Surfing

NSW CHEMISTRY 7&8

Module 8

APPLYING CHEMICAL IDEAS

CONTENT FOCUS

In this module you will:

- Appreciate that the identification and analysis of chemicals is important in many fields, including scientific research, medicine, environmental management, quality control, mining.
- Investigate methods used to identify and measure quantities of chemicals.
- Investigate and process data involving the identification and quantification of ions present in aqueous solutions.
- Deduce or confirm the structure and identity of organic compounds using data from reactions.
- Determine structural information using proton and carbon-13 nuclear magnetic resonance (NMR) spectroscopy.

61 Introduction To Inorganic Analysis

There is a whole branch of chemistry, called **analytical chemistry**, which is the study of the separation, identification and quantification of the chemical components of materials – all sorts of materials, from rocks, water and the atmosphere, to food, living tissue and manufactured products. Some tests are based on traditional techniques, others are based on the use of instruments, which allow more sensitive and accurate measurements. Some tests use micro techniques involving very small testing samples, others use larger quantities. Some can be carried out in the field, others in laboratories.

Analytical chemistry has applications in many fields such as environmental analysis and monitoring, forensic science, medical analysis, bioanalysis, materials analysis and quality control in industry.

You have already looked at a number of analytical techniques during this course including both quantitative and qualitative testing techniques.

Qualitative techniques include flame tests, precipitation tests, paper chromatography and thin layer chromatography (TLC). These aim at identifying the presence of substances but without measuring the amount present.

Quantitative techniques include gravimetric analysis, atomic absorption spectroscopy (AAS), colorimetry, mass spectrometry, gas chromatography and high performance liquid chromatography (HPLC). These techniques can not only detect the chemicals present, they can also measure the amount present.

Need for analysis and monitoring Measurement and analysis are fundamental to both theoretical chemistry and its applications. There are many reasons why we may want to analyse the composition of substances around us.

- Food needs to be analysed and labelled to show contents and energy values. People with allergies need to be able to avoid foods that contain any substance to which they are allergic (e.g. nuts, lactose or gluten).
- Biological samples such as blood and urine need to be analysed so that doctors can diagnose illness and also to detect any drugs used by athletes and measure drug or alcohol levels in drivers.
- Pollution of the environment must be monitored and the source of pollution found in order to prevent more pollution. Pollution in the atmosphere and water has adverse effects on humans and the environment.
- Crime scenes, and artefacts found there, need to be analysed by the forensic scientist to help determine whether people are innocent or guilty.
- The discovery and uses of pharmaceutical drugs involves analysing natural substances that are found useful so they can be manufactured synthetically.
- Soil needs to be analysed to ensure it contains all the minerals needed for the growth of crops, and no harmful substances such as heavy metals or asbestos. Crops need to be analysed to be sure there are no residues of pesticides or other contaminants.
- Water must be analysed. Our water supplies must be monitored to ensure the water is safe to drink. Waste water also needs to be constantly monitored to ensure that it is safe to be released into the environment and will not harm aquatic organisms or lead to eutrophication.
- Quality control depends on analysis, and this is essential not only for foods, but also other products such as building materials, and pharmaceuticals.
- During many industrial production processes, analysis and monitoring is continuous to ensure the safety of the process and also to ensure that the product produced meets the relevant standards. We need to be sure that products meet the claimed specifications, that they contain no impurities, and that they are safe to use.

To analyse the composition of substances for the presence of **inorganic ions**, there are many methods available. You can make use of flame tests, solubility rules (precipitation and complexing reactions), acid/base reactions, gravimetric analysis and titrations. Many of these you are already familiar with. You can also use instrumental analysis with procedures such as colorimetry, chromatography, ultraviolet-visible spectroscopy and atomic absorption spectroscopy.

QUESTIONS

1. What is analytical chemistry?
2. Distinguish between qualitative testing and quantitative testing and give two examples of each.
3. Identify two areas where the analysis and monitoring of substances is essential and explain why this is necessary.

62 Water Pollution and Monitoring

The ionic content of water varies with its source. The ions most commonly found in surface water are shown in Table 62.1.

Table 62.1 Ions in water.

Cations	Anions
Sodium (Na^+)	Chloride (Cl^-)
Calcium (Ca^{2+})	Sulfate (SO_4^{2-})
Magnesium (Mg^{2+})	Carbonate (CO_3^{2+})
Potassium (K^+)	Bicarbonate (HCO_3^-)

Trace elements may also be present such as copper, zinc, iodide and magnesium ions. Although essential for life in small quantities, larger concentrations of these ions can be harmful to both plants and animals. Many Australian aquatic organisms can only tolerate small variations in ion concentrations.

Sources of ions in water

Rocks and soils over which water flows and the rate of flow affect water content. Rivers leach out minerals from rocks and soils, delivering billions of tonnes of salts into the oceans every year. The minerals dissolved depend on the composition of the rocks over which the water passes. For example, water which contains dissolved carbon dioxide will be acidic and may dissolve carbonates from rocks such as limestone and thus add calcium and carbonate ions to the water.

$$CaCO_3(s) + 2H_2CO_3(aq) \rightarrow CO_2(g) + Ca(HCO_3)_2(aq) + H_2O(l)$$

Natural erosion and clearing land for agriculture or buildings also releases salt from the soil and ground water and increases the concentration of dissolved ions.

Sea spray is a source of ions in fresh water. These ions reach the atmosphere and fall again dissolved in rain.

Discharge of **wastes from mines, power stations and other industries** pollutes water.

Domestic sewage water, stormwater run-off and fertilisers are all discharged into waterways from septic tanks and overflow during floods. Inorganic fertilisers include nitrates and phosphates. Run-off from farms carries excess fertilisers into waterways where they can cause algal blooms and eutrophication.

Metals are released into the environment from industries such as metal mining and extraction, chrome plating and battery manufacture. Metals can react with other ions to form dangerous products. They can bond to organic compounds to form highly toxic products that are stored in fat cells and cannot be excreted by organisms.

Organometals such as methylmercury and tetraethyl lead, contain at least one carbon-metal bond. These are of extra concern as they are toxic, stable and they bioaccumulate – they build up in organisms, cannot be excreted, and accumulate in the food chain.

Heavy metals

The sediments of many of our rivers are highly contaminated with high levels of **heavy metals** which are metals with a density greater than 5 g/cm^3 such as lead, cadmium, mercury and arsenic.

It is essential to monitor the ion concentrations in our waterways, our water supplies and our beaches to check for the presence of pollution and ensure the water is safe to use.

Over recent years, two big problems with water pollution in New South Wales have been the development of increasing **salinity** of our waterways and the development of areas of **eutrophication**. Both of these problems are largely due to human activities.

Eutrophication

An increase in soluble nitrate and phosphate ions in waterways stimulates the rapid growth of algae and cyanobacteria. This is called algal bloom.

Figure 62.1 Algal bloom.

The algae die and decay using up the oxygen dissolved in the water during the decomposition process and leaving the water stagnant. This process is called **eutrophication**. Cyanobacteria (commonly called blue-green algae) are a particular problem as they produce chemicals that are toxic for aquatic life and unsuitable to drink. In humans they cause gastric upsets and rashes.

The increase in nitrates and phosphates that starts this eutrophication process is due to increased pollution from sources such as fertilisers, detergents, sewage and meat processing plants. Eutrophication is especially likely to occur during times of drought, when there is not enough water to flush out the river system.

Eutrophication can spread through waterways very quickly, especially during droughts when there is not enough water in the system to flush out rivers. It can also spread to estuaries and marine coastal environments. Eutrophication can lead to the death of fish and other aquatic organisms in the waterways, destroy fisheries. Animals, such as cattle, dogs, native animals and birds that drink from the waterway can become very ill and it cause rashes and illness in humans who drink the water or swim in it.

Monitoring of water discharges from farms and industries can help prevent this problem.

Salinity

In many areas, human activities such as land clearing and irrigation have led to rising water tables and increased salinity of the soil. This is a huge problem in Australia, where large areas of grazing and farming land have become unusable because of the increased concentrations of salts in the water and soil. The Murray-Darling Basin has been affected by salinity. To reduce the salinity, management practices have included changing land use practices, more efficient irrigation, lowering the water table in adjacent flood plains, planting trees and shrubs that are salt tolerant and pumping salty ground water into a basin where the salt can be harvested.

Figure 62.2 Effect of increased salinity near Mildura, Victoria. Photo: Arthur Mostead.

Both of these problems, eutrophication and increasing salinity, have occurred in the **Murray River**.

The **Murray River** is the third longest navigable river in the world and it flows through Victoria, New South Wales and South Australia. It has four major dams, supplying water to thousands of people and provides water to more than 50% of Australia's irrigated crops.

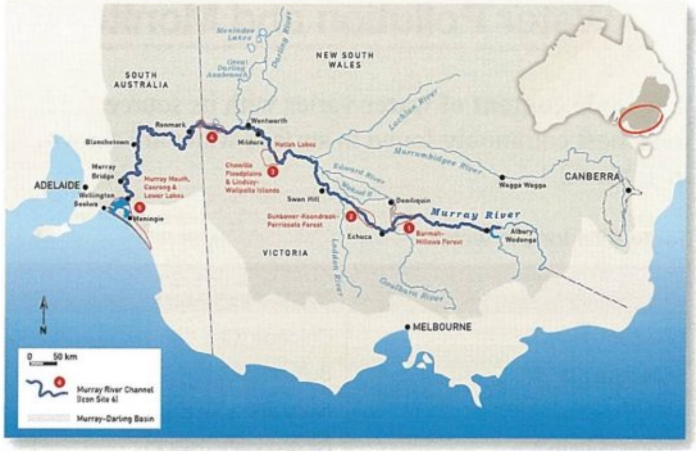


Figure 62.3 The Murray River.

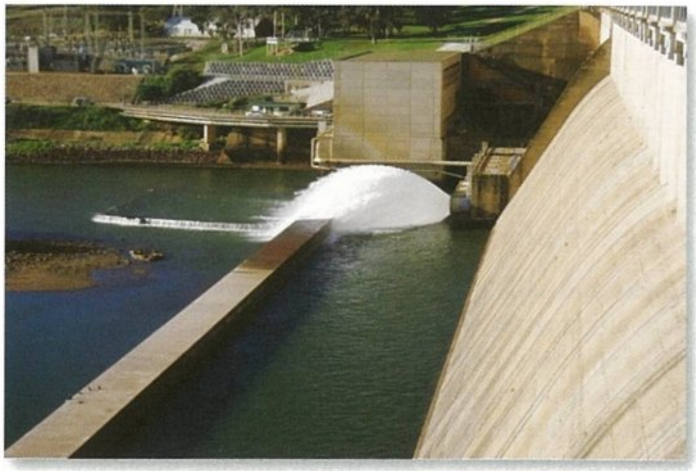


Figure 62.4 The Hume Dam on the Murray River at Albury with water being released downstream.

Two of the issues that are putting the Murray River under threat are increasing salinity and eutrophication. Both these issues are largely due to human activities.

Testing and monitoring of the ion content in rivers, dams and lakes can help us to assess the effects of human activities and find ways to improve affected areas and prevent further areas of eutrophication and salinity increases.

Treatment of water supplies

Water for towns and cities is collected over a large catchment area, stored in dams and sent to treatment plants to ensure it is of a high standard before it is used by the population. Treatment of water includes the following processes.

- Screening.
- Coagulation (flocculation).
- Filtration.
- Ion exchange treatment.
- Chemical treatment.

Screening – A sieve-like device removes solid objects such as twigs, weeds, eels and fish.

Coagulation (flocculation) – Chemicals such as iron(III) chloride or aluminium hydroxide and a cationic polymer are added to make fine suspended particles clump together so they can be more easily filtered out.

Filtration – In most filtration plants, sand filters remove the solids. Membrane filters are being introduced in some plants as, although they are initially more expensive, they are much more efficient and can also filter out micro-organisms.

Ion exchange treatment – Removing nitrates and sulfates. Nitrates are very stable and soluble so the conventional treatment processes of coagulation, precipitation, adsorption or filtration are not suitable. The two main processes used are ion exchange and biological denitrification.

In the **ion exchange process**, water is passed through a bed of synthetic resin beads which remove anions (negative ions such as nitrates and sulfates) from the water, exchanging them for equivalent amounts of chloride ions.

Biological denitrification uses naturally occurring bacteria that can use nitrates for respiration in the absence of oxygen.

Concentrations of sulfates must be monitored as they have a laxative effect which can be dangerous for infants. Small quantities can be removed by distillation or reverse osmosis, but large quantities are removed using ion exchange treatment.

Chemical treatment of water includes the following.

- Potassium permanganate ($KMnO_4$) can convert excess manganese ions (Mn^{2+}) to an insoluble form which can be filtered out.
- Sulfuric acid is added to break down any organic matter which can discolour the water.
- Aluminium and iron salts (Al^{3+} or Fe^{3+}) and cationic polymers can be added to coagulate fine particles so filtering will be more effective.
- Chlorine (often as sodium hypochlorite – $NaOCl$) is used to disinfect water when necessary. The hypochlorite ion (OCl^-) destroys bacteria and protozoa which can cause disease.
- Hydrogen peroxide (H_2O_2) is used to oxygenate surface waters and treat serious pollution.

Water is tested as it enters the plant to determine the treatment necessary. It is retested as it leaves the plant to ensure the treatment has been effective.

QUESTIONS

1. (a) What is meant by a chemical contaminant?
   (b) Identify two chemical contaminants found in our waterways.
2. All organisms need phosphorus and nitrogen compounds. However, too much of these can be harmful, causing algal bloom and eutrophication.
   (a) Why do organisms need phosphorus and nitrogen?
   (b) Research sources of excess nitrates and phosphates in waterways.
   (c) Why is eutrophication of concern?
   (d) Use a flow chart to show the process of eutrophication.
   (e) Outline how excess nitrate and sulfate ions can be removed from water.
3. Salinity is a problem in some Australian waterways.
   (a) Define salinity.
   (b) Salt occurs naturally in the Australian landscape. Salinity (saltiness) of rivers and soil can develop naturally, however when ecosystems are disturbed by humans the salinity of rivers and soil may accelerate. Identify some actions of humans that have led to an increase in salinity of rivers and soil in Australia.
   (c) Research some effects of salinity on buildings.
   (d) Research an area in Australia where salinity is a problem and explain the impact of this on society.
   (e) Research and outline two possible rehabilitation techniques.
4. Many towns and cities in Victoria add fluoride to their water supply.
   (a) Research the reason for the addition of fluoride to water supplies.
   (b) Determine whether fluoride is added to your local water supply.
5. Research an issue involving chemical contamination in the water supply of your local area.
6. Research the impact on concentration of ions in waterways. Draw up a table to summarise the effects using the headings provided as a proforma.

Human activity	Impact	Ion concentrations likely to be changed
Land clearing		
Farming		
Disposal of sewage		
Industries		
Waste disposal		

7. Water from some sources can be 'hard'. Read the following passage about hard water and answer the questions.

Water which contains a high concentration (over 200 mg L^{-1}) of calcium and magnesium ions will not lather easily with soap and is referred to as hard water. These ions form an insoluble scum with soap.

$Ca^{2+}(aq) + 2Na\ stearate(aq)\ (soap) \rightarrow Ca(stearate)_2(s) + 2Na^+(aq)$

Temporary hardness refers to hardness that can be removed by boiling the water. It is caused by the presence of calcium and magnesium hydrogen carbonate. These form the insoluble carbonate when heated, thus removing calcium ions from the water.

$Ca(HCO_3)_2(aq) \xrightarrow{heat} CaCO_3(s) + H_2O(l) + CO_2(g)$

Permanent hardness is caused by the presence of heat-stable salts such as sulfates. These cannot be removed by boiling.

Permanently hard water can be softened by adding sodium phosphate (calgon) or sodium carbonate (washing soda). Bath salts, used to soften bath water, are made of sodium carbonate, with perfume and colouring added.

$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

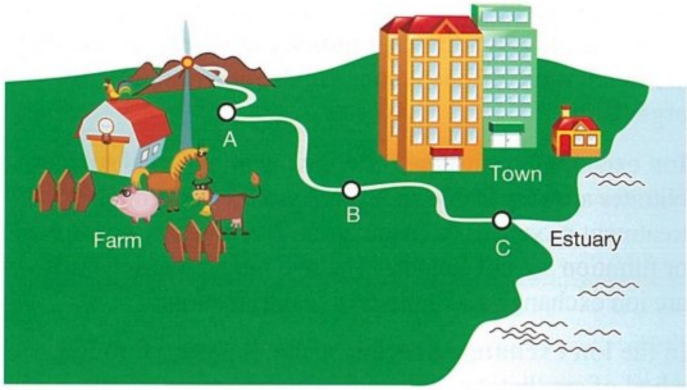
$3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)$

Other methods to remove dissolved substances and soften water include distillation, ion exchange, deionisers and membrane filters. Distillation will remove all dissolved substances. However, this uses a lot of energy so it is expensive for large scale use. In an ion exchange process hard water is passed through a bed of sodium zeolite (naturally occurring silicates) and the calcium and magnesium ions in the water are removed and replaced by sodium ions in the zeolites, leaving soft water.

A deioniser is an ion exchanger containing zeolites that soften water by replacing either calcium and magnesium ions with hydrogen ions, or negative ions with hydroxide ions.

(a) Describe the meaning of hard water.
(b) Distinguish between temporary and permanent hardness.
(c) Hard water poses some difficulties, however it also has advantages. Research and compare the advantages and disadvantages of hard water.
(d) An ion exchange process may be used to remove ions causing hardness of water. Outline how this works.
(e) Distillation removes all dissolved ions. Explain why distillation is not used for purifying water supplies.

8. The diagram below shows a river flowing from a mountain range, across a plain to the sea. Water samples are collected from sites A, B and C and analysed for chloride ion concentration, dissolved oxygen, turbidity, nitrogen and phosphorus content. Predict qualitatively any differences in these factors that you would expect to find in the water samples collected.



9. Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. Evaluate this with regard to water supply in Australia.

10. Check your knowledge with this quick quiz.
(a) Identify two gases that dissolve in water and contribute to acid rain.
(b) Name a rock that reacts with acid rain.
(c) Why are cyanobacteria (blue-green algae) a problem?
(d) The overgrowth of algae and their decay causes a process that results in stagnant water. Name this process.
(e) Identify two ions whose presence in high concentrations contributes to the development of algal bloom.
(f) Water polluted with sewage and industrial wastes would have a (high/low) level of dissolved oxygen.
(g) Filtration of water would separate out substances which were (soluble/insoluble) in water.

63 Collecting and Testing Water Samples

There are a number of reasons for collecting and analysing samples of water from the environment.

Figure 63.1 Collecting and analysing water samples in the field.

Sampling equipment

Appropriate, clean sampling equipment should be selected that will allow you to prevent the sample being contaminated before analysis. Field and laboratory instruments must be correctly calibrated and the manufacturer's instructions followed.

Health and safety precautions

Risk assessments should be made and safety protocols should be followed including the wearing of protective equipment if needed.

You should assume that all streams and waterways are polluted with sewage, toxic substances or harmful micro-organisms and act accordingly. Wear waterproof boots and gloves and wash your hands thoroughly with soap and water after collecting, handling or testing samples.

Sterile techniques

To enable accurate analysis of water, sterile techniques must be used in sampling and it is essential to be trained in using such techniques. This is necessary to protect the person doing the sampling as water may contain microbes, industrial waste or sewage. Using sterile techniques also prevents contamination of the samples being collected.

Clean, sterilised containers should be used and any containers that are damaged or may have been contaminated should be discarded at an appropriate time and place.
Containers should be labelled with a waterproof pen before collecting the sample and only opened when it is time to collect the sample. Be careful not to touch the inside of the collection bottle or lid. You should hold the lid rather than placing it on the ground where it could be contaminated. Then screw the top on the bottle firmly as soon as the sample has been collected. Containers should be stored under suitable conditions for transport to where they are to be tested.

Care should be taken to avoid contamination of the sample, not only at the time of collection but also during transportation to the laboratory. For the later analysis of some substances, it may be necessary to add preservatives to samples, cool them or freeze them. If samples are to be analysed by a commercial laboratory, then they may provide suitable, labelled containers. and preservatives if these are required.

Collecting samples

There are many factors to consider when planning to collect samples of water, including the type of container used, time and method of collection and also when and how samples are to be stored, transported and analysed.

Containers are usually made from glass or a polymer and the choice of which is used may depend on the type of substance to be looked for. For example, glass is suitable to use when looking for organics, however it is unsuitable if you are testing for trace inorganics as these can bind to active sights on the surface of the glass.

It is important to **document** the site and time of collection and also to record any observations of the surrounding area that may be relevant such as the use of the surrounding land and presence of any wildlife. Note the weather at the time as factors such as a recent storm could affect a sample.

Samples should **be collected over a period of time and in different areas**, as samples from any one time or place may not be representative of the whole area. For example, samples from an estuary will vary depending on tides, rainfall and the position of collection. Also pollution or microbes may be concentrated in only one small area and not representative of the whole waterway.

When collecting more than one sample within an area these should be collected several metres apart, so that sediments disturbed by previous sampling do not contaminate later samples.

It is also important to take samples at **different depths** as the composition of the water could vary at different depths depending on the presence or absence of currents and the degree of mixing of water layers. This is especially important in still water, as layers of water develop with varying densities.

Particles may sink or float at different levels depending on density, and also chemical composition can vary with depth. The presence of microbes can also vary with light penetration and thus with depth. Collection containers that can be remotely opened and closed are useful for sampling at different depths. Fast flowing water may be more homogeneous and require the taking of fewer samples.

Equipment for water testing

There is a vast range of equipment available for water collection and testing, depending on the reasons for testing, source of the water to be sampled – from swimming pools to industrial boilers, and the tests that are to be carried out. There are drop test kits and test strips, as well as meters for testing factors such as turbidity, conductivity, dissolved oxygen and pH.

Figure 63.2 Simple water quality test kits are available.

Common tests carried out at the time of collecting samples include measurements of pH, temperature, turbidity, dissolved oxygen, electrical conductivity and tests for the presence of some ions using ion selective electrodes.

Figure 63.3 Electrical conductivity meter.

Testing in the field has the advantage of providing rapid results without the risk of the sample changing as it is transported, e.g. chemicals decomposing or microbe populations either multiplying or dying.

However, precise measurements, particularly for detecting low levels (ppm or ppb) require laboratory analysis using techniques such as atomic absorption spectroscopy (AAS), chromatography, mass spectroscopy and titrations.

Testing samples

Some common analytical tests used include those listed in Table 63.1 and most of these can be carried out in situ.

Table 63.1 Water testing.

