.80 g of cheese was oxidised to $NH_4^+(aq)$ ion, which was then converted to $NH_3(g)$ by heating with NaOH(aq).

Step 2 The $NH_3(g)$ was distilled into a collection flask containing 50.00 cm^3 of 1.00 mol dm^{-3} HCl(aq).

Step 3 The solution formed was diluted to 250.0 cm^3 with deionised water.

Step 4 25.00 cm^3 portions of the diluted solution were titrated with 0.116 mol dm^{-3} NaOH(aq) using phenolphthalein as an indicator. An average of 22.85 cm^3 of NaOH(aq) was required to reach the end point.

a) Write the equation for the reaction between $NH_3(g)$ and HCl(aq) in *Step 2*.

$NH_3(g) + HCl(aq) \longrightarrow NH_4Cl(aq)$ (1)

or $NH_3(g) + H^+(aq) \longrightarrow NH_4^+(aq)$ (1)

b) State the colour change at the end point of the titration in *Step 4*.

From colourless to pink (1)

Topic Exercise (p.216)

20 (continued)

c) Calculate the percentage by mass of nitrogen in the sample of cheese. (Relative atomic mass: N = 14.0)

Number of moles of NaOH used to neutralise H^+ ion in 25.00 cm^3 diluted solution

$= 0.116 \text{ mol } dm^{-3} \times \frac{22.85}{1\,000} \text{ } dm^3$

$= 2.65 \times 10^{-3}$ mol (1)
= number of moles of H^+ ion in 25.00 cm^3 diluted solution

Number of moles of H^+ ion in 250.0 cm^3 diluted solution
$= 10 \times 2.65 \times 10^{-3}$ mol $= 2.65 \times 10^{-2}$ mol
= number of moles of H^+ ion left after reacting with NH_3 (1)

Number of moles of H^+ ion used in *Step 2* at start $= 1.00 \text{ mol } dm^{-3} \times \frac{50.00}{1\,000} \text{ } dm^3$
$= 0.0500$ mol
Number of moles of H^+ ion reacted with NH_3 = (0.0500 – 0.0265) mol
= 0.0235 mol (1)
= number of moles of NH_3 formed in *Step 1*

Mass of N in cheese $= 0.0235 \text{ mol} \times 14.0 \text{ g mol}^{-1}$
$= 0.329$ g
Percentage by mass of N in cheese $= \frac{0.329 \text{ g}}{8.80 \text{ g}} \times 100\%$
$= 3.74\%$ (1)

∴ the percentage by mass of nitrogen in the sample of cheese is 3.74%.

Topic Exercise (p.216)

21 a) Hydroxylamine ($HONH_2$) reacts with $Fe^{3+}(aq)$ ions under acidic conditions to form products including $Fe^{2+}(aq)$ ions and an oxide of nitrogen. An experiment, consisting of the following two steps, was carried out to deduce the oxidation number of N in the oxide.

Step 1 An aqueous solution containing 0.875 g of $HONH_2$ and excess $Fe_2(SO_4)_3$ was heated under an acidic condition until the reaction was complete. The resulting solution was then diluted to 250.0 cm^3.

Step 2 25.00 cm^3 of the diluted solution was acidified with excess $H_2SO_4(aq)$ and then titrated with 0.0282 mol dm^{-3} $KMnO_4(aq)$ until the end point was reached. The chemical equation for the reaction involved is as follows:

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

i) State the colour change at the end point of the titration.

Topic Exercise (p.216)

21 (continued)

a) ii) Four trials of the titration were carried out and the results are listed below:

Trial	1	2	3	4
Volume of $KMnO_4(aq)$ used (cm^3)	38.34	37.62	37.58	37.60

(I) Calculate a reasonable average of the volume of $KMnO_4(aq)$ used in the titration.

(II) Based on the experimental results, calculate the mole ratio of $HONH_2(aq)$: $Fe^{3+}(aq)$ required for the completion of the reaction in *Step 1*.
(Relative atomic masses: H = 1.0, N = 14.0, O = 16.0)

(III) Given that the oxidation number of N in $HONH_2$ is –1, and the oxidation numbers of H and O remain unchanged, deduce the oxidation number of N in the oxide.

iii) According to (ii)(III), suggest a reasonable empirical formula for the oxide.