Factor being tested	Test
Total dissolved solids	Gravimetric analysis. Electrical conductivity.
Insoluble solids	Gravimetric analysis.
Common ions	Precipitation tests. Flame tests. Gravimetric analysis. AAS for metal ions. Ion selective electrodes, e.g. to test for F^- and S^{2-} ions.
Dissolved oxygen (DO)	Meter with oxygen sensitive electrode.
Hardness (ability to lather with soap)	Gravimetric analysis – precipitate Mg^{2+} and Ca^{2+} ions as carbonates by adding Na_2CO_3.
Turbidity – cloudiness of water caused by suspended solids	Gravimetric analysis. Percentage light transmitted through a standard depth. Depth at which a Secchi disc can be seen.
Acidity	Indicators. pH meter and data logger.
Nitrogen to phosphorus ratio	Colorimetry. Titration. Gravimetric analysis.
Heavy metals	AAS (atomic absorption spectroscopy). Precipitation tests. Bioassay.

If you plan to collect water samples for testing, you should first consult your teacher as there are safety issues to consider and restrictions on collection of water by students that could be contaminated with substances such as sewage. Even if you feel sure the water is safe to collect, you should take precautions such as wearing gloves.

QUESTIONS

1. (a) Why is a risk assessment needed before collecting and analysing water samples in the field?
   (b) Suggest two safety precautions that could be implemented.
2. Identify three sterile techniques to use when collecting water samples in the field.
3. Is there any advantage in taking measurements in situ rather than taking specimens back to the laboratory to be tested?
4. What equipment would you use to test the following factors in the field.
   (a) Acidity.
   (b) Dissolved ions.
   (c) Turbidity.
5. Outline the importance of collecting water samples at various depths and locations when studying water in a lake.

64 Atmospheric Pollution and Monitoring

Layers of the atmosphere

The atmosphere consists of a mixture of gases surrounding the Earth. The atmosphere is layered (Figure 64.1). There are four layers, called the troposphere, stratosphere, mesosphere and thermosphere.

About 90% of the atmosphere occurs in the troposphere, which extends up about 15 km from the Earth's surface. The air in the troposphere is mainly nitrogen (about 78%). Oxygen makes up 21% and argon 0.9%. Other gases, such as carbon dioxide, are present in very small amounts. Clouds, rain and snow all form in the troposphere.

About 9% of the Earth's atmosphere is in a layer above the troposphere called the stratosphere. Most of the ozone occurs here. The remaining 1% of gas molecules that make up our atmosphere occurs in the mesosphere and the thermosphere.

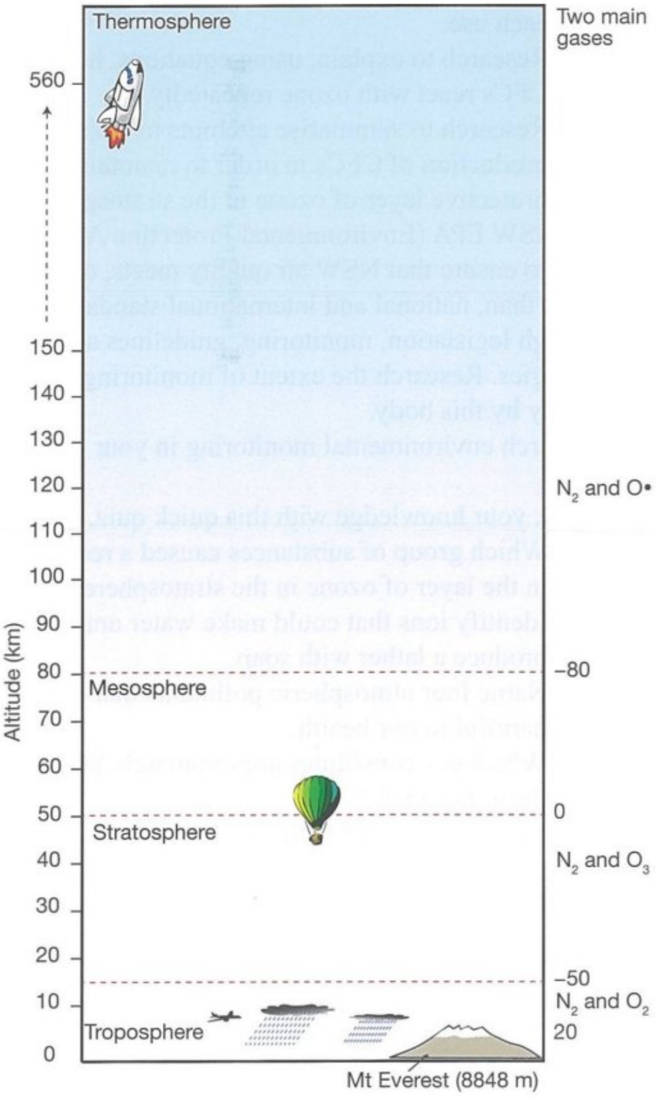


Figure 64.1 Layers of the atmosphere.

Human activities have changed the composition of the atmosphere. Most of the pollutants in the atmosphere have been added by the combustion of fossil fuels derived from petroleum and used in vehicles (cars, trucks, planes, boats) and in the production of electricity.

These pollutants can cause medical problems for us, for example:

- Sulfur dioxide irritates the respiratory system, causes lung damage and may cause asthma. It also contributes to acid rain. An increase in acid rain is causing an increase in acidity of waterways and oceans, which impacts numerous aquatic organisms. Some animals are unable to breed, toxic aluminium ions become more soluble and are released into waterways, the calcium carbonate shells of molluscs are dissolving, corals are bleaching and dying.
- Nitrogen oxides contribute to acid rain and photochemical smog, they decrease lung function, increase susceptibility to respiratory infections and sensitivity to asthma.
- Particles settle in the lungs and cause irritation. Some are carcinogenic.
- Volatile organic compounds contribute to photochemical smog and many are carcinogenic.
- Ozone (O_3) is a pale blue, toxic gas with a sharp, pungent odour. The atmosphere contains 2 ppb (by volume) of ozone, a tiny amount compared to nitrogen (8.8×10^8 ppb). All the ozone in the atmosphere would form a layer only about 3mm thick. Most of this ozone is high up in the stratosphere where it is beneficial as it absorbs UV light coming from the sun. About 10% is in the troposphere where it contributes to pollution and causes health effects such as irritation of our eyes and airways, an increase in respiratory diseases such as asthma, a reduction in lung function and increased susceptibility to infection. Ozone is made by the effect of sunlight on photochemical smog, by photocopying machines, laser printers, electrostatic precipitators and during electrical storms.

As well as these problems, since the beginning of industrialisation, the Earth has become warmer, mainly due to our production of methane, carbon dioxide and water vapour as we obtain and burn fossil fuels. These gases absorb the Sun's radiation and release it as heat. This warming effect is increasing the greenhouse effect, and this causes **global warming**. The temperature of our atmosphere and oceans is increasing, the frequency of extreme weather events is increasing, glaciers and polar ice are melting and causing a rise in sea levels.

Measuring and monitoring the levels of contaminants in our atmosphere, waterways and oceans has allowed us to gather evidence of these changes and to determine the harmful effects due to our burning of fossil fuels.

QUESTIONS

1. (a) List the three most common gases in the atmosphere in decreasing order of abundance. Beside each gas, write its formula and indicate its abundance in the atmosphere. Illustrate this with a pie graph.
   (b) Identify which of these gases is used by both plants and animals for the process of cellular respiration.
   (c) Oxygen gas makes up 20.9% of the Earth's atmosphere by volume, but 23.1% of the atmosphere by mass. Nitrogen on the other hand makes up 78.1% by volume but only 75.5% by mass. Explain.
2. Complete the table by researching natural and anthropogenic sources of common atmospheric pollutants. (Anthropogenic means made by humans and their activities.)

Pollutants	Anthropogenic sources	Natural sources
Nitrogen oxides (NO_x, e.g. NO and NO_2)		
Volatile organic compounds (VOCs)		
Carbon monoxide (CO)		
Carbon dioxide (CO_2)		
Sulfur dioxide (SO_2)		
Particles of matter		

3. Atmospheric pollution is of concern because of its effects on health and its contribution to the greenhouse effect.
   (a) Describe the effects on humans of inhaling each of the following substances.
      (i) Sulfur dioxide.
      (ii) Nitrogen oxides.
      (iii) Particles of matter.
      (iv) Volatile organic compounds.
   (b) When carbon monoxide is inhaled, haemoglobin in the blood combines with the carbon monoxide rather than with oxygen. Explain why this presents a serious health problem.
4. Atmospheric pollution is also of concern because of its contribution to the greenhouse effect.
   (a) Describe what is meant by the greenhouse effect.
   (b) Discuss the consequences of atmospheric pollution increasing the greenhouse effect.
   (c) Identify four gases that are considered to enhance the greenhouse effect.
5. (a) Identify the main source of atmospheric pollution.
   (b) Explain why the combustion of fossil fuels is considered to be an increasing problem.
   (c) In which layer of the atmosphere do these pollutants mainly occur?
6. Another group of chemicals that may be present in the atmosphere and need to be monitored is the haloalkanes called chlorofluorocarbons (CFCs). These are produced by human activities, and they rise up into the stratosphere where they destroy the ozone layer.
   (a) Research to identify some early ways in which CFCs were used. Include a named example of each use.
   (b) Research to explain, using equations, how CFCs react with ozone repeatedly.
   (c) Research to summarise attempts to stop the production of CFCs in order to maintain our protective layer of ozone in the stratosphere.
7. The NSW EPA (Environmental Protection Agency) aims to ensure that NSW air quality meets, or is better than, national and international standards through legislation, monitoring, guidelines and strategies. Research the extent of monitoring of air quality by this body.
8. Research environmental monitoring in your local area.
9. Check your knowledge with this quick quiz.
   (a) Which group of substances caused a reduction in the layer of ozone in the stratosphere?
   (b) Identify ions that could make water unable to produce a lather with soap.
   (c) Name four atmospheric pollutants that could be harmful to our health.
   (d) Which gas constitutes approximately 80% of the atmosphere?
   (e) Identify the layer of the atmosphere closest to the Earth's surface.
   (f) Name the third most common gas in the atmosphere.
   (g) What is the main source of atmospheric pollution?

65 Flame Tests

You will recall that a **flame test** is an analytical technique using the fact that, when heated, the atoms of different metals emit different frequencies of light which are seen as different colours. This is an example of **emission spectroscopy**. Flame tests can be used to check detect some metal ions present in solid samples or in solutions.

Table 65.1 shows some metal ions that can be identified by using a flame test and the colour of the flames produced by each ion.

Table 65.1 Flame tests for cations.

Cation	Positive result for flame test
Barium (Ba^{2+})	Apple-green flame
Calcium (Ca^{2+})	Orange/red flame
Copper (Cu^{+} and Cu^{2+})	Blue-green flame
Potassium (K^{+})	Lilac flame
Sodium (Na^{+})	Orange flame
Lithium	Mauve/purple flame

Cause of coloured light emission

Electrons orbit the nucleus in distinct energy levels. If energy is supplied to the atom, some electrons may absorb a quantum (a specific amount) of extra energy and jump to a higher (outer) energy level. Such electrons are then said to be in an excited state. Eventually the excited electron falls back to its original position – its ground state – giving out that extra energy as it drops back. That extra energy is emitted as visible light. How much energy is emitted determines the wavelength and hence the colour of the light.

Each element has its own unique electron configuration, so it has a characteristic pattern of wavelengths absorbed and emitted. This is called the element's spectrum and it can be used to identify the element and to measure how much of that element is present in a sample being tested.

QUESTIONS

1. The following diagram shows four methods of carrying out the flame test to identify cations (positive ions).
   (a) For each method, identify and explain one safety precaution.
   (b) Explain one other precaution necessary for all methods to prevent contamination.

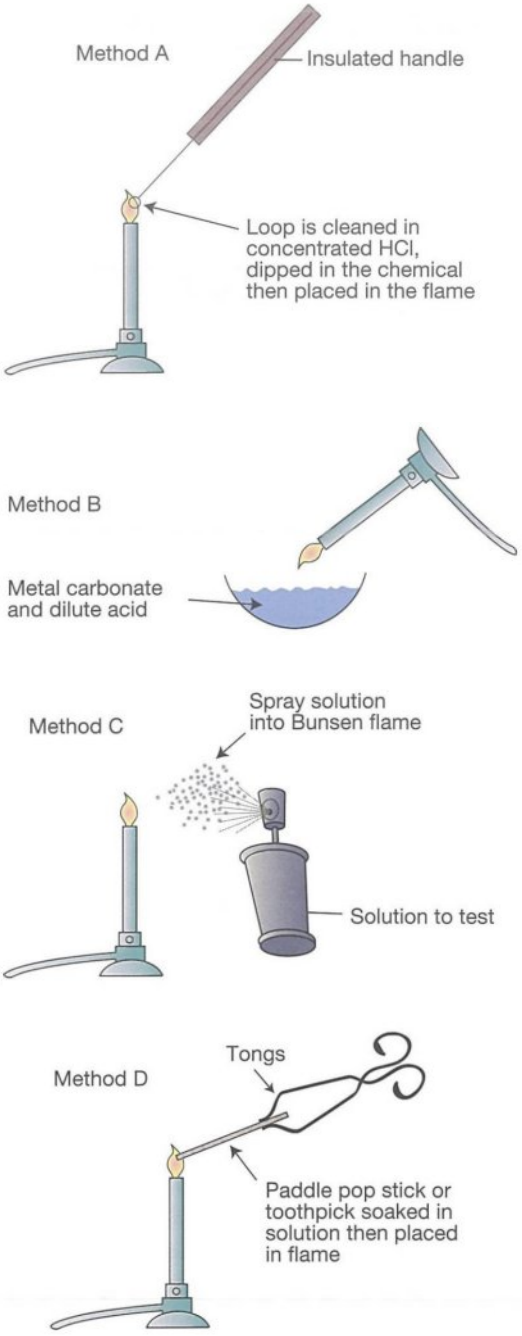


Figure 65.1 Flame tests.

2. Why is it not safe to test for the presence of lead by using the flame test?
3. What is happening at an atomic level to cause the emission of light in a flame test?
4. Complete the following quick quiz.
   (a) Which test involves heating a chemical in a flame and observing the colour of the flame?
   (b) Does the flame test rely on emission or absorption of light?
   (c) Describe the colour of the flame produced by the following ions.
      (i) Barium. (ii) Copper.
      (iii) Calcium. (iv) Potassium.

66 Using Solubility Rules

You are already familiar with solubility rules and the use of precipitate formation, and the colours of the precipitates formed to identify ions dissolved in solutions.

Table 66.1 Some solubility rules.

Soluble	Insoluble
• All nitrates • All acetates • All sulfates (except those of Ca, Ba, Pb, Hg and Ag) • All chlorides, bromides and iodides (except Pb, Hg, Ag) • All ammonium compounds • All sodium and potassium compounds	• All carbonates (except those of Na, K, NH_4^+) • All oxides and hydroxides (except Na, K, Ca, Mg, Ba and NH_4^+) • All sulfides (except those of Na, K, Mg, Ca, Ba and NH_4^+) • All phosphates (except Na, K, and NH_4^+)

Analysis technique

When you are given a solution and asked to identify the ions present, the traditional technique is to follow a flow chart.

A **flow chart** often starts by dividing ions into anions and cations. You will recall that **anions** are negatively charged ions such as chloride (Cl^-) ions and hydroxide (OH^-) ions, whereas **cations** are positively charged ions such as the metal ions, calcium (Ca^{2+}) ions and barium (Ba^{2+}) ions. The flow chart in Question 6 in this chapter shows possible steps to identify some cations.

The usual procedure is to take a sample of the unknown solution, carry out a test to remove some ions by precipitation. If no precipitate forms, then those ions were not present and you use the same sample to move on and carry out another test. If a precipitate does form, then you filter out any precipitate and then carry out the next step using the filtrate. You continue working on the same sample until you have identified all the ions present.

Here are a number of groups of cations whose members can easily be distinguished from each other using solubility rules.

Cations testing

Group 1 – Ag^+ and Pb^{2+}

Silver and lead both have insoluble white chlorides, so you can precipitate these ions out by adding **dilute hydrochloric acid**.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s) \text{ White}$$

Silver chloride goes mauve/violet on standing.

$$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s) \text{ White}$$

Lead chloride is also a white precipitate, it does not change colour on standing and it will dissolve in hot water. You can further confirm the presence of lead ions by adding potassium iodide which forms a yellow precipitate of lead iodide.

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s) \text{ Yellow}$$

You could also precipitate Ag^+ and Pb^2 ions out by **adding NaOH**, as their hydroxides are also insoluble.

$$Ag^+(aq) + OH^-(aq) \rightarrow AgOH(s) \text{ Brown}$$

Silver hydroxide will dissolve in excess ammonium hydroxide.

$$Pb^{2+}(aq) + 2OH^-(aq) \rightarrow Pb(OH)_2(s) \text{ White}$$

However, other ions also produce insoluble hydroxides.

Group 2 – Cu^{2+}, Fe^{2+}, Fe^{3+}

Iron and copper both form insoluble hydroxides. If you **add ammonium hydroxide** or sodium hydroxide to a solution, and it contains any of these ions, you will produce coloured precipitates.

Ion	Colour of precipitates
Fe^{2+}	Green
Fe^{3+}	Red-brown
Cu^{2+}	Deep blue

The colour of the precipitate will help you identify the original ion present.

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s) \text{ Green}$$
$$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s) \text{ Brown}$$
$$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s) \text{ Blue}$$

Copper hydroxide will dissolve in excess ammonium hydroxide.

Group 3 – Ba^{2+}, $Ca^{2+}$and Mg^{2+}

Barium and calcium have insoluble white carbonates which can be precipitated by adding **ammonium carbonate**.

$$Ba^{2+}(aq) + CO_3^{2-}(aq) \rightarrow BaCO_3(s) \text{ White}$$
$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s) \text{ White}$$

The presence of this group of ions in a sample can also be determined by **adding sulfate ions**, for example adding a solution of sodium sulfate or dilute sulfuric acid.

Barium and calcium will form white precipitates of barium sulfate and calcium sulfate. Magnesium will produce a solution of soluble magnesium sulfate.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s) \text{ White}$$
$$Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s) \text{ White}$$
$$Mg^{2+}(aq) + SO_4^{2-}(aq) \rightarrow MgSO_4(aq) \text{ White}$$

If a white carbonate or sulfate precipitate forms, then you can use the flame test to determine whether it is barium (apple-green flame) or calcium (brick-red flame) ions that are present. Magnesium does not produce a coloured flame.

Anion testing

Group 1 – Cl^-, Br^- and I^-

Chlorides, bromides and iodides form precipitates with a solution of silver nitrate. (Note that silver nitrate causes brown stains on skin that will not easily wash off.)

$$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s) \text{ White}$$
$$Br^-(aq) + Ag^+(aq) \rightarrow AgBr(s) \text{ Yellow}$$
$$I^-(aq) + Ag^+(aq) \rightarrow AgI(s) \text{ Yellow}$$

Silver chloride is the most soluble of these three chloride salts, it dissolves readily in ammonium hydroxide solution. Silver bromide and silver iodide do not readily dissolve in ammonium hydroxide.

Group 2 – CO_3^{2-}, SO_4^{2-}, CH_3COO^- and PO_4^{3-}

Carbonate and sulfate ions can be distinguished from each other by **adding dilute hydrochloric acid**. **Carbonate ions react** with dilute acid and release carbon dioxide gas.

$$CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O$$

Carbon dioxide gas can easily be identified by bubbling the gas through limewater; if the limewater goes cloudy, then the gas is carbon dioxide.

Sulfate ions will not produce any carbon dioxide gas with dilute acid.

Acetate/propanoate ions (CH_3COO^-) produce ethanoic acid when reacted with dilute sulfuric acid and this has a smell that you would recognise as vinegar.

$$CH_3COO^-(aq) + H_2SO_4(aq) \rightarrow HSO_4^-(aq) + CH_3COOH(aq)$$

Carbonates and sulfates can also be distinguished from other anions because they both **react with barium ions** (such as in barium nitrate or barium chloride) to produce insoluble white precipitates.

$$CO_3^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaCO_3(s) \text{ White}$$
$$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s) \text{ White}$$

Phosphates also form a precipitate with barium ions, but this precipitate will not form if a few drops of 6 mol L^{-1} acid is added.

A test to confirm the presence of **phosphate ions** is the **ammonium molybdate test**. Phosphate ions react with acidified ammonium molybdate solution to form a deep yellow precipitate of ammonium phosphate molybdate

$$12MoO_4^{2-}(aq) + 3NH_4^+(aq) + PO_4^{3-}(aq) + 36H^+(aq) \rightarrow$$
$$18H_2O(l) + (NH_4)_3PO_4.12MoO_3.6H_2O(s)$$

QUESTIONS

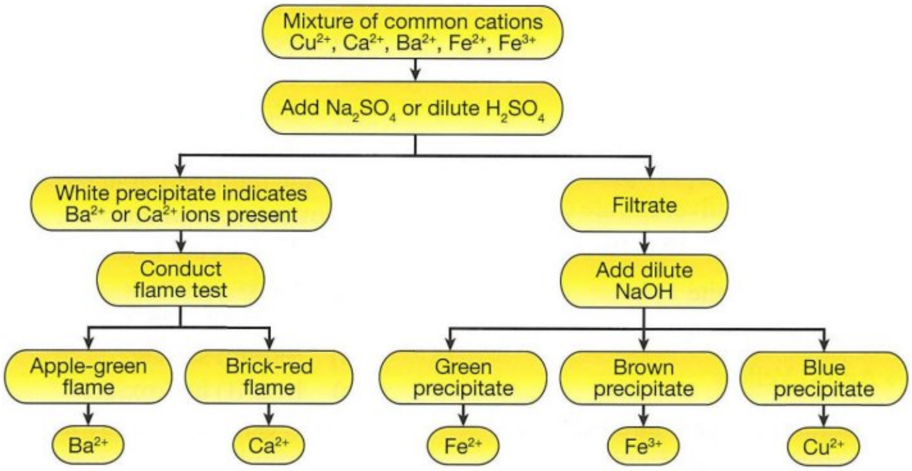
1. Analytical tests are sometimes divided into tests for anions and tests for cations.
   (a) Define anion and give four examples.
   (b) Define cation and give four examples.
   (c) Summarise the analytical tests you have carried out in class for anions and for cations.
2. Use the information in the text to describe the following precipitates.
   (a) Aluminium hydroxide.
   (b) Silver chloride.
   (c) Calcium carbonate.
   (d) Barium sulfate.
   (e) Iron(II) hydroxide.
3. Before carrying out any analysis in the laboratory you would have done a risk assessment to ensure safety when using chemicals.
   (a) Identify four basic handling procedures used in the laboratory.
   (b) Outline precautions needed when using hydrochloric acid to test for the presence of carbonate ions in a sample.
4. A solution is provided and the class carries out a number of tests to find out which ions are present.
   (a) The following results are obtained. Based on these results, identify a substance in the solution.

Test	Result
Add dilute hydrochloric acid	Gas produced that turns limewater milky.
Add ammonium hydroxide solution	A deep blue precipitate is obtained.

   (b) Use a diagram to show how you could use hydrochloric acid to test for the presence of carbonate ions.
5. Write the formula for each compound listed below. Then, based on information in the solubility table (Table 66.1), state whether each substance would be classified as soluble or insoluble.
   (a) Sodium nitrate.
   (b) Potassium carbonate.
   (c) Aluminium carbonate.
   (d) Magnesium sulfate.
   (e) Calcium sulfate.
   (f) Ammonium hydroxide.
   (g) Barium hydroxide.

6. Flow charts such as the one below can be used to help with the analysis of solutions to find out which anions and/or cations are present in solution. Use the information in this chart to answer the questions following.

Cation identification flow chart



Some students tested a local water supply for the presence of cations in solution.

(a) One group added dilute sulfuric acid to a sample of water collected. This produced a white precipitate. A flame test carried out then showed a brick-red flame. Which cations were present in this water sample?

(b) Another group also added dilute sulfuric acid but no precipitate was produced. They then neutralised the solution and added excess dilute sodium hydroxide. A green precipitate was produced which slowly turned brown. Identify the ions present in the sample.

7. A group of students tested water samples for the presence of dissolved anions such as chloride, sulfate, phosphate and carbonate ions. Their method and results are described here.

Method:

- Record observations at each step.
- Add dilute acid in excess.
- Add barium nitrate solution. If a precipitate forms, then add excess barium nitrate until there is no more precipitate being produced. Filter off any precipitate formed.
- To the filtrate, add silver nitrate.
- Filter off any precipitate formed.
- To the filtrate, add ammonium hydroxide solution until any acid is neutralised and the solution becomes basic.
- Add barium nitrate solution and record any observations.

Results:

A lot of bubbles were formed when the acid was added to the water sample.

No precipitate was formed when barium nitrate was added.

The only precipitate formed was a white precipitate formed with the addition of silver nitrate.

Questions:

(a) Construct a flow chart to show the method used by the students.

(b) Based on their results described here, were any anions present in the water sample? Explain.

(c) Sulfate ions and phosphate ions both form white precipitates with barium ions, but barium phosphate is soluble in acid, whereas barium sulfate is insoluble in acid. Predict the results students would observe, using the above method, if sulfate or phosphate ions had been present.

8. Check your knowledge with this quick quiz.

(a) Many compounds are white. Name five white compounds which you have seen in the laboratory.

(b) Name the cation used to test for the presence of chloride ions in water.

(c) Identify the anion which produces a yellow precipitate with lead ions (Pb^{2+}).

(d) When you add ammonium carbonate to an unknown solution, what are you checking for?

(e) What test would you use to distinguish between barium and calcium ions?

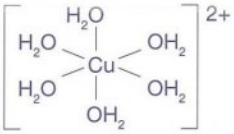
(f) Identify the cation used to test for the presence of sulfate ions.

67 Complex Ions

So far, we have assumed that most ions exist as single ions in solution, however, this is not what really happens, the reality is more complex than that.

Most metal ions, in solution, become bound to molecules of the solvent, forming a **complex ion**. Some complex ions are soluble, but others form precipitates.

For example, copper ions (Cu^{2+}) in solution bond with water molecules which surround it. This complex ion is called the hexaquacopper(II) ion, $[Cu(OH_2)]_6^{2+}$. This ion is blue and soluble in water.



Hexaquacopper(II) ion

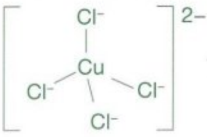
A **complex ion** is an ion which has a metal ion at its centre which is surrounded by other attached ions or molecules.

The solvent molecules attached to a metal ion can be replaced by other molecules or ions to form a new metal complex. Metal ions that form complex ions include Ag^+, Cu^{2+}, Fe^{2+} and Fe^{3+}.

A **complexation reaction** is a chemical reaction that takes place between a metal ion and a molecular or ionic particle that is called a ligand. A **ligand** is a complexing agent and it is a Lewis base (an electron pair donor) because it contains at least one atom with an unshared pair of electrons which it can donate to the central metal cation to form a bond called a dative covalent bond. The metal ion can be surrounded by 2, 4, or 6 ligands to form a complex ion. Complexing agents include CN^-, NH_3 and OH^-.

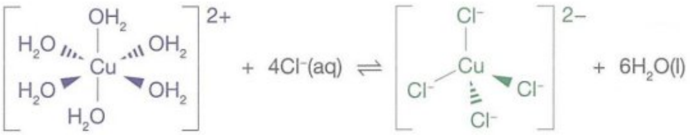
Other complex copper ions

Another complex copper ion is the green **tetrachlorocuprate(II) ion**. This ion is surrounded by four chloride ligands.

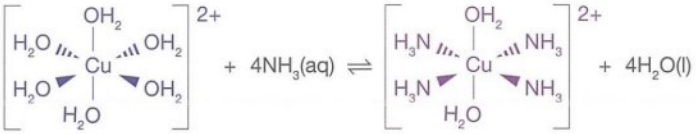


Tetrachlorocuprate(II) ion

The hexaquacopper(II) ion reacts with chloride ions to form a green complex ion, the tetrachlorocuprate(II) ion.



The hexaquacopper(II) ion also reacts with ammonia to form another complex copper ion which is a much darker blue. Because it is a strong base, ammonia can replace the water molecules in the hydrated copper ion to form a new complex ion.



The very distinct blue colour of **the copper-ammonia complex ion** can be used to identify the presence of Cu^{2+} ions. However, if ions such as Fe^{2+} are present, they could react with this complex and form a different product.

Silver ions also form a complex ion with **ammonia.**

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$

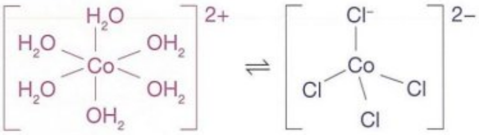
More complex ions

Many transition metal halides form complex compounds. You saw this when you observed equilibrium reactions earlier on in this course.

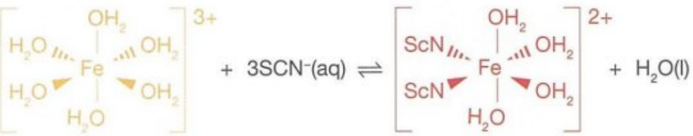
Pink hydrated cobalt chloride crystals ($CoCl_2.6H_2O$) turn blue when dehydrated. These are both complex ions.

$$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$$

Pink Colourless Blue



You also saw the formation of a **complex blood red iron ion** with the addition of a **thiocyanate solution**.



The addition of a solution of potassium cyanide to a solution of a transition metal salt, usually produces a precipitate of an insoluble metal cyanide.

Most complex cyanide ions are quite stable. For example, the blue colour of $CoCl_2$ disappears rapidly when water is added, however the complex ion $CoCl_4^{2-}$ keeps its blue colour when diluted. Such stable complex ions have a high K value.

QUESTIONS

1. Describe how you used complexation reactions and precipitations to analyse inorganic substances.
2. The formation of a complex can be used to identify some cations. Describe the complex formed between:
   (a) Copper and ammonia.
   (b) Iron(III) and thiocyanate ions.
   (c) Phosphate ions and ammonia.
3. A group of students are given a sample of a yellow/brown solid and asked to identify it. They are told that the cations present in their sample could be Ca^{2+}, Ba^{2+}, Pb^{2+}, Cu^{2+}, Ag^{+} or Fe^{3+} and anions present could be Cl^{-} or CO_3^{2-}.
   The table shows tests they carried out and their results.
   (a) Complete the table to show which ions each test eliminates.

Test	Results	Ions eliminated
Add NaOH	White ppte – does not dissolve in excess NaOH.	
Add NH_3	White ppte – does not dissolve in excess. (No complex formed)	
Add HCl(aq)	No reaction	

   (b) The students suspect that the unknown could be iron(III) chloride. Describe separate tests to confirm the existence of Fe^{3+} ions and Cl^{-} ions.

68 Gravimetric Analysis

You will recall that **gravimetric analysis** of a mixture is a technique that allows us to find out the composition of a mixture by separating out the components and weighing them. This allows us to calculate the percentage composition by weight of the component elements and/or compounds in a mixture.

Uses of gravimetric analysis

Gravimetric analysis has many uses such as determining the following:

- Mineral content of ores.
- Total dissolved chemicals in water.
- Suitability of bore water for crops and animals.
- Nutritional content of foods.
- Composition of soils.
- Pollutant concentrations in air and water
- Purity of products, e.g. medicines, industrial chemicals.
- Accuracy (or otherwise) of advertising claims.

Gravimetric analysis is a very slow technique, taking a long time to complete and it involves very careful weighing of the initial sample and the components isolated. The individual components are weighed and the percentage composition is calculated.

Often the mixture can be separated out by physical methods, e.g. if one component is soluble then water can be added to dissolve that component. Then the mixture is filtered, the soluble component being passed through in the filtrate, the insoluble component remaining in the filter paper. The components are then dried and weighed.

Sometimes one component may have to be removed from the mixture being analysed by a chemical reaction. For example, to find the amount of sodium chloride in a weighed sample of salty water, we could precipitate it out by reacting it with an excess of a silver salt such as silver nitrate. This produces a white precipitate of silver chloride that can be filtered, dried and weighed.

$$\text{Silver nitrate} + \text{sodium chloride} \rightarrow \text{silver chloride} + \text{sodium nitrate}$$

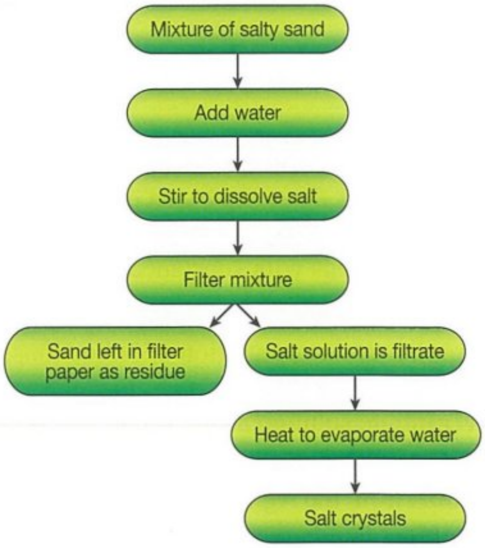
$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

QUESTIONS

1. (a) Define gravimetric analysis.
   (b) Research two uses of gravimetric analysis, explaining why each is necessary.
2. Outline a possible reason for wanting to know the:
   (a) Salinity of water.
   (b) Composition of soil.
3. A group of year 12 students is asked to collect and analyse two samples of a mixture collected from one source at the same time. They decide to collect samples of salt water, filter, evaporate the filtrate and weigh the salts collected. Their results are tabulated below.

Measurement	Sample 1	Sample 2
Mass of 100 mL salt water (g)	101.37	101.46
Mass of residue after filtering (g)	0.21	0.29
Mass of salt left after evaporation (g)	3.64	3.82
Percentage of salt in salt water (%)		

   (a) Calculate the percentage of salt in the students' two samples.
   (b) Justify their use of salt water as a mixture.
   (c) The teacher recommends repeating their experiment. Explain why.
   (d) Identify the property being used in this experiment to separate the mixture.
   (e) Comment on the students' results.
   (f) What assumption did the students make?
4. Another group of students carried out a gravimetric analysis of a mixture of salty sand using the method shown in the flow chart below.



   (a) Write out the method using procedural text type. Note that the flow chart does not indicate when it is necessary to weigh anything. You should add instructions for doing so to your method.
   (b) List the equipment needed to carry out their method.
   (c) Outline any necessary safety precautions.
   (d) Calculate the percentage composition of their mixture from the students' results:
   Weight of original mixture = 8.30 g.
   Weight of sand = 6.05 g.
   Weight of salt = 2.20 g.
   (e) Identify possible sources of error.

69 Precipitation Titrations

A **precipitation titration** is a form of volumetric analysis in which the formation of an insoluble coloured complex is used to indicate the end point of the titration.

The principle of a precipitation titration is that the amount of added precipitating reagent is equivalent to the substance being precipitated.

The end point is usually determined by a change in colour as a complex is formed or decomposed.

For example, to determine the concentration of **thiocyanate ions** in a solution, a sample of the solution could be titrated against a solution containing iron(III) ions (Fe^{3+}) until the red colour of the iron complex appears.

If a solution contains a cation that will form a **stable complex with ammonia (NH_3) or hydroxide ions (OH^-)** it can be titrated against ammonium or sodium hydroxide.

Table 69.1 Some complexes of cations with NH_3 and OH^-.

Cation	NH_3 complex	OH^- complex
Ag^+	$[Ag(NH_3)_2]^+$	—
Cu^{2+}	$[Cu(NH_3)_4]^{2+}$	—
Pb^{2+}	—	$Pb(OH)_3^-$

Precipitation titrations are often used to analyse **halide ion concentration** in solution for which different methods can be used. They are based on using **silver nitrate as the precipitating agent** as silver forms insoluble complex ions with substances such as halide ions and chromate or thiocyanate ions.

- Determining the concentration of halide ions, such as chloride ions (Cl^-), by using a standard solution of silver nitrate solution as the titrant and potassium chromate as indicator.

  Silver ions from the $AgNO_3$ react with any chloride ions (or other halide iions) in the solution being analysed.

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

  When all of the Cl^- ions in solution have reacted, silver ions from the next drop of silver nitrate solution react with the indicator's chromate (CrO_4^{2-}) ions and form a red precipitate of silver chromate.

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

  Note that the silver chloride is formed first because silver chromate is more soluble than silver chloride, and only after all the Cl^- has been used up can the first drop of excess silver ions react with the chromate to form the red silver chromate precipitate.

- An excess of silver nitrate is reacted with the halide in acidic solution. (Here X is used for a halide ion.)

  $Ag^+(aq) + X^- \rightarrow AgCl(s)$

  When all of the halide ion is converted to silver halide, the remaining silver halide is estimated by back titration against a standard solution of potassium thiocyanate.

  $Ag^+(aq) + SCN^- \rightarrow AgSCN(s)$

  This continues until all the silver has been converted to silver thiocyanate.

  The precipitate is filtered out and then the excess thiocyanate reacts with iron(III)ammonium sulfate forming a red complex.

  $Fe^{3+}(aq) + SCN^-(aq) \rightarrow Fe(SCN)^{2+}(aq)$

  The acid medium is used to prevent the formation of any precipitate of iron(III) hydroxide precipitate.

- A third method uses dyes that absorb onto the surface of AgCl to determine the end point. They have different colours when free in the solution and when adsorbed onto a precipitate.

Precipitation titration titrations can also be used for the analysis of mixtures as long as any precipitates that will form differ in solubility. The least soluble compound formed will precipitate first.

QUESTIONS

1. Outline the use of a precipitation titration that you discussed or performed in class.
2. One of the earliest precipitation titrations, carried out in the late 18th century was to analyse fertiliser material called potash. The potash contained potassium carbonate and potassium sulfate. A solution of calcium nitrate $Ca(NO_3)_2$ was used as the titrant. The end point of the titration occurred when adding more calcium nitrate could not produce any more precipitate.
   Write equations to identify the precipitates formed.
3. To determine the concentration of chloride ions in a sample, a precipitation titration is carried out using silver nitrate, in the presence of chromate ions.
   (a) Write an equation to show the formation of the first precipitate.
   (b) Why are chromate ions added?
   (c) How do you determine the concentration of chloride ions present?

70 Colorimetry and UV Visible Spectrometry

Modern **analytical techniques** in chemistry involve the use of various parts of the electromagnetic spectrum.

You will recall that the **electromagnetic spectrum** refers to a series of waves that are produced by fluctuating electric and magnetic fields and includes radio waves, microwaves, infra-red radiation, visible light, ultraviolet light, X-rays and gamma rays.

The waves of the electromagnetic spectrum all travel in straight lines at the same speed, 3×10^8 metres per second in space and through air. They vary in wavelength and frequency. The smaller the wavelength, the higher the frequency of a wave will be. The higher the frequency of a wave, the more energy it carries. So waves with short wavelength and high frequency carry the most energy.

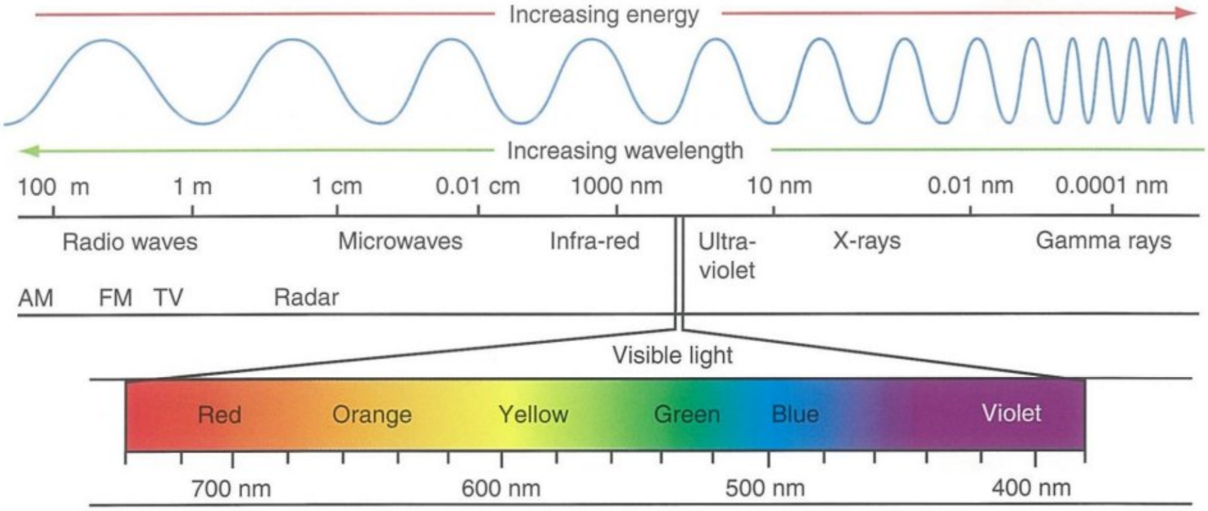


Figure 70.1 The electromagnetic spectrum.

Spectrometry

Spectrometry is the study of the interaction between matter and radiated energy. Original studies in spectrometry involved visible light. An instrument called a **spectroscope** was used to disperse (spread) light, forming a spectrum (band of light).

The general idea with using spectrometry for analysis is that you shine light through a sample, look at it with a spectroscope and then analyse the spectra produced to determine **which wavelengths** of electromagnetic radiation (EMR) have been absorbed and from this you can determine which substances are present in the sample. The **amount of a particular wavelength** absorbed is used to determine the quantity of that substance present.

Perception of colour

The colours that we see are based on the absorption and reflection of wavelengths of electromagnetic radiation in the visible range (around 380 to 780 nm). When visible light falls on an object some is usually absorbed – the rest is reflected and/or transmitted and this reflected and transmitted light is what we see and what determines the colour of an object.

When white light passes through a copper sulfate solution, some of the orange/red light is absorbed, so the light that makes it through the solution to our eyes looks blue.

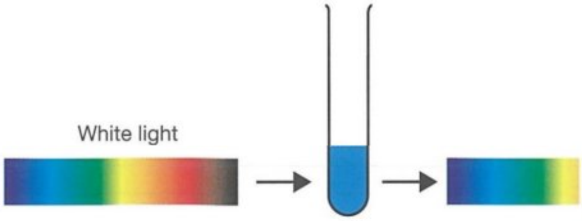


Figure 70.2 Copper sulfate solution looks blue because it absorbs orange light. The mixture of wavelengths that passes through the solution looks blue to us.

A more concentrated copper sulfate solution absorbs more orange/red light and looks a darker blue. We can estimate the depth of blue by eye or by comparison with standards. However, a colorimeter gives a more accurate measurement of concentration by actually measuring the amount of wavelengths absorbed by the object.

In spectrometry, the wavelength(s) of light passing through the solution being analysed can be varied. If the entire visible spectrum (white light) is used, the light transmitted is the complementary colour of the one absorbed.

For example, if you look at the colour wheel in Figure 70.3, you will see that when green light is absorbed by a transparent object, the light that is transmitted through will be the complementary colour which is red. So the object will look red to us.

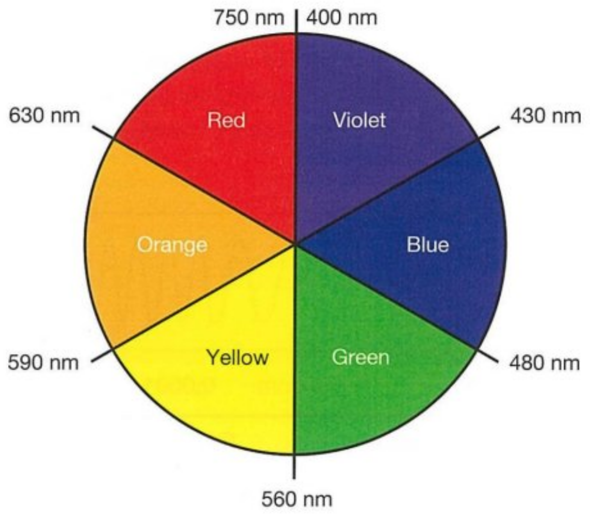


Figure 70.3 Complementary colours.

Analysis using colorimetry

Colorimetry is a method of identifying a coloured substance or determining its **concentration in solution** based on its ability to absorb parts of the visible electromagnetic spectrum. To do this, light of a particular wavelength is absorbed by the solution as it passes through and the intensity of the light is compared before and after being passed through the substance being analysed.

Figure 70.4 shows an absorbance spectrum produced when analysing a soft drink. Orange light (around 600 nm) is being strongly absorbed by the drink, so it will look blue.

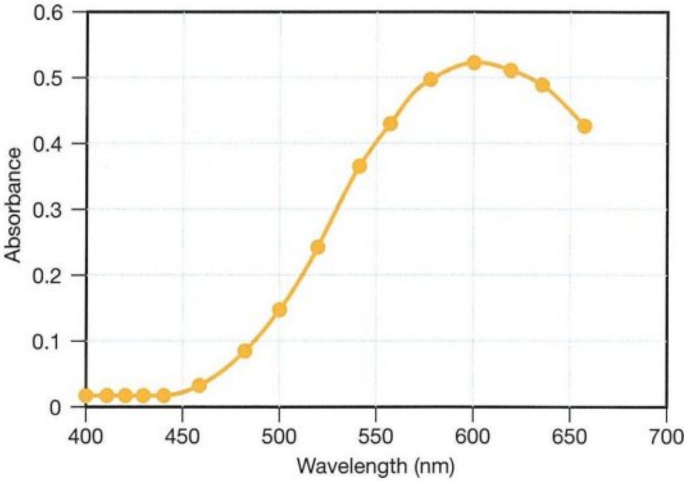


Figure 70.4 Absorbance spectrum for a soft drink.

For quantitative analysis, a **calibration** (absorbance) **curve** is used. This enables the conversion of the measured absorbance into concentration units such as mg/L or ppm. A number of solutions with different concentrations are made up of the chemical being analysed. Radiation with a range of wavelengths in the visible range is passed through a sample of the known substance. The amount of absorption of a specific wavelength is measured at different concentrations and a graph drawn which is called a calibration/absorbance curve. Notice that, although these graphs are called calibration curves, they are straight lines, as **absorbance is directly proportional to concentration** – a relationship called the **Beer-Lambert law**.