Topic Exercise (p.216)

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

21 (continued)

b) Many plants contain useful organic compounds which can be obtained by extraction using suitable solvents.
The leaf of a certain plant contains a useful organic compound S. S can dissolve gradually in a warm organic solvent, and can be extracted from the leaves by using this solvent.

i) 'Heating under reflux' is a method commonly used to carry out this kind of extraction.
State the advantage of this method.

ii) After extraction, the solvent can be removed from the extract by simple distillation.
Draw a labelled diagram for the set-up required for this simple distillation.

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

(HKDSE, Paper 2, 2017, 3(b), (c)(i))

Topic Exercise (p.216)

22 Chlorine was used in swimming pools as a bactericide.

The amount of chlorine present can be determined by adding excess KI(aq) to a known volume of swimming pool water. This reacts to form iodine:

$Cl_2(aq) + 2I^-(aq) \longrightarrow I_2(aq) + 2Cl^-(aq)$

The amount of iodine formed is then found by titration with $Na_2S_2O_3(aq)$ of known concentration.

A student added excess potassium iodide solution to 25.00 cm^3 of the swimming pool water, and titrated the iodine formed with 0.00100 mol dm^{-3} $Na_2S_2O_3(aq)$. The titre was 11.60 cm^3.

a) Briefly describe how the end point of the titration could be determined.

Add $Na_2S_2O_3(aq)$ to the reaction mixture until the mixture changes to a pale straw colour. (1)

Add starch solution. (1)

Add $Na_2S_2O_3(aq)$ dropwise until the mixture changes from dark blue to colourless. (1)

b) Write the equation for the reaction involved in the titration.

$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

Topic Exercise (p.216)

22 (continued)

c) Calculate the concentration of chlorine, in mol dm^{-3}, in the swimming pool water.

$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

0.00100 mol dm^{-3}

11.60 cm^3

Number of moles of $S_2O_3^{2-}$ ion reacted with the iodine formed

$= 0.00100 \text{ mol } dm^{-3} \times \frac{11.60}{1\,000} dm^3$

$= 1.16 \times 10^{-5}$ mol (1)

According to the equation, 1 mole of I_2 reacts with 2 moles of $S_2O_3^{2-}$ ion.

i.e. number of moles of I_2 reacted with $S_2O_3^{2-}$ ion

$= \frac{1.16 \times 10^{-5}}{2}$ mol

$= 5.80 \times 10^{-6}$ mol (1)

= number of moles of Cl_2 in 25.00 cm^3 of swimming pool water

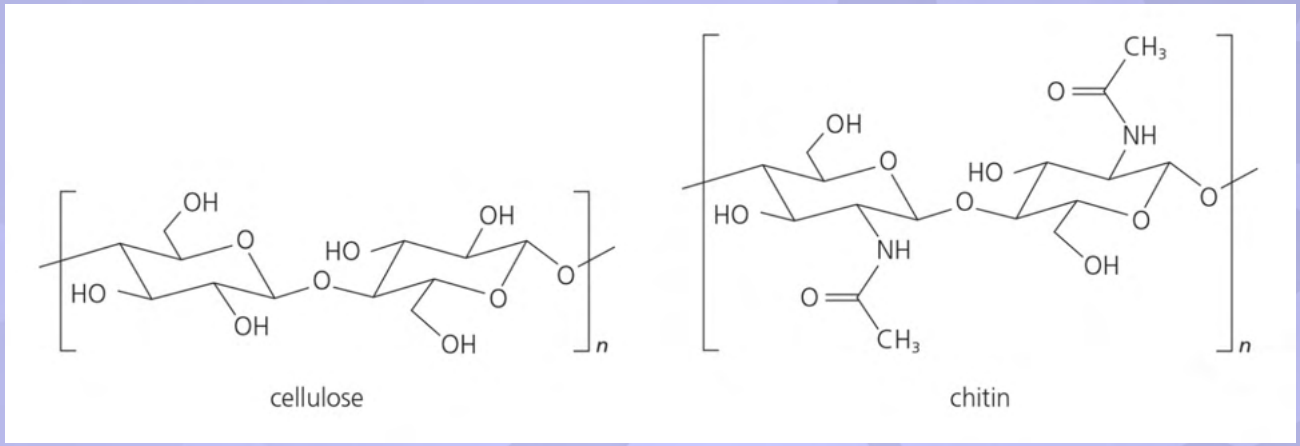
Concentration of Cl_2 in swimming pool water $= \frac{5.80 \times 10^{-6} \text{ mol}}{\frac{25.00}{1\,000} dm^3}$

$= 2.32 \times 10^{-4}$ mol dm^{-3} (1)

∴ the concentration of chlorine in the swimming pool water is 2.32×10^{-4} mol dm^{-3}.