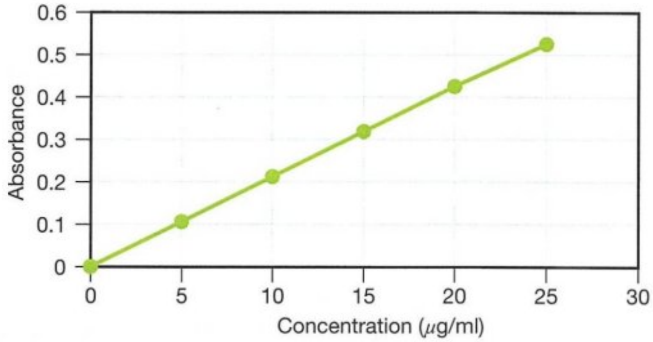


Figure 70.5 Calibration curve.

To measure the concentration of a chemical in a solution, radiation of the specific wavelengths in the visible range is passed through a sample of the substance being studied. The amount of absorption of that wavelength is measured and checked against the calibration curve. In Figure 70.5, you can see that if the absorbance is 0.3 then the concentration of the substance being analysed will be 14 micrograms per litre.

Many compounds such as nitrates and phosphates can be **converted to coloured compounds** using reagents so they can be analysed using a colorimeter. For example, phosphate can be reacted to form a blue complex with molybdenum. The depth of colour is directly proportional to the concentration of phosphate ions present in the solution.

Colorimetry is a **simple**, **low cost method** of analysis and the colorimeters used for analysis are usually small portable devices, convenient to use in the field. They can detect small colour differences that are impossible for the human eye to see. Colorimetry (like UV/V spectrometry), also has the advantage that you **do not have to isolate the substance** from a mixture to measure its concentration. If the coloured substance to be studied is part of a mixture, it does not have to be separated out first.

Colorimetry is widely used in medical laboratories and for industrial purposes including the analysis of water. It is used in hospitals and in the food, petrochemical, medical and pharmaceutical industries as it can analyse a diverse range of substances such as blood, urine and fuels. It is often used in conjunction with mass spectrograms.

Substances which can be analysed using colorimetry include both organic substances such as glucose and protein and also inorganic substances such as phosphate ions and ferric (Fe^{3+}) ions. It is used to analyse inks and dyes used for colour printing and textile and paint manufacturing. This method can also be used to determine reaction rates and the point at which a reversible reaction reaches equilibrium, by analysing the concentrations of all species present at any given time.

Originally this technique only used visible light for analysis (with wavelengths from about 400 to 800 nm).

If monochromatic light or a narrow band of radiation is used for analysis the instrument used is called a spectrophotometer. Modern **spectrophotometers** also operate in the UV and near infra-red regions. The spectrophotometer can be programmed to measure a range of specific substances, with the wavelengths to be used and the calibration curves needed being programmed in for each substance.

Analysing using ultraviolet and visible (UV/V) spectrometry

Ultraviolet and visible spectrometry refers to analysis of solutions using light in the **visible and ultraviolet** (UV) **ranges** of the electromagnetic spectrum. Any substance which dissolves in a solvent such as water, alcohol or hexane and which absorbs UV or visible light, can be analysed using this method.

UV/V spectrometry is used in analytical chemistry to:

- Confirm the presence of a particular compound by comparing its absorption spectrum, in solution, with that of known compounds.
- Determine the concentration of a compound in solution. As with colorimetry, the spectrum produced is compared with spectra of known concentrations, and the absorbance is directly proportional to the concentration of the chemical present.

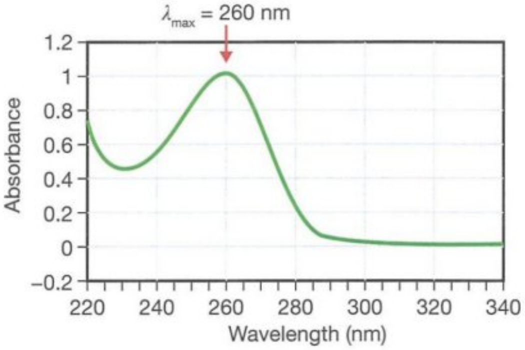
UV visible spectrometry is a sensitive method and can accurately measure very low concentrations of chemicals. It can be used to measure concentrations of transition metal ions, organic compounds and biological macromolecules as these substances all absorb light in the UV and/or visible regions of the electromagnetic spectrum.

For example, **transition metals** occur in different oxidation states with different electronic structures and different numbers of electrons in their d orbitals. This causes different amounts of energy and different wavelengths of radiation (and thus different colours of light) to be absorbed, producing a characteristic UV absorption spectrum.

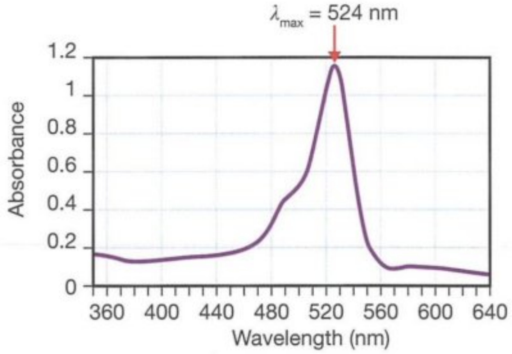
Organic compounds containing unsaturated groups, such as –N=N–, $–NO_2$, C=C and C=O bonds, absorb in the UV range. This ability to absorb UV light can be used to detect colourless organic compounds. Because they absorb in the UV range, our eyes cannot detect any change – we cannot see that any radiation has been absorbed because our eyes cannot detect UV light.

Different structures have different absorbance curves. Some examples for organic compounds are shown in Figure 70.6.

(a) For an important biological molecule called nicotinamide adenine dinucleotide (NAD).



(b) For a red food dye.



(c) Absorption spectrum for beta carotene.

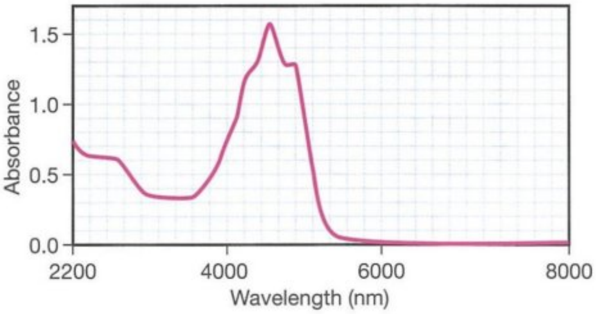


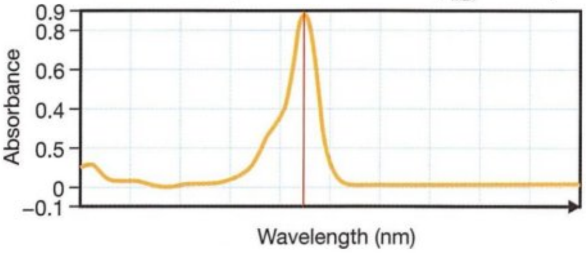
Figure 70.6 UV/V absorption spectra.

Organic compounds such as steroids, drugs and amino acids absorb different wavelengths of UV light depending on their structure, so their absorption spectra can be used to detect and identify them.

QUESTIONS

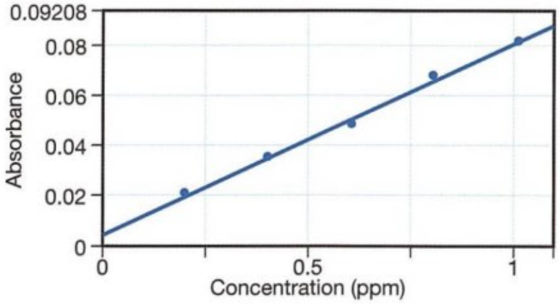
1. (a) Define the electromagnetic spectrum.
   (b) Order the following types of electromagnetic radiation in order of increasing frequency. Visible light, X-rays, radio waves, ultraviolet light, infra-red light, gamma rays.
   (c) Outline the relationship between wavelength, frequency and energy carried by a wave.
2. Outline uses and advantages of colorimetry as an analytical technique.
3. (a) Why is UV/visible spectrometry able to detect colourless organic compounds and metals in solutions?
   (b) Research to identify the range of ways in which spectrometry can be used.
   (c) Research to describe the use of UV/V spectrometry in one specific area.
4. Tartrazine is a chemical which has been in the news. It has a UV spectrum as shown.

Standard UV spectrum of tartrazine (λ_{max} 426 nm)



   (a) What is tartrazine and why is it of concern?
   (b) Use the calibration curve below to determine the concentration of tartrazine in a sample of food with absorbance of 0.05.

Calibration curve for tartrazine

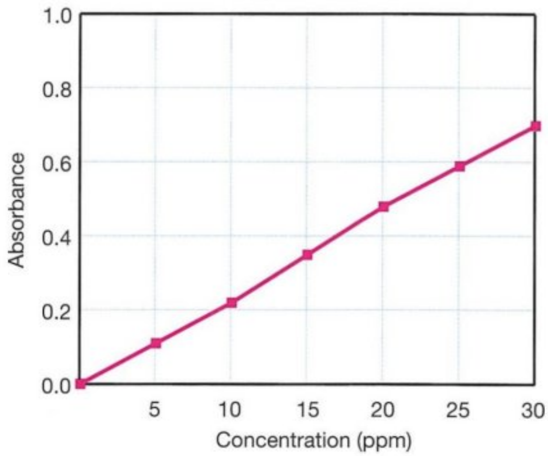


5. A river is suspected of pollution with inorganic phosphate. Two samples are taken at each of three different locations and each is diluted by a factor of 10.

Samples	Absorbance	Average absorbance
1	0.10, 0.09	
2	0.28, 0.28	
3	0.35. 0.36	

   (a) Fill in the table to calculate the average absorbance for each of the three diluted water samples.
   (b) Use the calibration curve provided to determine the diluted inorganic phosphate concentration for each of the diluted water samples.

Calibration curve



   (c) Calculate the inorganic phosphate concentrations in each of the original water samples.
   (d) What do these test results suggest about the possibility of phosphate contamination of the river?
   (e) Suggest a consequence of high phosphate content in river water.
   (f) What would you have to do in order for colorimetry to be a suitable method of analysis of phosphate ion concentrations?
6. Check your knowledge by naming the following.
   (a) A continuous band of colours of light.
   (b) A spectrum of colours with dark bands.
   (c) A dark background with bands of colours.
   (d) Identify three bonds that will absorb in the UV/V range.

71 Atomic Absorption Spectroscopy

Spectroscopy and spectra

Spectroscopy is the absorption, emission or scattering of electromagnetic radiation by matter in order to study either the matter itself (atoms, molecules, ions) or physical processes taking place.

There are two types of spectra: absorption spectra and emission spectra.

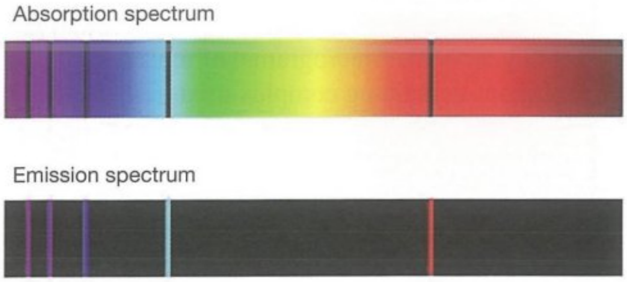


Figure 71.1 Absorption and emission spectra.

An **emission spectrum** consists of a series of bright lines against a dark background. It is produced by a gas which is made incandescent by heating it or by passing electricity through it. The **flame test** is an example of emission spectroscopy. It is a qualitative test, identifying substances present but not measuring how much.

An **absorption spectrum** consists of a series of dark lines superimposed on a continuous spectrum. This type of spectrum is produced when white light passes through a gas which absorbs some wavelengths of light, leaving a dark line where that wavelength has been absorbed and thus is not transmitted. An example of absorption spectroscopy is the use of an atomic absorption spectrometer (**AAS**). For any substance, each dark line in an absorption spectrum is at the same frequency as a bright line in an emission spectrum.

Atomic absorption spectroscopy (AAS)

An atomic absorption spectroscope/spectrometer is used in industry, in research and in monitoring the purity of substances such as air, water and food. AAS is a **quantitative technique** as it can be used to measure the **concentration** of metal ions in solution. It can both detect and measure very small concentrations of metal ions – parts per million (ppm) and even parts per billion (ppb).

In **atomic absorption spectroscopy** the sample to be analysed is split into atoms by heating it to a high temperature. If the concentration in the sample of a metal such as mercury is being measured, then radiation with a wavelength suitable to excite mercury electrons is passed through the sample. This energy is absorbed by the electrons in any mercury atoms present, making the electrons jump to a higher energy level. The intensity of light energy absorbed depends on the concentration of the mercury in the sample.

Figure 71.2 shows a simplified diagram of an atomic absorption spectrometer.

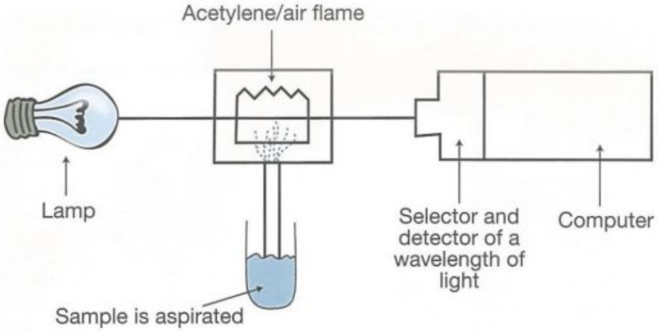


Figure 71.2 Atomic absorption spectrometer.

The lamp emits the mix of wavelengths of light that can be absorbed by the atoms you are trying to detect. The sample is aspirated (sucked up) and sprayed into the flame where an acetylene/air flame vaporises atoms. Some light is absorbed by the metal in the sample. The greater the concentration of metal ions in the sample, the more light will be absorbed. A detector measures the intensity of the wavelength of light selected to be studied. A computer compares the light before and after passing through the flame and calculates the amount of this wavelength of light that has been absorbed by the sample. From this the concentration of the particular metal ions in the sample can be calculated.

Using an atomic absorption spectrometer

Using an atomic absorption spectrometer is a quick and simple process. The main steps involved are listed below.

1. The operator chooses a lamp that emits light of a wavelength that can be absorbed by the metal being measured.
2. The operator makes up very accurately a series of solutions with different concentrations of the metal for which they are testing. These solutions of accurate, known concentrations are called **standards**.

3. Each of these standard solutions is **aspirated**, one at a time, and the light absorbed by each solution is measured and recorded. The light absorbed is called the **absorbance**. Absorbance is graphed against concentration. This process is called **calibrating the atomic absorption spectrometer**.
4. Each unknown sample is aspirated. The computer compares the light absorbed by the samples with that absorbed by the standards and reads from the graph the concentration of metal in the sample.

Periodically the operator will run a standard solution through again to check that the measurements are reliable.

Figure 71.3 A spectrometer being used in pharmacy quality control.

QUESTIONS

1. (a) AAS is a technique suitable for quantitative analysis rather than just qualitative analysis. Explain.
   (b) Explain why it is necessary to heat the sample to high temperatures.
   (c) What is meant by 'the sample is aspirated'?
   (d) The detector in an AAS receives two rays of light; one has come through the heated sample and the other has come directly from the lamp. Explain why.
2. Read the boxed passage about AAS then answer the questions below.
   (a) Find the following terms used in the passage and explain their meaning.
      (i) Wavelength.
      (ii) Absorption.
      (iii) Trace elements.
      (iv) Enzymes.
      (v) Monitoring.
      (vi) Heavy metals.
      (vii) Gravimetric analysis.
      (viii) Spectroscopy.
   (b) Outline three uses of atomic absorption spectroscopy in industry.
   (c) Describe the use of an atomic absorption spectroscope in detecting concentrations of metal ions in solutions.

Atomic absorption spectroscopy is a technique that uses the absorption of light to measure the concentration of gaseous atoms in a sample being analysed. AAS revolutionised quantitative analysis and has been described as the most significant advance in chemical analysis in the 20th century.

AAS was developed by **Dr Alan Walsh** at the CSIRO during the 1950s. It is a very sensitive technique, being able to detect the concentrations of tiny amounts (micrograms) of metals in solutions containing complex mixtures. It can measure concentrations as small as one part per billion without having to extract the substance from the sample. The sample being analysed is vaporised and the intensity of absorption of light of a particular **wavelength** is measured. Each element has its own characteristic **absorption** spectrum that depends on the energy levels of its electrons.

AAS is used in industry and in environmental monitoring. It measures the concentration of metals in alloys, minerals, soils and living tissues. It is also used to analyse wine for trace components such as fluoride, lead, arsenic and boron.

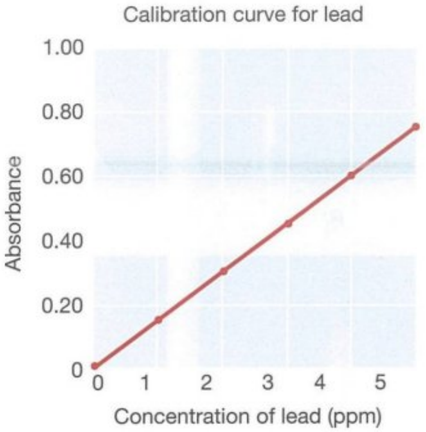
Atomic absorption spectroscopy has played an important role in the understanding of the effects of **trace elements** such as copper, zinc, boron, cobalt, molybdenum, iron and iodine and also the concentrations of these required for healthy development of crops and livestock. Organisms need tiny amounts of trace elements for the action of **enzymes**. Experiments are carried out with different growth media using AAS to compare uptake to yield in processes such as photosynthesis and respiration.

Heavy metal pollution is of concern and **monitoring** the concentrations of heavy metals such as lead, mercury and cadmium in soils, water, atmosphere and tissues is necessary. This was previously carried out by **gravimetric analysis** of multiple samples, which is a tedious and relatively inaccurate method, especially when dealing with low concentrations. AAS allows a simple and routine analysis, providing fast and reliable results.

AAS has a number of **advantages** over other analysis techniques. It is a relatively simple technique, relatively inexpensive to operate (once you have the equipment), does very fast analysis (but only for one metal at a time), is extremely accurate and very sensitive.

(d) Assess the impact of AAS on scientific understanding of the effects of trace elements.
(e) Name the Australian scientist who developed the atomic absorption spectroscope.
(f) Outline the advantages of AAS over gravimetric analysis.
(g) Outline one disadvantage of AAS.

3. Atomic absorption spectroscopy is an important technique in chemistry. It involves the use of a calibration curve such as the one shown below.



(a) What does this calibration curve tell us?
(b) Outline how this curve would be produced.
(c) How would a scientist use this graph?

4. A chemist uses atomic absorption spectroscopy to analyse the calcium concentration of two water samples. She uses the following method.

Method

(i) Choose a **lamp** and filter that emits light of a wavelength that will be absorbed by calcium; this is 422.7 nm. Install it and turn it on so it shines through any solution to be tested.
(ii) Make up five **standard solutions** very accurately (ones with known concentration). The chemist decides to use solutions of 1, 2, 3, 4 and 5 ppm.
(iii) Turn on the acetylene/air flame and spray each solution, one at a time, into the flame.
(iv) The detector measures how much light has been absorbed by each solution (the **absorbance**).
(v) Graph absorbance against concentration. This graph is called a **calibration curve**.
(vi) Spray each of the unknown solutions into the flame and record the absorbance of each.

(a) Define each of the terms in bold print.
(b) The table below shows some results obtained with an AAS testing for calcium. The computer has run three tests on each standard solution. Work out the average absorbance for each and then plot a calibration curve.

Absorbance of standard solutions.

Conc. of standard (ppm)	Absorbance readings			Average absorbance
1	0.072	0.072	0.072	
2	0.145	0.145	0.145	
3	0.216	0.216	0.214	
4	0.284	0.283	0.284	
5	0.350	0.349	0.349	

(c) The average absorbances for each of the unknown solutions were:
Water sample A: 0.2612
Water sample B: 0.2738
Use your calibration curve and these absorbance values to determine the concentration of calcium in each sample.
(d) What absorbance value would you expect for a sample with a concentration of 3.0 ppm?
(e) When testing a number of unknown samples, the chemist will want to check the reliability of her results. How could she do this?

5. Evaluate the claim that atomic absorption spectroscopy represents the most significant advance in chemical analysis in the 20th century.

6. Research two heavy metals to explain why it is necessary to be able to test for the presence of heavy metals and identify the types of samples that may need to be tested.

7. Check your knowledge with this quick quiz.
(a) What does AAS stand for?
(b) Name the process that involves measuring the amount of light absorbed in order to measure the concentration of atoms in a substance.
(c) Name three trace elements in the body whose presence can be monitored by the technique of AAS.
(d) Name a heavy metal whose concentration in the atmosphere or water can be monitored by AAS.
(e) Name two techniques for analysing the concentration of a mineral in an ore.
(f) What determines the type of lamp used in AAS measurement?

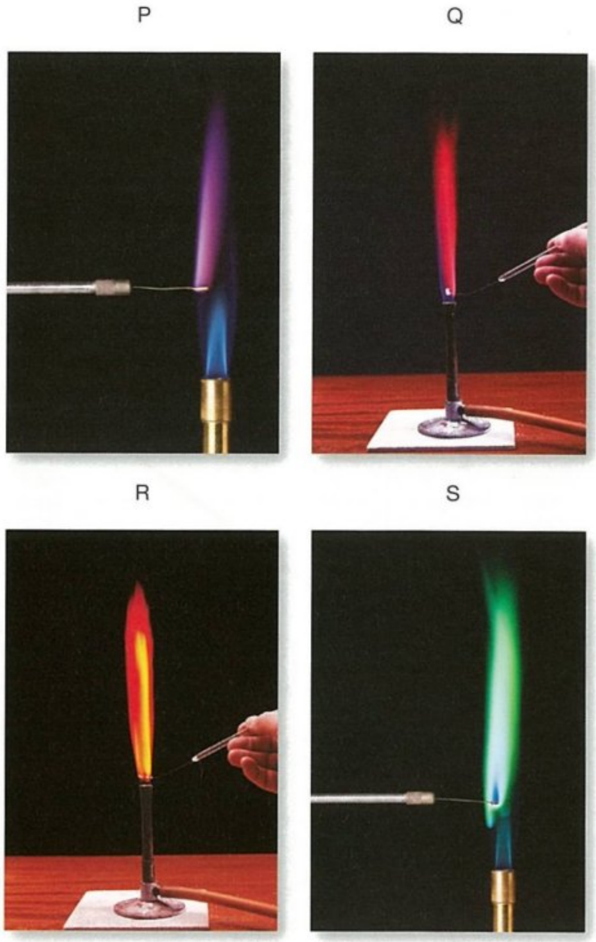
72 Revision Of Analysis Of Inorganic Substances

Analysis is an integral part of chemistry. Being able to determine what is present in a substance and in what concentration is a very important skill for anyone studying chemistry. To be able to do this you need to know about the properties and chemical reactions of a wide variety of substances.

This topic builds on ideas and techniques such as flame tests and the use of solubility. Some wet laboratory analysis techniques, and also instrumental analysis techniques were included in the year 11 books, in case your teacher preferred to introduce them at that stage. However, you will have noticed that they are included again here for completeness, so you do not have to refer back to previous texts.

QUESTIONS

1. Which statement about ozone is most correct?
   (A) Most ozone occurs in the troposphere.
   (B) Ozone formed in the troposphere causes health problems.
   (C) Ozone is useful wherever it occurs.
   (D) Ozone is a form of oxygen that we can breathe.
2. Which of the following pairs of ions causes eutrophication when present in rivers?
   (A) Sulfates and carbonates.
   (B) Nitrates and phosphates.
   (C) Mercury and lead.
   (D) Aluminium and chloride.
3. The gas with the highest concentration in the atmosphere is:
   (A) Nitrogen.
   (B) Oxygen.
   (C) Carbon dioxide.
   (D) Ozone.
4. The atmospheric pollutant which is the main cause of acid rain is:
   (A) Carbon monoxide.
   (B) Nitrogen monoxide.
   (C) Methane.
   (D) Sulfur dioxide.
5. The major source of atmospheric pollution is considered to be:
   (A) Building construction.
   (B) Mining activities.
   (C) Combustion of fossil fuels.
   (D) Industrial waste.
6. The photographs show the results of flame tests carried out on substances containing four cations.



The cations present in the samples tested were:

Sample	P	Q	R	S
(A)	Calcium	Barium	Potassium	Lithium
(B)	Sodium	Copper	Calcium	Barium
(C)	Calcium	Magnesium	Lithium	Copper
(D)	Potassium	Lithium	Calcium	Barium

7. Two test tubes contain solutions of sodium carbonate and sodium chloride. These could be distinguished by:
   (A) Using AAS to determine the ions present.
   (B) Adding iodide ions and looking for a yellow precipitate.
   (C) Adding dilute hydrochloric acid to see if a gas is produced.
   (D) Carrying out a flame test and comparing the flame colours.
8. Eutrophication of a waterway would most likely be associated with:
   (A) Low biochemical oxygen demand
   (B) Low levels of nitrates.
   (C) High nitrogen : phosphorus ratio.
   (D) High acidic oxide levels.

Questions 9 to 12 are based on the following solubility rules.

Soluble	Insoluble
• All nitrates • All acetates • All sulfates (except those of Ca, Ba, Pb, Hg and Ag) • All chlorides, bromides and iodides (except Pb, Hg, Ag) • All ammonium compounds • All sodium and potassium compounds	• All carbonates (except those of Na, K, NH_4^+) • All oxides and hydroxides (except Na, K, Ca, Mg, Ba and NH_4^+) • All sulfides (except those of Na, K, Mg, Ca, Ba and NH_4^+) • All phosphates (except Na, K, and NH_4^+)

9. The list which contains only insoluble salts is:
(A) Calcium sulfate, mercury chloride, magnesium carbonate.
(B) Sodium carbonate, sodium hydroxide, sodium phosphate.
(C) Magnesium carbonate, barium carbonate, potassium carbonate.
(D) Ammonium phosphate, lead(II) oxide, silver bromide.

10. The ions which would react to produce a precipitate are:
(A) Mg^{2+} and SO_4^{2-} (B) CH_3COO^- and Pb^{2+}
(C) S^{2-} and Ag^+ (D) NO_3^- and Ba^{2+}

11. Iron, chromium and copper can all be detected in a solution by the formation of coloured precipitates on the addition of:
(A) Sodium chloride.
(B) Ammonium hydroxide.
(C) Dilute hydrochloric acid.
(D) Pure water.

12. The presence of salt (sodium chloride) in water can be detected by the white precipitate that forms and then darkens on the addition of:
(A) Silver nitrate. (B) Hydrochloric acid.
(C) Potassium hydroxide. (D) Reactive cations.

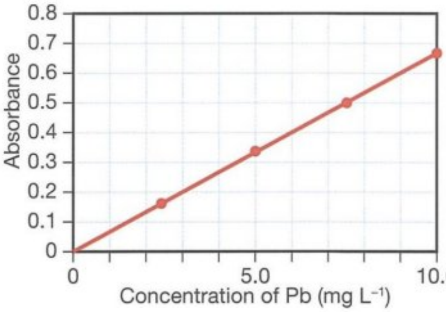
13. Measurement and analysis are important in:
(A) Monitoring pollution and also chemical processes in industry.
(B) Investigating crime scenes.
(C) Diagnosing illness and detecting drug use.
(D) All of the above.

14. In an investigation involving gravimetric analysis, The precipitate was weighed before it was completely dried. The impact of this would be:
(A) The mass of the substance being investigated would appear lower than the correct value.
(B) The mass of the substance being investigated would be higher than the correct value.
(C) Minimal because the water would not weigh very much.
(D) Minimal because the water would form part of the crystals.

15. A substance whose presence could not be investigated using gravimetric analysis involving precipitation is sodium nitrate. This is because:
(A) All sodium salts are soluble.
(B) All nitrate salts are soluble.
(C) All sodium salts and all nitrate salts are soluble.
(D) None of the above.

16. Gravimetric analysis was used to find the sodium chloride content of a tin of soup. Silver nitrate was added to precipitate out any chloride ions as silver chloride. The mass of silver chloride precipitate collected was found to be lower than expected. This could be because:
(A) The precipitate was not washed before being dried and weighed.
(B) The soup contained other sodium salts as well as sodium chloride.
(C) The soup contained other chloride salts as well as sodium chloride.
(D) Not enough silver nitrate was added to precipitate out all of the chloride ions.

17. The lead calibration curve obtained using atomic absorption spectroscopy is shown below.



The concentration of lead in a soil sample was measured using atomic absorption spectroscopy, and was found to have an absorbance of 0.4. What was the concentration of lead in the soil in mg L^{-1}?
(A) 5.5 (B) 6.0 (C) 0.26 (D) 0.05

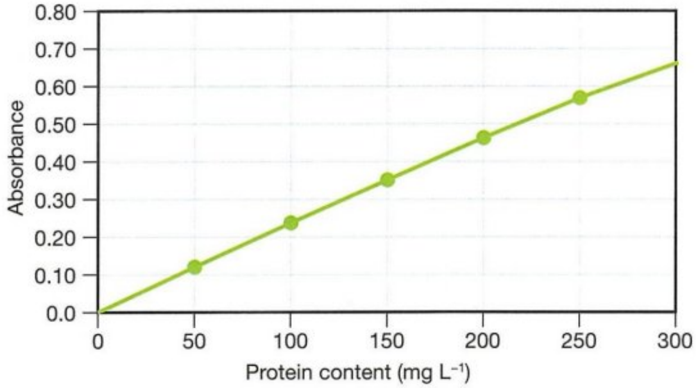
18. Small amounts of sodium chloride are added to bottled water to 'improve' its taste. If atomic absorption spectroscopy shows a sodium ion concentration of 4 moles L^{-1} in a bottle of water, what will be the concentration of chloride ions in moles L^{-1}?
(A) 2 (B) 4 (C) 6 (D) 8

19. Which is the most correct statement about atomic absorption spectroscopy (AAS)?
(A) AAS uses emission spectroscopy to distinguish between metal and non-metal ions.
(B) AAS uses absorption spectroscopy to estimate the atmospheric carbon pollution.
(C) AAS uses emission spectroscopy to detect and measure the concentration of any metal ions present.
(D) AAS uses absorption spectroscopy to detect and measure the concentration of any metal ions present.

20. Colorimetry involves analysis of the absorption of:
(A) Ultraviolet light.
(B) Gamma radiation.
(C) Visible light.
(D) Infra-red light.

21. Which type of radiation in the electromagnetic spectrum has the highest energy?
(A) Ultraviolet.
(B) Visible.
(C) Infra-red.
(D) Radio waves.

22. Below is a calibration (absorbance) curve obtained using a UV-visible spectrometer to measure protein content in solutions of different concentration.



A scientist wants to measure the concentration of this protein in a sample of liquefied food. The sample was diluted ×20 and tested using UV visible spectrometry. Its absorbance was found to be 0.40. What was the concentration of protein in the sample, measured in grams L^{-1}?
(A) 0.4 (B) 8.0 (C) 175 (D) 3.5

23. Which one of the following is an example of quantitative analysis using atomic absorption spectroscopy?
(A) Using gravimetric analysis to find the concentration of sodium chloride in the water of a lake.
(B) Analysing the alcohol content of the blood of a speeding motorist.
(C) Detecting mercury ions in the water and sediments of Port Phillip Bay.
(D) Measuring the level of a banned drug in Olympic athletes.

24. An advantage of AAS over gravimetric analysis is that in AAS:
(A) The sample does not have to be separated from the mixture.
(B) The analysis is very sensitive.
(C) The method is quick and accurate.
(D) All of the above.

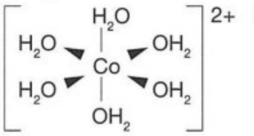
25. The figure shows data about absorbance and complementary colours of visible light. Use this information to answer the next TWO questions.

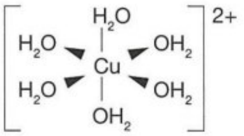
Wavelength (nm)	Absorbed colour			Complementary colour
650-780	Red	🟥	🟩	Blue-green
595-595	Orange	🟧	🟦	Greenish blue
560-595	Yellow-green	🟨	🟪	Purple
500-560	Green	🟩	🟥	Red-purple
490-500	Bluish green	🟩	🟥	Red
480-490	Greenish blue	🟦	🟧	Orange
435-480	Blue	🟦	🟨	Yellow
380-435	Violet	🟪	🟨	Yellow-green

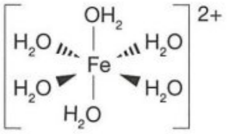
Based on the information in the diagram above, colorimetry of a yellow-green coloured solution of chlorophyll would absorb light which is:
(A) Red-purple.
(B) Violet.
(C) Purple.
(D) Yellow.

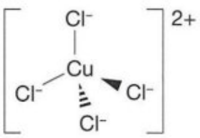
26. If the chlorophyll solution were further diluted, and then again analysed, the following observation would be made.
(A) Different wavelengths of light would be absorbed and emitted.
(B) More of the same wavelength of light would be absorbed.
(C) Less of the same wavelength of light would be absorbed.
(D) The emitted light would be a deeper colour.

27. The complex ion that is deep blue in colour is:

(A)


(B)


(C)


(D)


INQUIRY QUESTION

How are the ions present in the environment identified and measured? Develop a summary of this section, no more than one page long, that includes all the techniques you have covered and examples of substances you could detect and/or measure using each technique.

73 Sources Of Organic Pollution

It is not only ionic substances that pollute our water and atmosphere. Organic pollutants are also present and we need to be able to detect and measure these substances. Organic contaminants found in the atmosphere and water include insecticides, pesticides, dioxins, oil spills and particles of decomposing plastics.

These contaminants are a problem, not just because of their toxicity, but also because many can bind strongly to sediments, allowing them to persist in the environment for long periods of time without detection. We will look at a few of these organic pollutants.

Dioxins

Dioxins are a group of hundreds of related carbon compounds that are highly persistent in the environment, e.g. 2, 3, 7, 8-tetrachlorodibenzo para dioxin (TCDD). They include the group of chemicals called **PCBs (polychlorinated biphenyls)** and were the main constituent in Agent Orange, used as a defoliant during the Vietnam War.

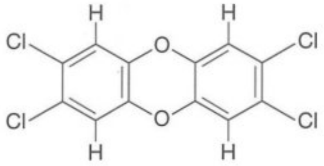


Figure 73.1 The dioxin TCDD.

PCBs are **highly toxic** chemicals, they cause development problems, interfere with hormones, damage the immune system and are carcinogenic.

They persist in the environment and in organisms because they are very stable and can be absorbed by fat tissue. Babies are particularly vulnerable, as they have rapidly developing organs and systems, and these chemicals are even found in human milk.

Dioxins are **produced naturally** for instance by volcanoes and bushfires. However, the majority of environmental dioxins are **synthetic** and released as **by-products of manufacturing processes** such as the manufacture of herbicides and pesticides, the manufacture of paper and smelting and also by the **incomplete combustion of wastes**. Dioxins exist in the environment, with the heaviest concentrations in soil and sediment.

PCBs were **used** in hydraulic fluids, coolant and insulation fluids in transformers and plasticisers in paints and cement. They also leach out of plumbing pipes, fittings and storage tanks over time. They are not water soluble. In many countries their use is restricted. Recently in Australia they have been banned for use in products such as baby bottles and products. More than 90% of human exposure to dioxins, including PCBs is through foods, especially meat, dairy products, fish and shellfish. It can be introduced to the food chain via contaminated animal feed.

Insecticides and pesticides

These are chemicals used to kill insects and other organisms. There are a number of types of insecticides. The best known is probably DDT (dichlorodiphenyltrichlorethane) which was introduced in 1944 to replace the lead and arsenic compounds being used to kill mosquito carriers of the disease malaria. DDT is an example of a **chlorinated hydrocarbon**. These compounds target the nervous system of insects. DDT and related chemicals have now been banned in most countries because of their harmful effects on wildlife, their potential for damage to human health and their persistence in the environment. For example, DDT has been shown to cause thinning of bald eagle eggs so that they easily break. Also, studies have shown a wide range of health defects in humans with even low exposure to DDT and its breakdown products. Other chlorinated hydrocarbons include aldrin, chlordane, dieldrin and lindane.

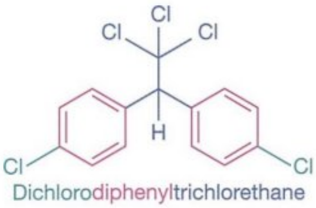


Figure 73.2 DDT.

Organophosphates and carbamates are two other types of toxic insecticide which also target the nervous system.

Pyrethrins are less toxic than organophosphates and chlorinated hydrocarbons and are used on household pests.

Biological insecticides are chemicals made by plants that repel insects. Plants that are claimed to repel insects include mint, lemon grass, citronella, geraniums, marigolds, basil, catnap and lavender.

Insecticides and pesticides do **benefit** us by increasing food production and decreasing the costs of food production. They also destroy household pests that could do damage and carry disease such as termites and fleas. However, many have nasty side effects and many persist in the environment. We should limit our exposure as far as possible.

Oil spills

An oil spill occurs when liquid petroleum is released into the environment, either on land or into water. These may be accidental discharges or planned releases from oil tankers, offshore oil rigs or ships.

Oil spills spread over large distances on water, destroying the environment and killing birds and other organisms. Oil spills can contaminate drinking water, can be a fire hazard and have an economic impact on neighbouring countries by loss of tourism in the area and loss of industries such as fishing and oyster farming.

Figure 73.3 A turtle coated with petroleum.

Clean-up programs are difficult and expensive. Some of the oil can be skimmed off or dredged. Chemicals can be used to absorb the oil, or to break up and disperse it, some may be burnt off, bacteria can be used to break down some of the oil.

Other organic pollutants

There are many other organic pollutants in our environment – even in our homes. One example is the flame retardant chemicals that are used to treat our clothing, curtains, and furniture. Others include components of paints, polishes, glues and dyes, as well as some perfumes.

Organic pollutants are especially dangerous because they are stored in fatty tissue of animals (including us). This is called **bioaccumulation**. They also accumulate along food chains, being present in increasing concentrations at higher levels of food chains. This is called **biomagnification**.

We are being continually exposed to persistent organic pollutants (called POPs) many of which are potentially harmful. They can cause changes in our immune system, as well as hormonal, respiratory and reproductive disorders. Many are also carcinogens and can increase our risk of cancer.

Research is needed to establish whether there are safe levels of exposure to such substances.

QUESTIONS

1. (a) Why are organic pollutants a problem?
   (b) Identify three types of organic compounds that can be found in water as contaminants. Identify two examples of each, their sources and harmful effects. Tabulate your answer.
   (c) Identify two examples of organic substances that occur naturally and can pollute waterways.
2. PCBs are a group of compounds called polychlorinated biphenyls.
   (a) Some PCBs were used as plasticisers in paints and cement. What is the function of plasticisers in these products?
   (b) Research the origin and effects of other PCBs.
3. Research a large oil spill and discuss the following.
   (a) Where did the oil come from, how much entered the environment and how was it released?
   (b) What attempts were made to clean up this oil spill and were they successful?
   (c) What effects did this spill have on the environment?
4. Research the following.
   (a) Determine what DDT is and why it has now been banned.
   (b) Research the impact of the book *The Silent Spring*, by the scientist Rachel Carson (published 1962), which became a best seller.

   (c) Research the use of genetically modified, insect resistant crops.
5. Tons of organic plastic waste is discarded into the environment every year, and as the world's population increases, so do our waste materials. It goes into landfill, it gets into the soil, the atmosphere, waterways and the ocean and in all of these environments it causes problems. Research the following:
   (a) Pollution by chemicals used to manufacture plastics.
   (b) Plastic pollution in the atmosphere.
   (c) Plastic pollution in the ocean.
   (d) What can we do to reduce plastic pollution?

74 Chemical Tests For Functional Groups

Chemical tests can be carried out for functional groups such as carbon-carbon double bonds found in alkenes; hydroxyl groups found in alcohols and for the carboxyl group in carboxylic acids.

Carbon-carbon double bonds

You have already seen, in Module 7, that to test for a –C=C– bond, you need to add bromine water, in the absence of light.

If any carbon-carbon double bonds are present in the substance being tested, then the yellow-brown bromine water will be decolourised, changing from a yellow-brown solution to a colourless solution.

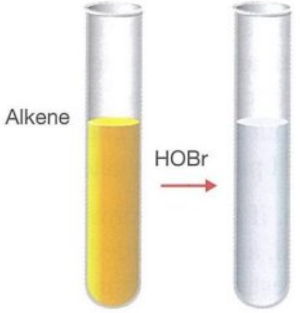
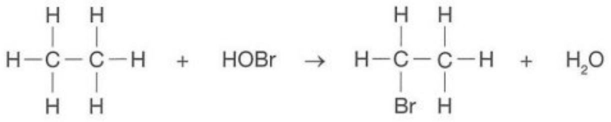


Figure 74.1 Addition of an alkene with bromine water.

$$Br_2(l) + H_2O(l) \rightleftharpoons BrOH(aq) + H^+(aq) + Br^-(aq)$$

$$H{-}\overset{H}{C}{=}\overset{H}{C}{-}H + HOBr \rightarrow H{-}\underset{OH}{\overset{H}{C}}{-}\underset{Br}{\overset{H}{C}}{-}H$$

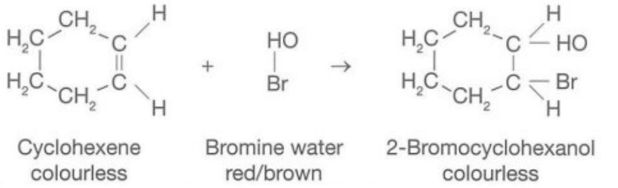
This reaction can also happen with an alkane, which does not have –C=C– bonds. However, the reaction will be very slow, especially if shielded from UV light.



$$H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H + HOBr \rightarrow H{-}\underset{Br}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H + H_2O$$

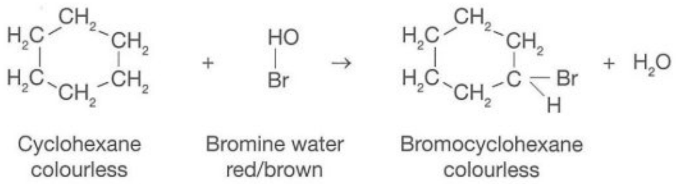
In the school laboratory, cyclic alkanes and alkenes are usually used to demonstrate the difference between the reaction of alkanes and alkenes with bromine water. The chemicals most readily available are cyclohexane and cyclohexene. These substances are used as they are liquids at room temperature and less volatile than some other organic molecules. However, it must be remembered that these are toxic chemicals if inhaled or swallowed and they can also be absorbed through the skin. Gloves, goggles and a fume cupboard should be used during their use to prevent skin or eye contact and also to prevent inhalation. They are also flammable, so no flames should be present during their use. As with other organic substances, any waste must be placed in designated containers and not poured down the sink.

Under dark or light conditions, cyclohexene will decolourise bromine water as an addition reaction occurs.



Cyclohexane will show no reaction with bromine water under dark conditions, so the yellow-brown colour will not change.

Under **UV light, a substitution reaction can occur between cyclohexane and bromine water**, and the yellow-brown colour will fade to colourless.



Alcohols

1. The distinguishing test for alcohols is that they react with active metals, forming hydrogen gas and a salt.

   $2Na(s) + 2C_2H_5OH(l) \rightarrow 2C_2H_5ONa(aq) + H_2(g)$

   Sodium + ethanol → sodium ethoxide + hydrogen

   If the solution is evaporated, the sodium ethoxide will form a white solid.

   Sodium ethoxide is strongly alkaline, it has a high pH. It is alkaline because the ethoxide ion $C_2H_5O^-$ attracts hydrogen ions from water molecules, leaving hydroxide ions.
   $C_2H_5O^-(aq) + H_2O(l) \rightarrow C_2H_5OH(aq) + OH^-(aq)$

   Of course, sodium gives the same reaction with water and with an acid – only in those cases the reaction is more violent.

   You would not carry out this test unless you were absolutely certain that there was no water present and the liquid being tested was neutral to indicators (not an acid).

2. Once you have determined that your unknown substance is an alcohol, you may also wish to know whether it is a primary, secondary or tertiary alcohol.

   To determine whether an alcohol is a **primary, secondary or tertiary alcohol**, you could add the oxidising agent, acidified potassium dichromate solution. Potassium dichromate, acidified with dilute sulfuric acid, is an orange solution.

   To carry out this test, place a few millilitres of the acidified potassium dichromate into a test tube, warm in a hot water bath, then add a few drops of the solution to be identified.

A primary alcohol will produce a green colour as it is oxidised to the aldehyde and then, if the oxidation reaction continues, it forms the carboxylic acid.

For example, ethanol is converted to ethanal and then to ethanoic acid.

$$3CH_3CH_2OH \xrightarrow{[O]} 3CH_3CHO(aq) + 7H_2O(l)$$

$$3CH_3CH_2OH \xrightarrow{[O]} 3CH_3CHO(aq) + 11H_2O(l)$$

A secondary alcohol will also produce a green colour as it is oxidised to a ketone. For example, propan-2-ol is oxidised to propanone.

$$CH_3CHOHCH_3 \xrightarrow{[O]} CH_3COCH_3$$

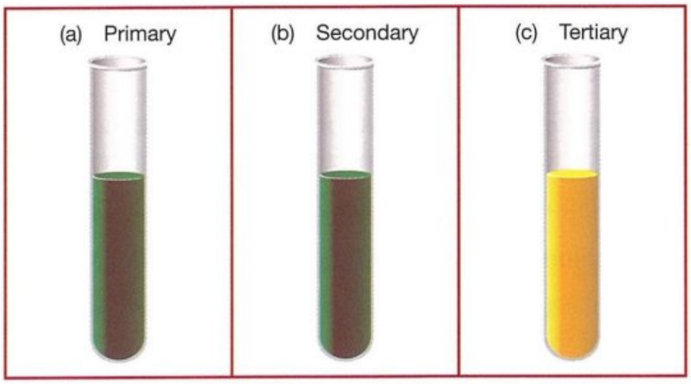


Figure 74.2 Acidified potassium dichromate with alcohols.