Topic Exercise (p.216)

23 Both cellulose and chitin are natural polymers. Their structures are shown below:



By referring to the data given in the table below, suggest ONE similarity and ONE difference between the infrared spectra of cellulose and chitin.

Characteristic infrared absorption wavenumber ranges (stretching modes)

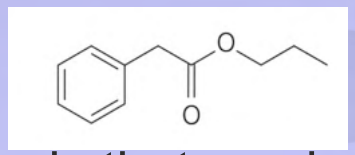
Bond	Compound type	Wavenumber range (cm^{-1})
C=C	alkenes	1 610–1 680
C=O	aldehydes, ketones, carboxylic acids and derivatives	1 680–1 800
C≡C	alkynes	2 070–2 250
C≡N	nitriles	2 200–2 280
O–H	acids (hydrogen-bonded)	2 500–3 300
O–H	alcohols, phenols (hydrogen-bonded)	3 230–3 670

(HKDSE, Paper 2, 2016, 3(a)(iii))

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

Topic Exercise (p.216)

24 The structure of ester E is shown below.



X and Y are two compounds that can be made by hydrolysis of E.

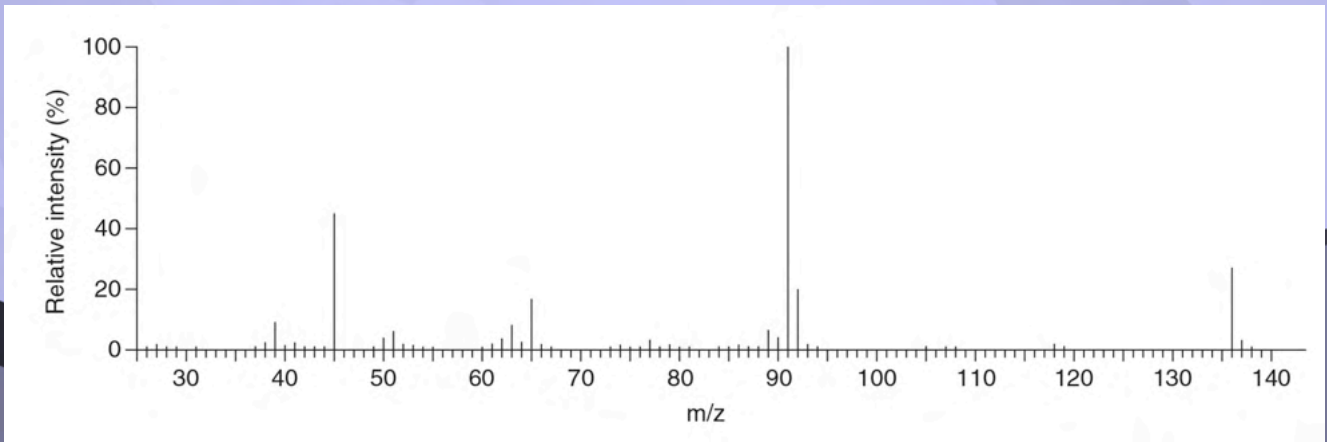
a) Give the systematic name of E.

1-propyl 2-phenylethanoate / 1-propyl phenylethanoate (1)

b) X has the following composition by mass:

C 70.6% H 5.9% O 23.5%

The mass spectrum of X is shown below.



Topic Exercise (p.216)

24 (continued)

b) i) Calculate the empirical formula of X.
(Relative atomic masses: H = 1.0, C = 12.0, O = 16.0)

There are 70.6 g of carbon, 5.9 g of hydrogen and 23.5 g of oxygen in 100 g of X.