However, a tertiary alcohol will show no change in colour. It cannot be oxidised.

Carboxylic acids

Depending on what you want to distinguish it from, there are a number of tests that can be used to identify a carboxylic acid.

1. Carboxylic acids **act on indicators**, for example, they turn blue litmus red, and have no effect on red litmus.

2. Carboxylic acids **react with carbonates and hydrogen carbonates** to produce carbon dioxide gas, a salt and water.

$$2CH_3COOH(aq) + Na_2CO_3(s) \rightarrow CO_2 + 2CH_3COONa(aq) + H_2O(g)$$

Ethanoic acid + sodium → carbon + sodium + water
carbonate dioxide ethanoate

$$CH_3COOH(aq) + NaHCO_3(s) \rightarrow CO_2 + CH_3COONa(aq) + H_2O(g)$$

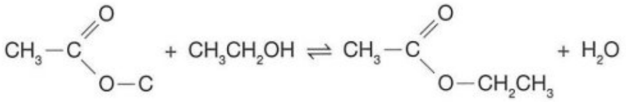
Ethanoic acid + sodium → carbon + sodium + water
bicarbonate dioxide ethanoate

So, to confirm your unknown chemical is a carboxylic acid, you can add it to sodium carbonate or sodium hydrogen carbonate. If a gas is produced, simply bubble the gas through limewater. If it goes milky/cloudy, then the gas is carbon dioxide and your original chemical was an acid.

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

3. Carboxylic acids react with alcohols to produce an ester. Esters have very distinctive smells. In a fume cupboard, mix a small amount of your unknown chemical with an alcohol such as ethanol, and add a few drops of concentrated sulfuric acid and warm slightly. If your unknown chemical is a carboxylic acid, you will produce an ester.

   For example, if your unknown chemical was ethanoic acid, and you added ethanol, you would produce the ester ethyl ethanoate which smells like an organic solvent or glue.



$$CH_3-C(=O)-O-C + CH_3CH_2OH \rightleftharpoons CH_3-C(=O)-O-CH_2CH_3 + H_2O$$

   If the smell of the alcohol or acid overpowers the ester smell, add a little water. The alcohol and acid will dissolve in water, and the ester will form a layer on top as it is less soluble and less dense than water. This stops the reverse reaction from taking place, giving you more time to identify the presence of the ester.

   If you need to collect the ester, you will need to carry out this reaction under reflux conditions and separate out the ester using fractional distillation.

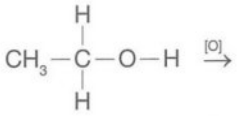
QUESTIONS

1. Describe the tests you carried out to determine if an unknown organic substance:
   (a) Contained a double –C=C– bond.
   (b) Contained an hydroxyl group.
   (c) Was a carboxylic acid.
   In each case include equations using structural formulas to show a positive result and include information on safety precautions needed.

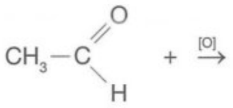
2. Complete the table to summarise information about the distinguishing tests you carried out.

Functional group to be identified	Reagent used	Positive result
–C=C– bond		
–OH group		
R–COOH		

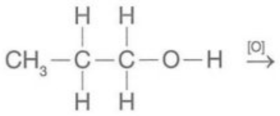
3. (a) Complete the equations using structural formulas to show the oxidation of ethanol.



$CH_3-\overset{H}{\underset{H}{C}}-O-H \xrightarrow{[O]}$



(b) Complete the equation using structural formulas to show the oxidation of a secondary alcohol. Name the alcohol and the product.



$CH_3-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H \xrightarrow{[O]}$

(c) Account for the fact that a tertiary alcohol cannot be oxidised, whereas a primary and secondary alcohol can be oxidised.

4. Identify three tests that could be used to identify a carboxylic acid.

5. Complete the table to match the functional group of an organic homologous series with a reagent that could be used to identify it.

Functional group	Identifying reagent
–C=C–	
–OH	
–COOH	

75 Mass Spectroscopy

Measurement and analysis are fundamental to both theoretical chemistry and its applications. There are many reasons why we may want to analyse the composition of substances around us.

- Food needs to be analysed and labelled to show contents and energy values. People with allergies need to be able to avoid foods that contain any substance to which they are allergic (e.g. nuts, lactose or gluten).
- Biological samples such as blood and urine need to be analysed so that doctors can diagnose illness and also to detect drugs used by athletes.
- Monitoring pollution of the environment and finding the source of pollution in order to prevent more pollution.
- Crime scenes, and artefacts found there, need to be analysed by the forensic scientist to help determine whether people are innocent or guilty.
- The discovery and uses of pharmaceutical drugs involves analysing natural substances that are found useful so they can be manufactured synthetically.

In this and the next few chapters you will be looking at some analytical techniques – starting with mass spectroscopy.

Revision

Before you study mass spectroscopy you should be sure that you know and understand the following.

- Positive ions are called **cations**. These include ions of individual elements, e.g. Ca^{2+} and larger particles, e.g. CHO^+.
- A **magnetic field** (or an electric field) can affect the path of any moving ions within its field. The effect of a magnetic (or electric) field on a moving ion depends on the strength of the field, the mass of the ion and the charge on the ion.
- An element can occur as **isotopes** – atoms with the same atomic number but different mass numbers because they have different numbers of neutrons. The atomic mass of an element is the mass of its atoms relative to atoms of the carbon-12 isotope.
- A compound can be split into a series of particles, e.g. methanol (CH_3OH) could be split into many different positive particles including CH^+, CH_2^+, CH_3^+, OH^+, CHO^+, CH_3OH^+. This is called a fragmentation pattern. Conditions are controlled carefully, so that no two substances will produce the same fragmentation pattern.

Mass spectroscopy

Mass spectroscopy is a technique used in analytical chemistry to identify and measure the type and amount of chemicals present in a sample and to determine molecular structure. Mass spectroscopy is expensive, but it can measure very small concentrations accurately and the results are relatively easy to interpret.

This technique measures the relative abundance of charged particles with different mass-to-charge ratios (m/z). It is useful for:

- Identifying and measuring the abundance of **isotopes**.
- Measuring the mass of particles produced when molecules are broken up. High energy particles such as electrons can be used to smash molecules.

  The collision between gaseous molecules and the ionising electrons in the spectrometer causes fragmentation of the molecules, forming a mixture of ions with different m/z ratios. The pattern of fragments produced can help to work out the **structure of the original molecule**. Note that these particles can have no charge or a positive charge, but they cannot be negatively charged. (However, negative charges can be separated when an electric field is used instead of the traditional magnetic field.)

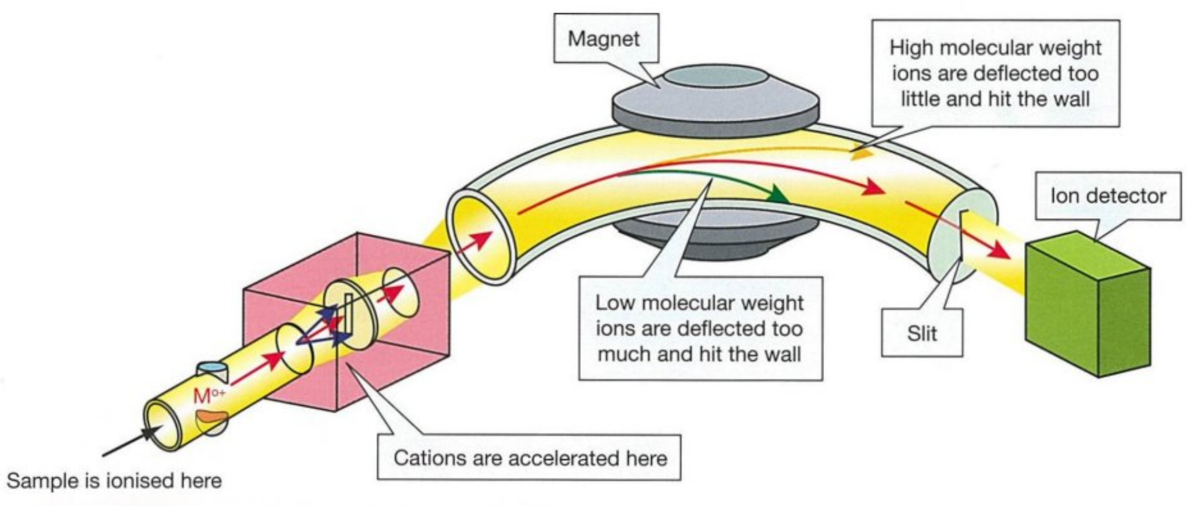


Figure 75.1 A mass spectrometer.

- Analysing the **composition of mixtures**, often after parts have been separated out by a technique such as gas chromatography. Mass spectroscopy can separate ionised particles of different masses and determine the amounts of each particle present in the mixture.

In a mass spectrometer, a magnetic or electric field is used to make any charged particles present travel in a circular path. This is illustrated in Figure 75.1 (you do not need its details, but the diagram may help you to visualise the process).

As the magnetic or electric field of the spectrometer is varied in strength, particles of different mass and charge will reach the detector. The radius of their paths is determined by the size of the particles – **lighter ions and ones with a higher charge are deflected the most**. Changing the strength of the electric or magnetic field allows different sized particles to be analysed. This produces a **mass spectrum** (or **spectrogram**).

The mass spectrum

The **mass spectrum (or spectrogram)** produced by a mass spectrometer is used to identify the particles present in the substance being analysed and to compare their abundance. The patterns of fragments shown on a spectrogram/spectrum can be used to analyse, identify the existence and abundance of isotopes, or to determine the composition and identity of a compound being analysed.

Each **vertical line** represents an ion with a specific mass-to-charge ratio (*m/z*). The height of each line indicates the relative abundance of that ion.

The strongest signal (tallest line) – called the **base peak** – is the most common fragment formed. This can be set at 100%, and the abundance of other particles is relative to this base peak. The ion which forms the base peak is usually either a particularly stable ion or one that can be formed in different ways so there are lots of them formed.

The **parent ion peak** is the peak formed by the parent ion. It is usually the peak furthest to the right and is used to determine the mass of the molecule. It is also called the **molecular ion peak**.

Identifying isotopes

The **mass spectrum** of an element shows lines to represent the isotopes of that element.

Bromine isotopes. Figure 75.2 shows a mass spectrogram analysis of the element bromine which shows that there are two isotopes of bromine, ^{79}Br and ^{81}Br. The horizontal axis is mass per charge (*m/z*).

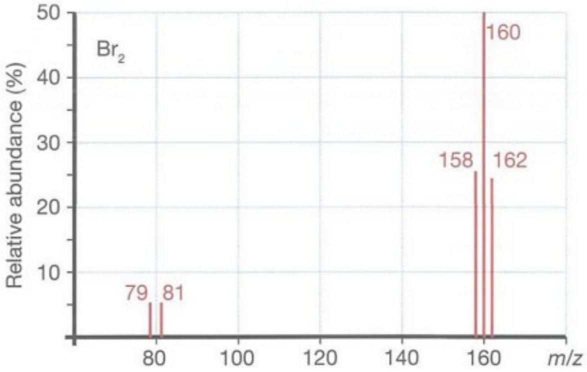


Figure 75.2 Mass spectrum for bromine.

You can see that there are **five ion peaks** in this spectrum, indicating five fragments have been produced at different *m/z* ratios as shown in Table 75.1.

Table 75.1 Fragmentation pattern for bromine.

Position of molecular ion peaks (m/z)	Fragment causing that peak	Abundance (%)
79	79 Br$^+$	5
81	81 Br$^+$	5
158	[79Br 79Br]$^+$	26
160	[79Br 81Br]$^+$	50
162	[81Br 81Br]$^+$	24

The base peak is at 160 *m/z* and the parent ion peak (or molecular ion peak) is at 162 *m/z*.

To estimate the relative atomic mass of the bromine atoms, it can be seen from the spectrum that ^{79}Br$^+$ and ^{81}Br$^+$ ions are in equal abundance. ^{79}Br$_2^+$ and ^{81}Br$_2^+$ are also similar in percentage abundance, therefore:

$$A_R = \frac{50}{100} \times 79 + \frac{50}{100} \times 81 = 80 \text{ amu}$$

Copper isotopes. Here is another example. Figure 75.3 shows the mass spectrum for copper with its two isotopes, copper-63 and copper-65.

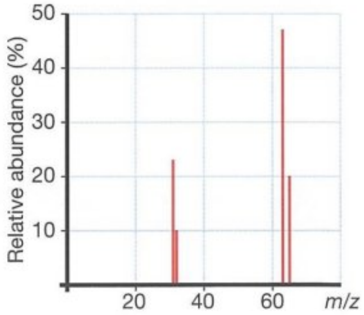


Figure 75.3 Mass spectrum for copper.

There are four peaks because it forms ions with a charge of 1 and 2.

Table 75.2 Fragmentation pattern for copper.

Position of peaks (*m/z*)	Fragment causing peak	Abundance (%)
31.5	$63Cu^{2+}$	23
32.5	$65Cu^{2+}$	10
63	$63Cu^{+}$	47
65	$65Cu^{+}$	20

There is a total of 23 + 47 = 70% Cu-63 and

10 + 20 = 30% Cu-65.

We can use these values to calculate the relative atomic mass for copper.

$$\text{Relative atomic mass } (A_R) = \frac{(70 \times 63)}{100} + \frac{(30 \times 65)}{100} = 63.6$$

Identifying some compounds

Carbon dioxide. Figure 75.4 and Table 75.3 show information obtained by the mass spectroscopy of the gas carbon dioxide. In this spectrum you will see that the base peak has been taken as 100 and other peaks are given relative to the base peak. The first thing you need to do is to work out the ions that could have formed and which line each ion will produce. All the ions have a charge of +1. For example, a line at 12 is likely to be carbon, at 16 it is likely to be oxygen.

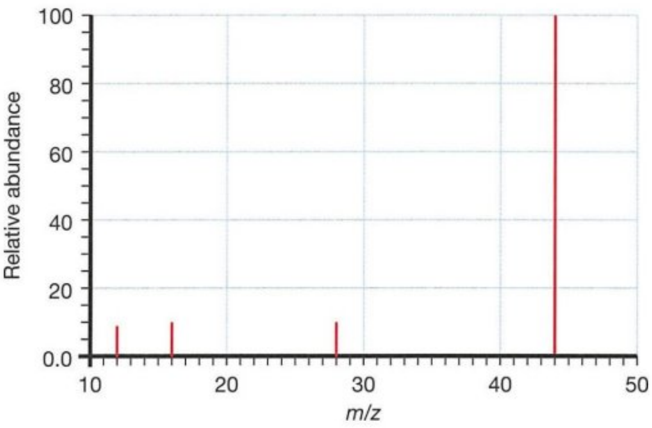


Figure 75.4 Mass spectrum of CO_2.

Table 75.3 Fragmentation pattern for CO_2.

Peaks (*m/z*)	Fragment	Abundance (%)
12	C^+	8
16	O^+	10
28	$[CO]^+$	10
44	$[CO_2]^+$	100

The parent ion peak is at 44 *m/z*, so we know that the molecular mass = 44.

(And from the formula, 12 + 2 × 16 = 44.)

Propane. Propane (C_3H_8) has the structure $CH_3CH_2CH_3$.

Think about how it could split into fragments, and where you might find them on a mass spectrum.

Then look at Table 75.4 which shows some of the main fragments that would be produced.

Table 75.4 Fragmentation for propane.

Fragment	Expected position of peak (*m/z*)
$[C_3H_8]^+$	44
$[C_3H_7]^+$	43
$[CH_2CH_3]^+$	29 (typical for an ethyl ion)
$[CH_2CH_2]^+$	28
$[CH_3]^+$	15 (typical for a methyl ion)
$[CH_2]^+$	14

Figure 75.5 shows a simplified mass spectrum for propane with the fragments mentioned in the above table. Notice the position of the parent ion peak at 44 *m/z* indicating a molecular mass of 44 (12 × 3 + 8 × 1).

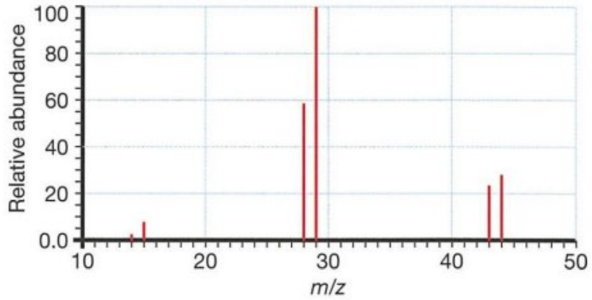


Figure 75.5 Simplified mass spectrum for propane.

Another alkane. Now try and work out the identity of another alkane which was analysed to produce the simplified mass spectrogram shown in Figure 75.6.

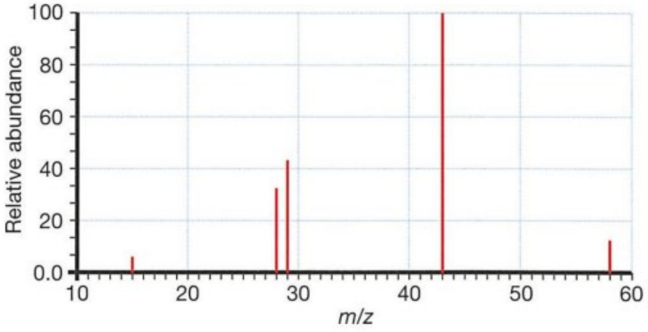


Figure 75.6 Simplified mass spectrum of an alkane.

Look at the parent ion peak. With a *m/z* ratio of 58, its molecular mass is probably 58, and it is an alkane, so what could its formula be?

It has to be C_4H_{10} ($4 \times 12 + 10 \times 1$). So it is **butane**.

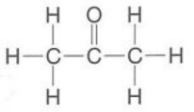
Can you work out what the most abundant fragment is likely to be (the base peak)? With $m/z = 43$, this base peak fragment could be $[CH_3CH_2CH_2]^+$.

You might also notice the production of the ethyl ion (at 29) and methyl ion (at 15) as these are commonly produced.

Stability of ions. Some ions are more stable than others so are more likely to form. For example, tertiary ions are more stable than secondary ions, which are more stable than primary ions.

An ion formed from a carbonyl C=O group is also relatively stable.

Ketones. Propanone (acetone) is the ketone with molecular formula C_3H_6O and the following structural formula.



CH_3COCH_3

Compare its mass spectrum with that of propane.

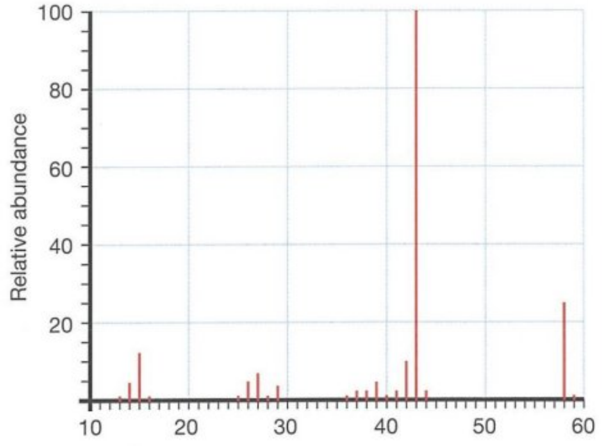


Figure 75.7 Mass spectrum of propanone.

In this case, the main ion produced is $[CH_3C{=}O]^+$ at $m/z = 43$ (the base peak) and its molecular mass = 58 as shown by the parent ion peak.

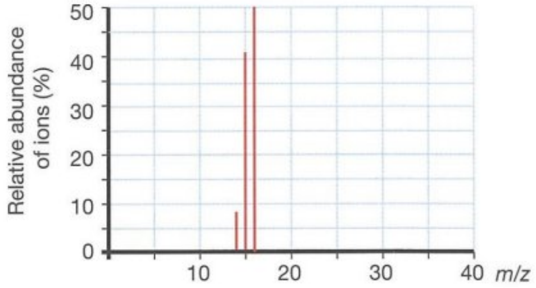
QUESTIONS

1. What is a mass spectrometer?
2. (a) Define ionisation.
   (b) What is a cation?
   (c) Did early mass spectrometers use positive or negative ions?
3. Outline three factors that can affect the path of a charged particle through a magnetic field in a mass spectrometer.
4. Mass spectroscopy of a sample of rubidium shows the existence of two isotopes, rubidium-85 with a relative abundance of 72% and rubidium-87 with relative abundance of 28%.
   (a) What is meant by an isotope?
   (b) Calculate the relative atomic mass of rubidium based on these results.
5. The mass spectrum of a sample of chromium shows four peaks. Use the data in the table to calculate the relative atomic mass of chromium in the sample analysed.

m/z	50	52	53	54
Abundance (%)	4.3	83.8	9.5	2.4

6. A simplified mass spectrum for methane is shown below. Complete the table using the results in the spectrogram.

Simplified mass spectrum of methane

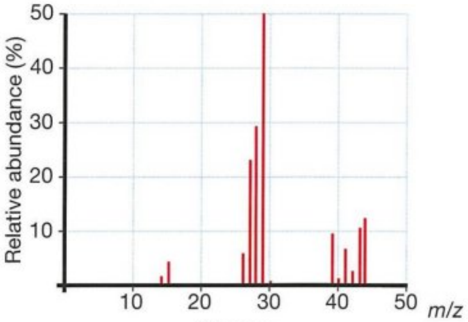


Fragment	Mass/charge ratio (*m/z*)	Relative abundance
$[CH_4]^+$	16	
$[CH_3]^+$		41
$[CH_2]^+$	14	

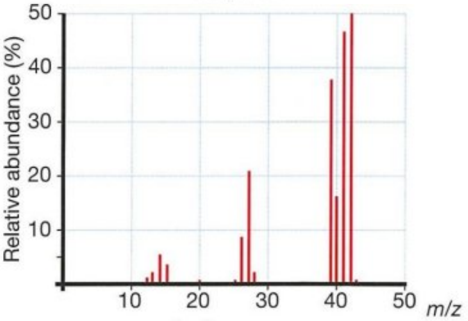
7. Distinguish between the meaning of the pattern of lines in the mass spectrum of an element and the mass spectrum of a compound.
8. Research a specific use of mass spectroscopy in each of the following areas.
   (a) Forensics.
   (b) Medicine.
   (c) Pollution.

9. Each substance produces its own distinctive mass spectrum. For example, you can see from the mass spectra below that although propane and cyclopropane are quite similar in size and composition, their spectra are quite distinct. Answer the questions about these spectra.

Mass spectra for propane and cyclopropane.



Propane



Cyclopropane

(a) Distinguish between a base peak and a parent ion peak on a mass spectrum.

(b) Compare the parent ion peaks on these two spectra.

(c) Compare the base peaks on these two spectra.

10. In a mass spectrum of an organic acid, the most common fragment has a *m/z* value of 28. Deduce the most likely identity of this fragment and include your reasoning.

11. A compound B is analysed by a mass spectrometer and forms the parent ion B^+.

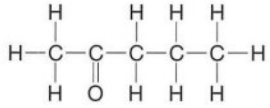
Some of the parent ions fragment as shown:

$B^+ \rightarrow D^+ + G$ and $B^+ \rightarrow D + G^+$

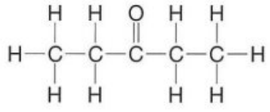
(a) Which ions will appear on the spectrum?

(b) If the molar mass of B is 32, and the molar mass of G is 12, at what *m/z* values would the mass spectrum show peaks?

12. Pentan-2-one and pentan-3-one are ketones with their C=O groups in different positions.

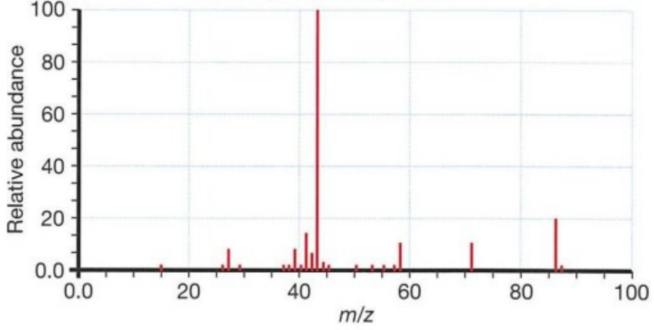


Pentan-2-one

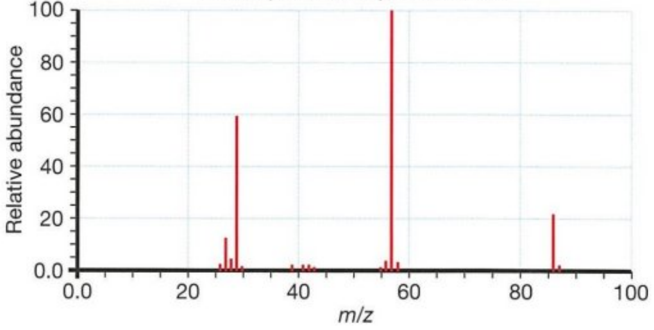


Pentan-3-one

Mass spectrum of pentan-2-one



Mass spectrum of pentan-3-one



(a) Account for these two spectra each having identical parent ion peaks.

(b) Account for the formation of the base peak in each of these spectra.

13. Check your knowledge with this quick quiz.

(a) The instrument that measures the mass-to-charge ratio of charged particles in a sample is called a ....

(b) Converting an atom to an ion is called ....

(c) What deflects ions in a mass spectrometer?

(d) Two factors which affect the deflection of ions in a mass spectrometer are .... and ....

(e) Different forms of the same element with different numbers of neutrons are called ....

(f) The original mass spectrometers studied ions which were (positively/negatively) charged.

76 Infra-Red Spectroscopy

Infra-red (IR) radiation is a very small part of the electromagnetic spectrum, with wavelengths from about 10^3 nm to 10^6 nm and a frequency between 430 THz and 300 GHz. Infra-red radiation can help us to find out about the structure of molecules, even though we cannot see either the molecules or the infra-red radiation.

The energy associated with infra-red radiation is mostly not high enough to excite electrons and make them change their energy levels, but it can make covalently bonded atoms and groups vibrate and it can make covalent bonds within molecules stretch and bend. Each atom, group of atoms or bond has its own natural vibration frequency – a frequency at which it can vibrate, bend or stretch. It absorbs energy at this natural frequency.

Infra-red spectrometer

In an infra-red spectrometer, a beam of infra-red light is passed through a sample of the substance being studied. If the frequency of the IR radiation matches the natural frequency of the substance then that energy will be absorbed.

To find out which IR frequencies have been absorbed, the radiation which enters the sample is compared to the radiation which leaves the sample. Then the IR spectrum produced is compared to spectra of known substances which are stored in a data bank.

Initial studies of IR spectrometry used only one frequency of infra-red light at a time as shown in Figure 76.1.

The monochromator selects one frequency of infra-red light – this is split so some goes through the sample being studied and the rest goes unchanged to the detector and recorder. A computer compares the two spectra electronically to see what effect the sample has had on the IR light – how much has been absorbed. The process is repeated many times, using a different frequency of infra-red radiation each time.

These days, rather than just looking at the effect of one wavelength at a time, a technique called Fourier transformation analysis is used. This technological development allows for the analysis of many radiation frequencies simultaneously and thus achieves much faster analysis of the sample.

The **wave number** is used as a unit in IR spectroscopy. The wave number is the number of wave peaks in 1 cm of a wave.

$$\text{Wave number} = \frac{1}{\text{wavelength}}\ \text{cm}^{-1}$$

Wave number is directly proportional to the energy involved – a higher wave number corresponds to a higher energy.

For example, a wave with wavelength 5×10^{-4} cm would have a wave number of $\frac{1}{0.0005} = 2000\ \text{cm}^{-1}$.

Interpreting results

The way that a bond can vibrate, bend and stretch when exposed to infra-red radiation depends on the **strength and length of the bond and the mass of the atoms** at each end of the bond. Stretching (changing bond length) requires more energy than bending (changing the angle between two bonds in a molecule).

For example, a **molecule of carbon dioxide** (CO_2) will vibrate when subjected to infra-red radiation. As it absorbs the radiation, the two C=O bonds stretch and bend relative to each other, changing the length and shape of the molecule. This can be symmetrical or asymmetrical. The amount of infra-red radiation absorbed provides a measure of carbon dioxide concentration, for example in blood.

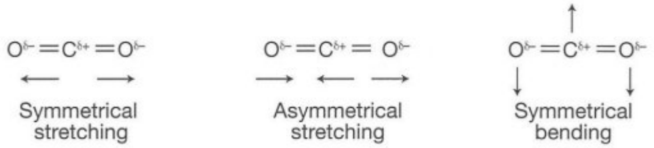


Figure 76.2 Model of bending and stretching of CO_2 molecule when exposed to IR radiation.

A diatomic **molecule such as hydrogen chloride** (HCl) can stretch, but not bend. This is because there is only one bond present and bending refers to changes in the angle between two bonds.

The **stronger the bond within a molecule, the more energy needed to make it vibrate**. For example, in Table 76.1, HCl has the highest bond enthalpy, indicating the most energy needed to break the bonds and thus the strongest bonds present. HCl also absorbs the radiation with highest frequency and thus highest energy indicating the strongest bonds.

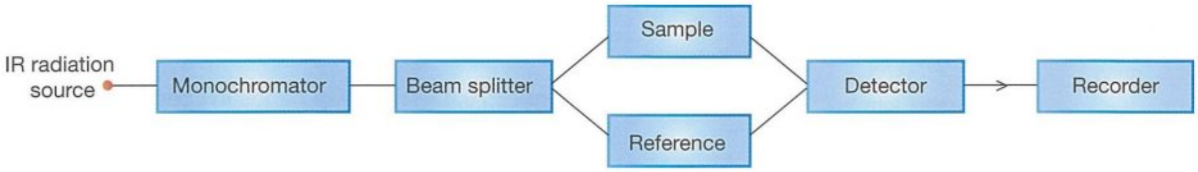


Figure 76.1 An infra-red spectrometer.

Table 76.1 Comparing bond strength using infra-red spectrometry.

Molecule	Bond enthalpy (kJ mol^{-1})	Absorption (cm^{-1})
H–Cl	431	2886
H–Br	366	2559
H–I	299	2230

Absorption within a particular range of infra-red radiation can be used to predict the presence of particular bonds. For example, see Table 76.2.

Table 76.2 IR radiation absorbed by bonds.

Bond	Wave number absorbed (cm^{-1})
C–O	1050 to 1411
C–H	2850 to 3000 (in alkanes) 3000 to 3100 (in alkenes)
C=O	1700 to 1750
O–H	2500 to 3300 (in carboxylic acids) 3200 to 3600 (in alcohols and phenols)

Such information will indicate bonds that are present, but gives no information about the number of such bonds in the molecule.

Note that molecules which are **non-polar**, such as hydrogen (H_2) cannot absorb infra-red radiation.

Interpreting an infra-red spectrum

Infra-red spectroscopy makes use of the way in which molecules absorb different frequencies that are characteristic for their structure. The **spectrogram /spectrum** produced shows the amount of energy absorbed at each frequency.

Different types of bonds vibrate at different frequencies so they absorb infra-red light with different wavelengths. We can see this in an infra-red spectrum such as in Figure 76.3. The interpretation of spectral data uses the characteristic absorption bands to identify bonds present in the compound being analysed.

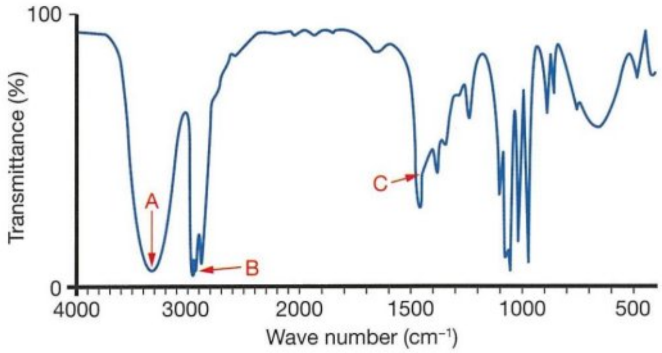


Figure 76.3 A typical infra-red spectrum.

When you look at an infra-red spectrum, such as in Figure 76.3, you should first notice two things:

- The horizontal scale increases from right to left, not from left to right.
- The left and right sides look different. On the left side, above about 2000 cm^{-1}, there are usually fewer peaks whereas on the right there are usually a lot more peaks.
- The vertical axis is percentage transmission, therefore an absorption peak shows as a decrease in transmission.

On **the left side of the spectrum**, a peak at wave number above 3000 cm^{-1}, in the area labelled A, indicates energy being absorbed as O–H bonds stretch. This tells you that an **OH group** is present in the compound being studied.

Also on the left, just below 3000 cm^{-1}, in the area labelled B, the drop indicates energy being absorbed by the stretching of **C–H bonds**. This tells you that there are saturated carbon atoms present.

Not many groups absorb between about 2800 and 2000 cm^{-1}, so there is often no peak in this region. If there are peaks in this region they are most likely to be from **nitrile groups** (such as in amines and amides) or from the **triple carbon-carbon bonds** of alkynes.

The **right half of the spectrum**, in the area where the wave number is less than 2000 cm^{-1}, often has many peaks which differ in intensity. This area is called the **fingerprint region** because almost every organic compound produces a unique pattern in this area and this can be used to confirm identity of substances. A peak at around 1200 cm^{-1} can indicate the presence of a **C–O bond**. Also, if there is a strong peak around the 1700 value, this indicates the presence of a **carbonyl group** (C=O).

Figure 76.4 summarises how the position of some of these peaks in the spectrum can help you to identify compounds.

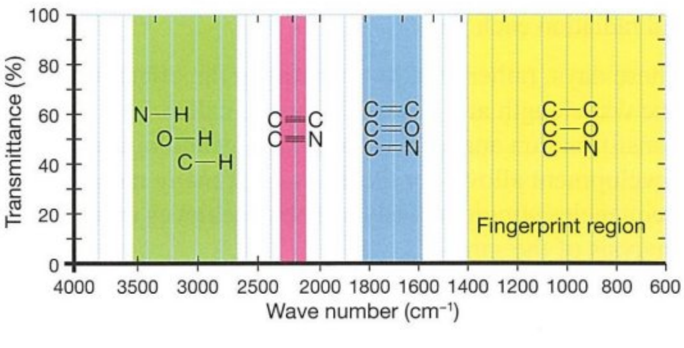


Figure 76.4 IR radiation bands in spectrum and bonds that absorb it.

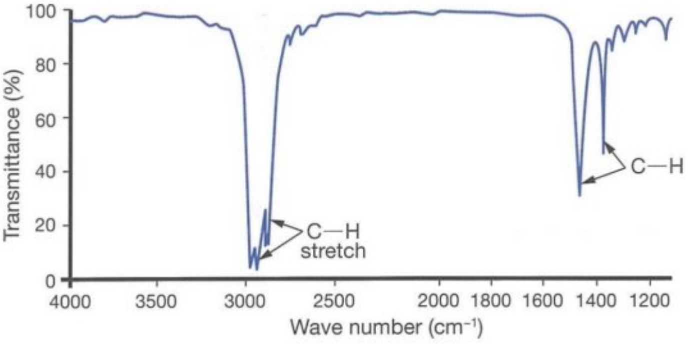
There are a few more things you should be aware of:

- The actual wavelength which is absorbed by any bond can vary. For instance, the greater the mass of the attached atoms, the lower the frequency of the infra-red radiation where absorption will occur. Conversely, bonds between lighter atoms vibrate at higher frequencies. Also, stronger bonds absorb at higher frequencies.
- Non-polar, symmetrical molecules such as hydrogen (H_2) cannot absorb infra-red radiation. The greater the polarity of a bond, the stronger its IR absorption.
- The IR spectrum tells us the types of bonds present, but it cannot indicate how many of each type of bond is present in the substance being analysed.

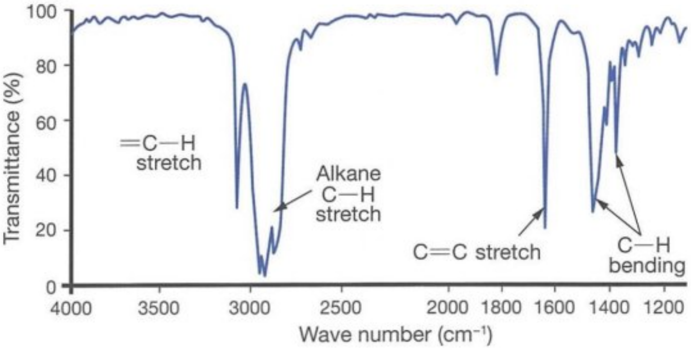
Examples of IR spectra

Below are IR spectra of compounds which belong to five different homologous groups. See if you can recognise them.

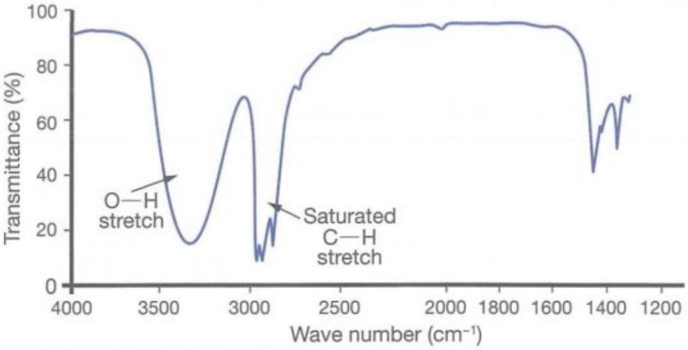
An **alkane** – notice C–H stretch (on the left) and C–H bending (on the right) causing absorption.



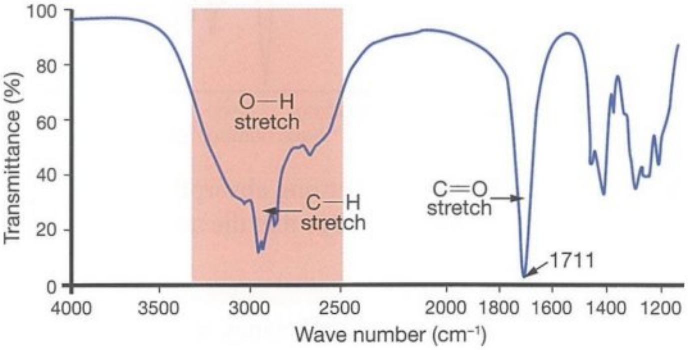
An **alkene** – notice absorptions caused by the C=C stretch at about 1600 to 1700, a C–H stretch at about 3000, and C–H bending at about 1400.



An **alcohol** – notice the broad band between about 3000 and 3700 cm^{-1} indicating an O–H bond and C–H stretch just before 3000.



A **carboxylic acid** – notice the broad band between about 3800 and 3000 cm^{-1}, indicating the presence of an OH bond, and the C=O stretch is at about 1700. Both of these bonds occur in a carboxylic acid (COOH).



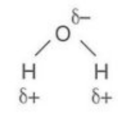
Uses of infra-red spectrometry

IR spectrometry is a reliable technique which can be used in inorganic and organic chemistry. Small measuring devices have been developed which allow studies in the field. It is used in research, in industry and in forensic analysis. Some uses include the following.

- Determining blood alcohol levels.
- Identifying how much a polymer has broken down or degraded.
- Monitoring the concentration of carbon dioxide in blood during surgery.

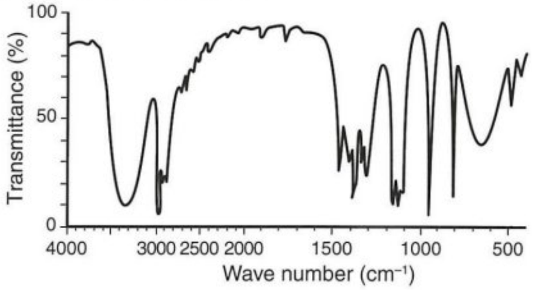
QUESTIONS

1. Outline what is meant by the following.
   (a) Infra-red radiation.
   (b) An infra-red spectrometer.
2. Use the information in Table 76.2 together with anything else you know about C–H and C=O bonds to predict which bond would absorb the higher energy infra-red radiation.
3. Infra-red radiation will be absorbed by a water molecule. What effect, if any, will this have on the polarity of the molecule?

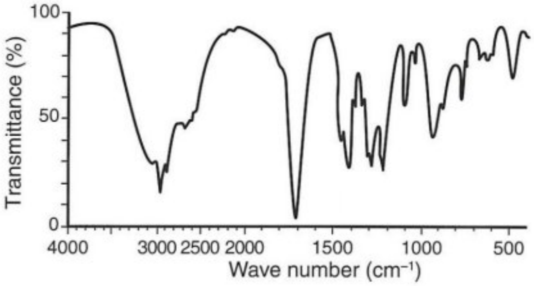


4. Examine the IR spectra below. Use the information in Table 76.2 to label, on each spectrum, absorption bands which would indicate the presence of C–O. C–H, C=O and O–H bonds.

(a)



(b)

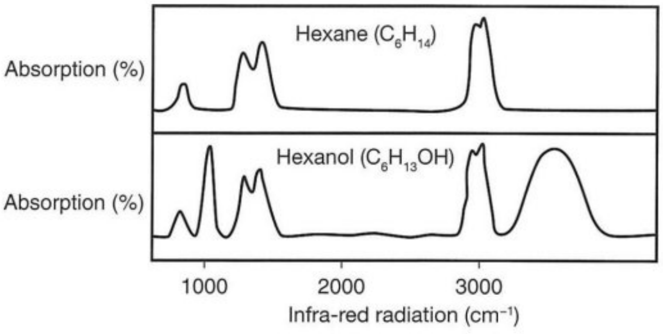


5. An IR spectrum shows strong absorption at around 1700 cm^{-1}. Does this prove that the substance under study is an ester?

6. Research an example of an advance in technology which has improved the efficiency with which we can identify chemicals.

7. Samples containing one of the two following compounds undergo IR spectroscopy.
Compound 1: $C_3H_7COOC_2H_5$
Compound 2: $C_3H_7COC_2H_5$
The samples show a strong absorbance at 1000 to 1300. Does this indicate the presence of compound 1 or compound 2 in the samples? Explain.

8. The diagram shows the infra-red spectrum for hexane (C_6H_{14}) and hexanol ($C_6H_{13}OH$).

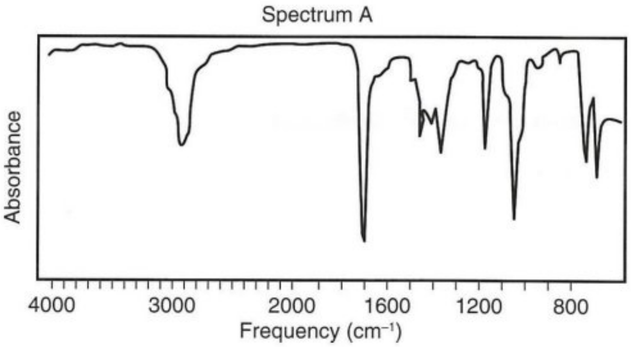


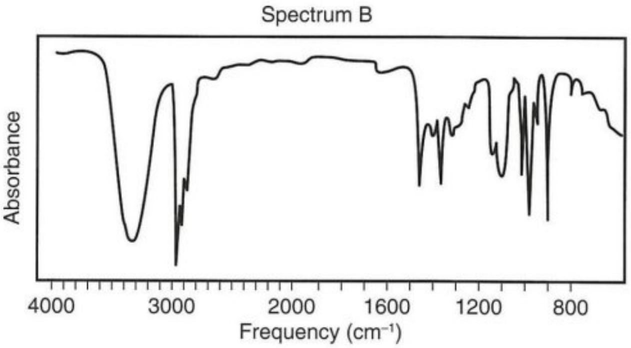
(a) What causes the peaks that are seen in the infra-red spectra?
(b) The spectrum of hexanol has two more peaks than the spectrum of hexane. Explain.
(c) What property of the structure of a molecule causes the absorption of energy in the technique of infra-red spectroscopy?

9. Some covalent bonds have characteristic infra-red stretching frequencies which are evident in their spectra. These include the following.

Bond	Found in	Frequency (cm^{-1})
C–H	Alkanes	2850 to 2950
O–H	Alkanols	3200 to 3400
C=O	Alkanals and alkanones	1680 to 1750

Two infra-red spectra are illustrated below. One is butanone and the other is butan-2-ol. Identify which is which and justify your answer.





10. Check your knowledge with this quick quiz.
(a) Radiation with wavelength less than microwaves and greater than visible light is called ....
(b) An instrument that measures the absorption of infra-red radiation to analyse structure of molecules and identify chemicals is called ....
(c) Infra-red radiation causes covalent bonds to .... and ....
(d) The higher the frequency absorbed the (stronger/weaker) the bond.

77 Introduction To NMR

Nuclear magnetic resonance analysis (NMR) is a research and analysis technique that makes use of the magnetic properties of some atomic nuclei, to determine the physical and chemical properties of atoms in molecules.

Background information

- You will recall from your studies on atomic structure that electrons spin as they orbit an atom. Particles in the nucleus of atoms also spin. If atoms have paired particles spinning in opposite directions they cancel each other out and the nucleus has no overall spin, for example in atoms of carbon-12. But some other atoms do have **net nuclear spin**, for example the isotopes **hydrogen-1, carbon-13, fluorine-19 and phosphorus-31**. Here we will focus on ^{1}H and ^{13}C.
- Any **charged particle in motion will develop a magnetic field**, so atoms of these isotopes with nuclear spins will be magnetic.
- If you place a small magnet in a large magnetic field it will move, e.g. a compass needle (a tiny bar magnet) moves in the Earth's magnetic field and points due north.
- In a similar way, if these atomic nuclei are not in a magnetic field – as in Figure 77.1 (a) – they will be randomly oriented. This just means that their poles will point every which way.