	Carbon	Hydrogen	Oxygen	
Mass of element	70.6 g	5.9 g	23.5 g	
Relative atomic mass	12.0	1.0	16.0	
Number of moles of atoms	$\frac{70.6\text{ g}}{12.0\text{ g mol}^{-1}} = 5.88\text{ mol}$	$\frac{5.9\text{ g}}{1.0\text{ g mol}^{-1}} = 5.9\text{ mol}$	$\frac{23.5\text{ g}}{16.0\text{ g mol}^{-1}} = 1.47\text{ mol}$	(1)
Mole ratio of atoms	$\frac{5.88\text{ mol}}{1.47\text{ mol}} = 4$	$\frac{5.9\text{ mol}}{1.47\text{ mol}} = 4$	$\frac{1.47\text{ mol}}{1.47\text{ mol}} = 1$	(1)

$\therefore$ the empirical formula of X is C_4H_4O.

ii) Deduce the molecular formula of X.

Let $(C_4H_4O)_n$ be the molecular formula of X.

Relative molecular mass of X = n(4 x 12.0 + 4 x 1.0 + 16.0)
= 68n

i.e. 68n = 136
n = 2 (1)

$\therefore$ the molecular formula of X is $C_8H_8O_2$.

Topic Exercise (p.216)

24 (continued)

b) iii) Suggest ONE chemical species corresponding to each of the signals at m/z = 45 and 91.

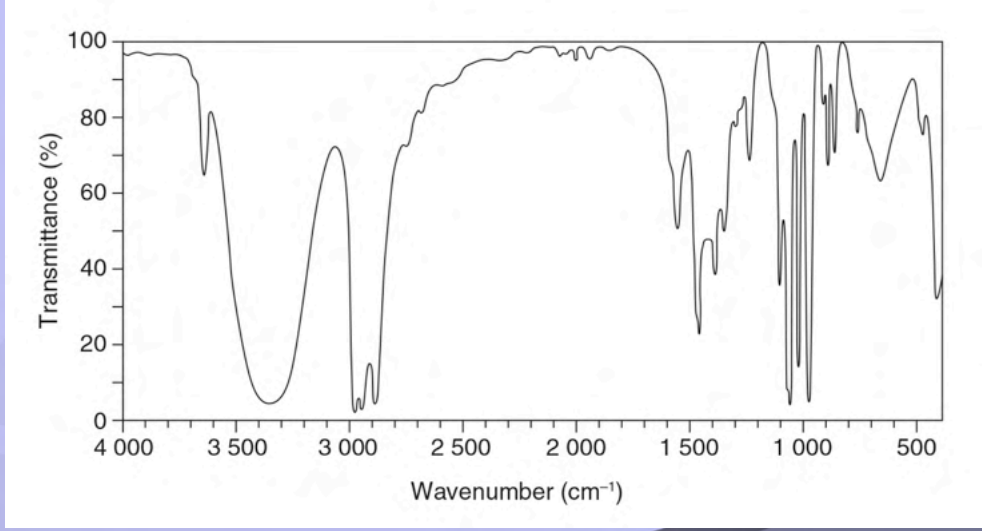
The peak at m/z = 45 corresponds to $COOH^+$ ion. (1)

The peak at m/z = 91 corresponds to $C_6H_5CH_2^+$ ion. (1)

iv) Write an equation for the fragmentation of the parent ion to give the ion which produces the signal at m/z = 91.

$[C_6H_5CH_2COOH]^{+\cdot} \longrightarrow C_6H_5CH_2^+ + \cdot COOH$ (1)

c) The infrared spectrum of Y is shown below.



(Refer to the information given in Table 54.1.)

Topic Exercise (p.216)

24 (continued)

c) i) Give the structure of Y and explain how the infrared spectrum confirms the identity of the functional group present.

The structure of Y is $CH_3CH_2CH_2OH$. (1)
The broad and strong absorption peak at about 3 230–3 670 cm^{-1} indicates the presence of O–H bond (alcohol). (1)

ii) Give the structure of X and explain how its infrared spectrum differs from that of Y.

The structure of X is $C_6H_5CH_2COOH$.
The broad and strong absorption peak at about 2 500–3 300 cm^{-1} indicates the presence of O–H bond (acid). (1)
There is also a strong absorption peak at about 1 680–1 800 cm^{-1} due to C=O bond. (1)

Topic Exercise (p.216)

25 X and Y are isomeric compounds with their structures shown below:

a) Suggest, with explanation, how X and Y can be differentiated from their respective mass spectra.

b) The melting point of X is 50 ˚C while that of Y is 77 ˚C. Both of them are insoluble in water but soluble in dichloromethane. When treated with dilute $Na_2CO_3(aq)$, no reaction occurs for X but reaction occurs for Y to form a soluble salt.

i) 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.

ii) Suggest how you can identify that the solid obtained in (i) is pure compound Y.

(HKDSE, Paper 2, 2016, 3(c))

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

Topic Exercise (p.216)

26 Compound X is the main component of cinnamon oil. Some chemical tests are carried out to find the structure of X.

Test 1 X decolourises both aqueous bromine and acidified aqueous solution of potassium permanganate.

Test 2 X gives a positive result when tested with 2,4-dinitrophenylhydrazine.

Test 3 X gives a positive result when tested with Tollen's reagent.

a) With reference to the result of each test, suggest ONE functional group that may be present in X.

i) *Test 1* C=C bond (1)
ii) *Test 2* Carbonyl group (1)
iii) *Test 3* Aldehyde group (1)

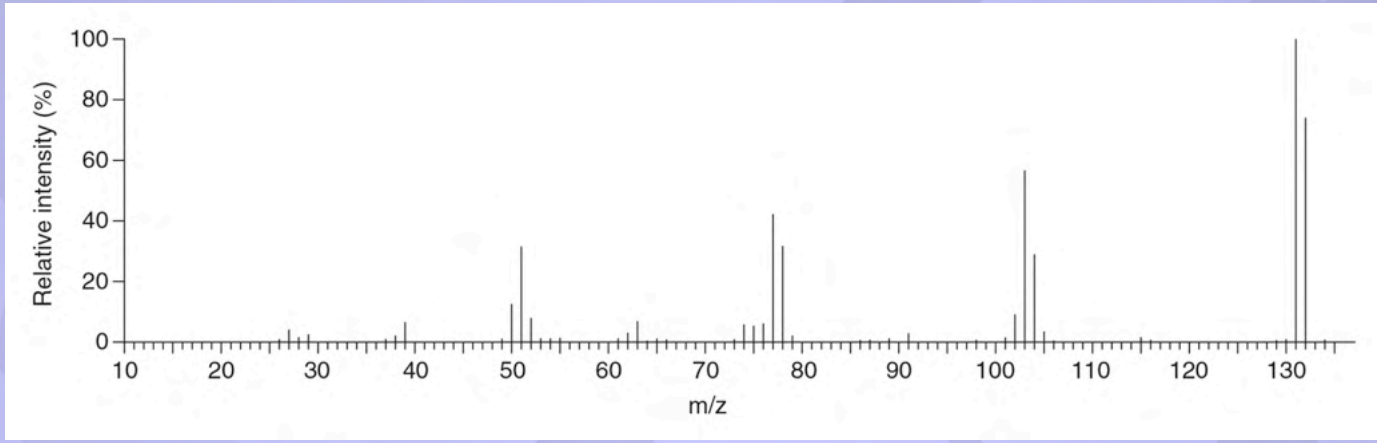
b) State the expected observation in *Test 3*.

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

Topic Exercise (p.216)

26 (continued)

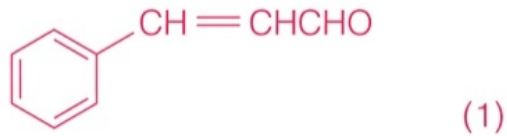
c) X has the empirical formula C_9H_8O and its mass spectrum is shown below.



i) Suggest ONE chemical species corresponding to each of the signals at m/z = 77 and 103.

m/z value	Corresponding chemical species	
77	$C_6H_5^+$	(1)
103	$C_8H_7^+$	(1)

ii) Draw a possible structure of X.



(1)

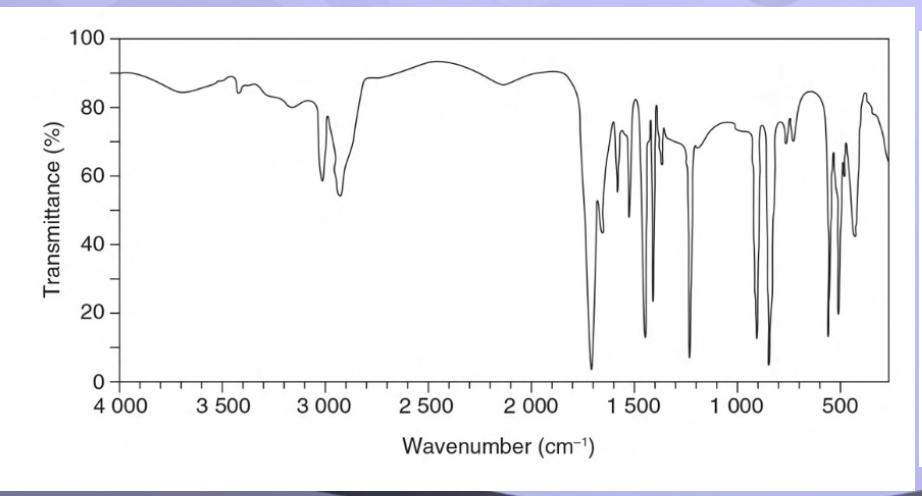
Topic Exercise (p.216)

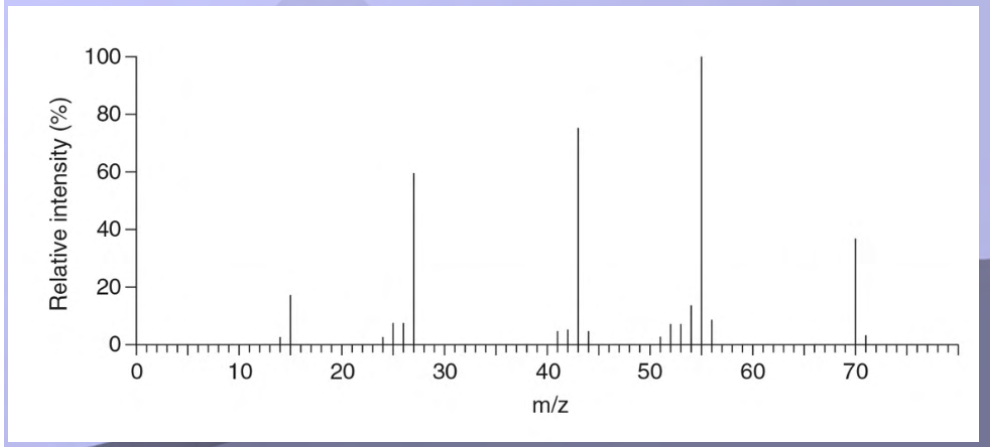
27 A liquid mixture consists of two organic compounds X and Y:

	X	Y
Molecular formula	C_4H_6O	C_4H_8O
Boiling point (°C)	81.4	79.6

a) Explain why fractional distillation is NOT a suitable method to separate X from the mixture.

b) X gives the following infrared spectrum and mass spectrum:





Topic Exercise (p.216)

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

27 (continued)

b) i) By referring to the infrared spectrum and the information given in the table below, deduce one functional group that may be present in X.

Characteristic infrared absorption wavenumber ranges (stretching modes)

Bond	Compound type	Wavenumber range (cm^{-1})
C=C	alkenes	1 610–1 680
C=O	aldehydes, ketones, carboxylic acids and derivatives	1 680–1 800
C≡C	alkynes	2 070–2 250
C≡N	nitriles	2 200–2 280
O–H	acids (hydrogen-bonded)	2 500–3 300
C–H	alkanes, alkenes, arenes	2 840–3 095
O–H	alcohols (hydrogen-bonded)	3 230–3 670
N–H	amines	3 350–3 500

ii) By referring to the mass spectrum, suggest one chemical species corresponding to each of the signals at m/z = 43 and 55.

iii) According to (i) and (ii) above, draw a possible structure of X.

c) Compound Y shows a positive result in 2,4-dinitrophenylhydrazine test, and a negative result in Tollens' reagent test. Deduce what Y may be.

(HKDSE, Paper 2, 2018, 3(c))