  But if you place these same nuclei in a strong magnetic field, they will all line up, the spin axis of each nucleus becoming parallel to the magnetic field. They might all point in the same direction as the magnetic field (as shown in Figure 77.1(b)), or they may all be against the magnetic field.

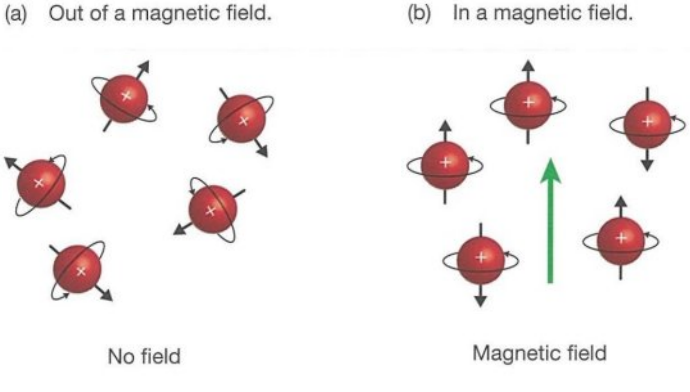


Figure 77.1 Spinning nuclei of atoms such as those of ^{1}H and ^{13}C.

It is this magnetic property of the nuclei of atoms that is used in nuclear magnetic resonance spectroscopy.

- When radio waves are applied to nuclei in a magnetic field, the nuclei absorb the energy of the radio waves. This energy changes the direction in which they point (their orientation) – it changes their spin energy, which we call their **spin state**. There is a very small difference in energy between the two possible spin states.
- The nuclei lined up in the direction of the magnetic field have a lower energy state than those lined up against the field.

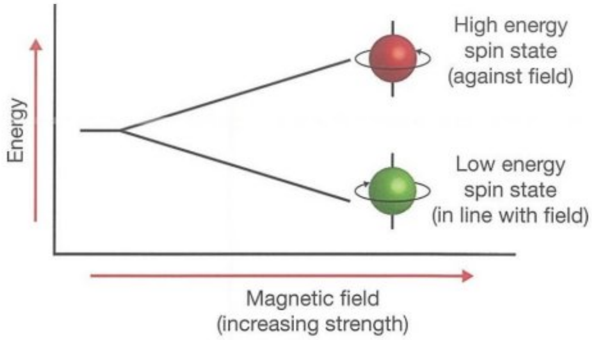


Figure 77.2 Spin states.

- At the higher energy level, the nuclei are unstable. They soon flip back to their original base level, **releasing the energy** they had absorbed.
- The magnetic field strength and the frequency of the radio waves which the nuclei absorb provide information about the structure of the compound being analysed. For instance, a hydrogen attached to a carbon atom and a hydrogen attached to an oxygen atom would absorb at different frequencies.
- The **frequency of the radiation used in NMR** is similar to that used for radio or television broadcasting (approximately 60 to 1000 MHz) because its energy level is similar to the difference between the high and low energy states of the nucleus when it is aligned and not aligned – in other words when it is in different spin states.

NMR spectroscopy

Nuclear magnetic resonance spectroscopy is an analytical technique which uses the magnetic properties of nuclei, such as hydrogen-1 and carbon-13.

Samples are placed in a strong **magnetic field**, and **electromagnetic radiation** in the radio/television frequency band is applied. The nuclei absorb the electromagnetic radiation and an NMR spectrum is produced which shows this absorption in a spectrum.

Notice that this **differs from ultraviolet, visible and infra-red absorption** where the outer electrons (rather than the nuclei) are involved in the absorption.

An **NMR spectrum** is a plot/graph of the shift in the radio frequency, which has been applied to the substance being analysed, against the absorption by the substance being analysed. Absorptions appear as sharp peaks or signals. The peaks represent **resonance** energies for nuclei in a molecule – the specific frequency absorbed.

The position in the spectrum where the absorption occurs for each hydrogen or carbon atom in the molecule, is referred to as the **chemical shift** from a known **standard**. Different chemical groups have different chemical shifts so the observed position and number of chemical shifts helps to determine the structure of a molecule.

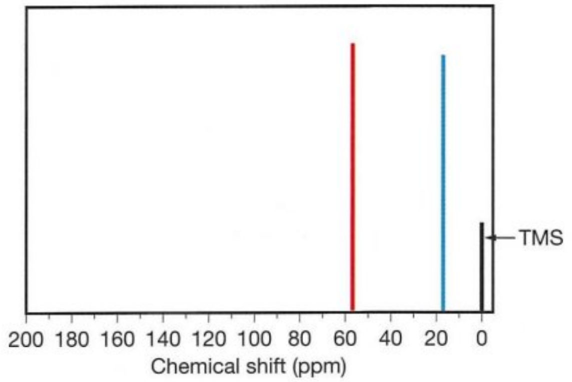
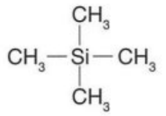


Figure 77.3 An NMR spectrum for ethanol obtained using carbon-13.

The standard against which chemical shifts are compared is always **tetramethylsilane** (TMS). The peak for TMS is given a shift value of 0 on the spectrum as shown in Figure 77.3.


$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$

Tetramethylsilane

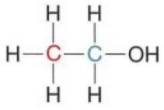
TMS is used because it is a symmetrical and chemically inert molecule, soluble in most organic solvents and very volatile (so it can be easily removed after testing and re-used). All of its 4 carbon atoms have the same chemical environment, as do its 12 hydrogen atoms, so a single intense peak is produced from this molecule. It is also non-toxic and is unreactive so it will not affect the sample being analysed.

This reference standard (TMS) is mixed with the solution being investigated. The frequency of radiation emitted by the sample being analysed is then read as a chemical shift (in ppm) from this standard.

Shielding and the environment

The movement of an electron cloud around a nucleus creates a small magnetic field which opposes the magnetic field being applied to it. This reduces the field that is experienced by the nucleus. The electron is said to **shield the nucleus**. Because of this shielding effect, the energy at which each nucleus resonates depends on its surrounding electron clouds – its **environment**.

The **chemical environment** of a nucleus refers to the types of atoms around it – for example, the environment could refer to a nearby carbon chain, an oxygen atom, a hydroxyl group or one or more hydrogen atoms.


$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$

Ethanol

For example, in a molecule of ethanol, there are two carbon atoms, and each has a different environment. The red C has three H attached and is close to a CH_2OH group. The blue C has 2 H and an OH group attached and is close to a CH_3 group.

In Figure 77.3, the red line on the left shows the shift caused by the C in the CH_3 group, and the blue line is caused by the C in the CH_2OH group.

Uses of NMR

NMR is used to investigate the molecular structure of both organic and inorganic molecules, to analyse the composition of mixtures and to study the physical properties of substances such as solubility and diffusion. It can be used in research, to determine the purity of substances, to design drugs, to screen for the presence of drugs, for quality control in industry. It is used to study membrane structures and protein folding, and to study metabolic pathways – determining how chemicals in the body are synthesised and broken down.

In the next chapter we will compare the spectra produced by two types of NMR, using carbon-13 (^{13}C NMR) and hydrogen-1 (^{1}H NMR).

QUESTIONS

1. (a) What is NMR?
   (b) Outline uses of NMR.
   (c) Identify two advantages of NMR.
   (d) Define a chemical shift in NMR.
   (e) What is the spin energy of a nucleus?
2. How does the resonance frequency in NMR spectra help determine the structure of molecules?
3. (a) Of what use is tetramethylsilane (TMS) in nuclear magnetic resonance?
   (b) List reasons why TMS is selected for this purpose?
4. NMR is being used with increasing frequency in medicine and is the basis of the body scanner called an MRI (magnetic resonance imager). Research the use of NMR in medicine.

78 Nuclear Magnetic Resonance

You have seen that nuclear magnetic resonance (NMR) is a research and analysis technique that makes use of the magnetic properties of some atomic nuclei, to determine the physical structure and chemical properties of atoms in molecules. The main isotopes used are carbon-13 and hydrogen-1. Here we will look at the spectra produced using each of these isotopes.

The ^{13}C NMR spectrum

The carbon-13 isotope is used in NMR to determine the **type and number of carbon atoms in a molecule and their environments**. NMR using the carbon-13 isotope can give information about any molecule present in the sample being analysed that contains carbon atoms. However, in C-13 NMR spectra you cannot draw any conclusions based on the heights of the peaks.

Figure 78.1 shows the spectrum for ethanol obtained using the ^{13}C isotope that we saw in the last chapter. Carbon atoms show chemical shifts between 0 and 200 ppm and each peak on the spectrum shows a carbon atom in a different environment within the molecule. Notice that **on NMR spectra the horizontal scale increases to the left, not to the right.**

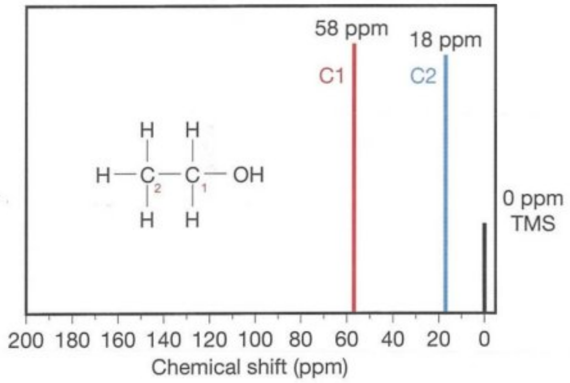


Figure 78.1 A ^{13}C NMR spectrum for ethanol.

Each carbon atom in the structure being analysed produces a peak on the spectrum. The position of the peak depends on the environment of that C atom. In ethanol there are two C atoms with different environments, so two peaks are produced.

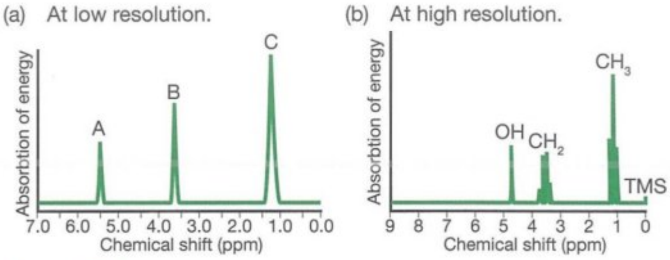
In a chemical data book you will find a table that tells you where in the spectrum each type of carbon atom will produce a peak. The part of that table relevant to ethanol is shown in Table 78.1.

Table 78.1 ^{13}C NMR data.

Type of carbon	Chemical shift (ppm)
$R{-}CH_3$	8 to 25
$R{-}CH_2{-}OH$	50 to 90

The ^1H NMR spectrum

Figure 78.2 shows a spectrum for ethanol obtained using the ^1H isotope. NMR using the hydrogen-1 isotope gives information about any molecule containing hydrogen atoms. It is used to determine the **type and number of H atoms in a molecule and their environments**. You will see that most protons (hydrogen ions) absorb between 0 and 10 ppm, and this is different to absorptions involving carbon atoms. Notice that here also the horizontal scale increases to the left, not to the right.

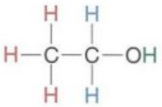

(a) At low resolution.

(b) At high resolution.

Figure 78.2 A ^1H NMR spectrum of ethanol.

The zero point on the scale is where the peak for tetramethylsilane occurs. Everything else is compared to this. All other peaks are downfield (to the left) of TMS, because to produce resonance, all other substances need smaller magnetic fields than TMS and resonate at a higher chemical shift.

There are three other shifts suggesting that the protons (H's), in the structure, occur in three different **chemical environments** and thus each needs different magnetic fields to resonate.


Ethanol

The spectrum in Figure 78.2 is consistent with the structure for ethanol. It contains an H attached to O, 2H's which form part of a CH_2 and 3H's forming part of a CH_3. Hydrogen atoms in these three different environments produce three peaks in three different areas of the ^1H NMR spectrum.

Before you go on, you should make sure you understand the differences between the spectra for ethanol produced by NMR when using hydrogen-1 and carbon-13. If you are unsure, you should talk to your teacher.

In an ^1H NMR spectrum, protons in the same environment (attached to the same groups) give the same signal. This means that in a spectrum:

Number of different NMR signals = Number of protons in different environments

Here are some more examples of this.

Table 78.2 Types of protons and number of signals in different molecules.

1 type of H 1 NMR signal	2 types of H's 2 NMR signals	3 types of H's 3 NMR signals
$\underset{\overset{\uparrow}{H_a}}{CH_3}{-}O{-}\underset{\overset{\uparrow}{H_a}}{CH_3}$	$\underset{\overset{\uparrow}{H_a}}{CH_3}\underset{\overset{\uparrow}{H_b}}{CH_2}{-}Cl$	$\underset{\overset{\uparrow}{H_a}}{CH_3}{-}O{-}\underset{\overset{\uparrow}{H_b}}{CH_2}\underset{\overset{\uparrow}{H_c}}{CH_3}$

A chemical data book can show possible chemical environments for protons (H's) that correspond to various chemical shifts. For example:

- A **chemical shift of between 0.8 and 1.0 ppm** is typical for a hydrogen in the environment of a **CH_3 group**, so a peak in this area on the spectrum tells us that the sample contains a CH_3 group (as in Figure 78.2).
- A **shift between 1 and 6** can indicate an H attached to an **OH group**.
- A shift between 3.3 and 4.5 can indicate an H in a CH_2 group attached to an OH group (as in Figure 78.2).
- A **shift between 9 and 10 ppm** indicates the presence of a molecule containing a **carbonyl (C=O) group**. The chemical shift is greater for this environment than for the CH_3 environment because there is an electronegative oxygen atom close by – it means that a smaller magnetic field will achieve resonance. Remember, the smaller the magnetic field needed, the higher the chemical shift will be.

You may however notice that the position of some groups is different in different sources. In an exam, just be sure to use the data table you are given.

Area under the peak. In an ^1H NMR spectrum, the **relative heights of the peaks and the relative area under each peak** represent the number of nuclei that were present to cause the peak. The area under each peak of an ^1H NMR spectrum corresponds to the ratio of the number of hydrogen atoms in a particular environment in a molecule. So a peak with twice the area will have twice as many nuclei. This is very useful when working out the structure of a chemical being analysed.

Peak splitting patterns. The absorptions of hydrogen atoms on nearby carbon atoms tend to interfere with each other and split some absorptions into a number of closely grouped peaks. These are called peak splitting patterns.

What appears to be a single peak in an ^1H NMR spectrum, when examined at low resolution as in Figure 78.2 (a), may be split into a cluster of peaks when looked at under high resolution as in Figure 78.2 (b).

There are four main types of peak splitting patterns.

You can use the $n + 1$ rule to find what the peak splitting pattern tells you about the number of hydrogen atoms **attached to** the **next carbon atom** in the molecule.

$N + 1$ rule. The number of subpeaks in a cluster is one more than the number of hydrogen atoms attached to the next door carbon atom.

Table 78.3 Peak splitting patterns.

Number of subpeaks in each cluster	Pattern
1 peak	Singlet
2 peaks	Doublet
3 peaks	Triplet
4 peaks	Quartet

Table 78.4 The $n + 1$ rule.

Pattern	What it tells you about the next carbon in the molecule
Singlet	Next C has no H attached
Doublet	Next to a CH group
Triplet	Next to a CH_2 group
Quartet	Next to a CH_3 group

For example, think about the spectra produced by **$BrCH_2CH_2Br$** and **$BrCH_2CH_2Cl$**.

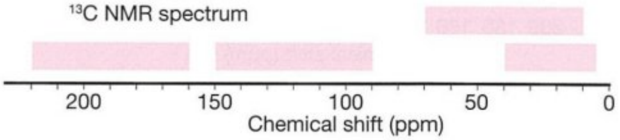
The ^1H NMR spectrum of **$BrCH_2CH_2Br$** would have **one singlet** as all H's are in the same chemical environment- they are each attached to a C with a Br atom and another H atom attached.

However, the ^1H MHR spectrum of **$BrCH_2CH_2Cl$** would have **two sets of triplets** because each CH_2 group has a different environment – one has a Br attached and the other has a Cl attached. There will be two peaks and each will split to form triplets under high resolution showing that each C has two hydrogens ($3 - 1 = 2$) on the adjacent C.

Notice that the presence of an **OH group** would produce a **singlet**. The H on the OH group does not interact with any hydrogens on the adjacent carbons so it does not produce splitting.

QUESTIONS

1. What is meant by ^1H NMR and ^{13}C NMR?
2. The figures show a simplified version of regions where you would expect to find the chemical shift for some main carbon groups on an NMR spectrum produced using hydrogen-1 and carbon-13. Fill in the boxes to show where you would find the following: C=O, C–C alkyl (C–C) groups, C–X (halogen), and C=C groups.

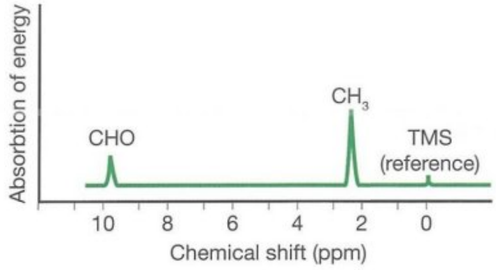


3. (a) What is meant by the chemical environment?
   (b) Complete the table to demonstrate the number of peaks each of the compounds would have on an ^1H NMR spectrum and on a ^{13}C NMR spectrum.

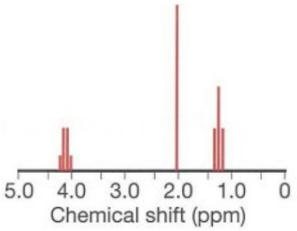
Molecular formula	Number of peaks on spectrum	
	^1H NMR	^{12}C NMR
$C(CH_3)_4$		
$CH(CH_3)_2Cl$		
CH_3COOCH_3		

4. An organic compound with molecular formula $C_4H_{10}O$ undergoes ^{13}C NMR.
   (a) Use structural formulas to show four isomers which all have this molecular formula.
   (b) For each of these isomers, determine the number of environments for the carbon atoms and hence deduce the number of peaks you would expect to find in a ^{13}C NMR spectrum.

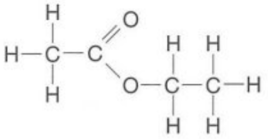
5. The spectrum shows a low resolution ^1H NMR analysis for a sample containing either ethanal (CH_3CHO) or ethanol (CH_3CHOH). Identify which substance is present and justify your conclusion.



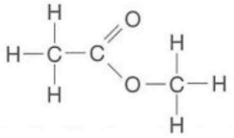
6. (a) Outline the $n + 1$ rule.
   (b) What is a triplet?
   (c) This ^1H MHR spectrum has three peak areas. What does this indicate?



   (d) The formula for this compound is shown. Indicate which part of the formula is responsible for producing each peak on the spectrum.

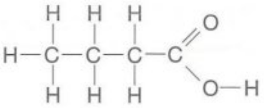


7. Consider the molecule shown.
   (a) Name this compound.
   (b) If this compounds undergoes nuclear magnetic resonance:
      (i) How many sets of peaks would you expect to find in an ^1H NMR spectrum?
      (ii) How many sets of peaks would you expect to find in a ^{13}C NMR spectrum?

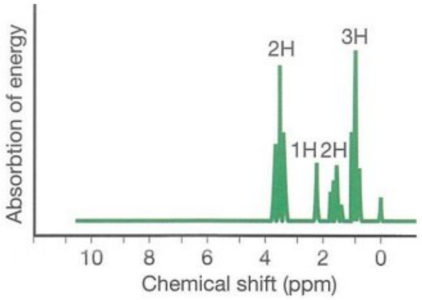


8. An organic compound has the molecular formula of $CH_3CH_2CH_2CH_3$.
   (a) Name this compound.
   (b) If this compound undergoes nuclear magnetic resonance:
      (i) How many sets of peaks would you expect to find in an ^1H NMR spectrum?
      (ii) How many sets of peaks would you expect to find in a ^{13}C NMR spectrum?

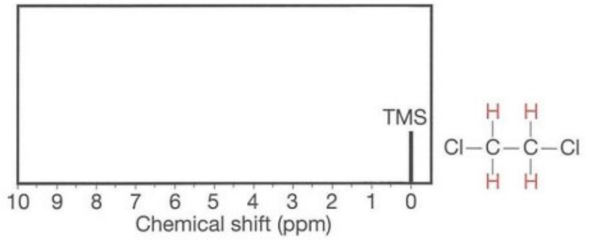
9. The molecule shown is an organic compound.
   (a) Name this compound.
   (b) In an ^1H NMR spectrum, how many chemically different proton environments would be present?
   (c) In a ^{13}C NMR spectrum, how many chemically different carbon environments would be present?



10. A high resolution ^1H NMR analysis is carried out and the resulting spectrum is illustrated. Could this spectrum represent propan-1-ol or propan-2-ol or both? Explain.



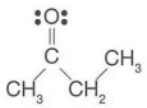
11. Use the appropriate table of ^1H NMR data in a chemical data book to complete the diagram showing a spectrum for 1,2-dichloroethane.

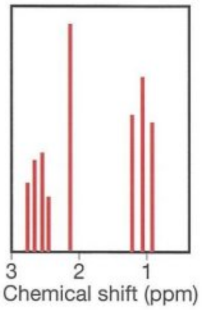


12. Research the following topics.
   (a) Why does the ethanol (–OH) group have such a wide range of occurrence on the ^1H NMR?
   (b) Why does the H in H–Cl absorb radiation at a higher frequency than the H in H–I?

13. An organic compound, with molecular formula C_3H_8O undergoes analysis by mass spectrometry, nuclear magnetic resonance and infra-red radiation. The mass spectrum shows that the molecular mass of the compound is 60, based on the mass of the heaviest fragment produced.
The ^1H NMR spectrum shows four hydrogen environments.
The IR spectrum shows that an O–H bond is present. Deduce the structural formula of its molecules and name the compound.

14. The diagram shows the structural formula of an organic compound and the spectrum produced when this compound undergoes ^1H NMR.
Indicate which area of the compound gives rise to each of the peaks shown.





79 Chromatography

Last year you studied the basics of the analysis technique called chromatography. It is being revised here because chromatography is useful in the separation of both inorganic and organic molecules so they can be analysed. Thus chromatograpy is often used in conjunction with other analytical techniques.

Chromatography is an analysis technique used to separate out pure components of a mixture so as to analyse its composition. It identifies and quantifies components of a mixture.

Terminology

In chromatography, two phases are used – a **stationary and a mobile phase**.

The substance being analysed is called an **analyte**. The analyte is dissolved in a **solvent** (eluent) and together they make up a **mobile phase** which moves through the solid **stationary phase**. The mobile phase that carries the sample components with it is called the **eluent**. The combination of the mobile phase and the sample components is called the **eluate**.

The **mobile phase** can be either a pure solvent or a mixture of solvents. In gas chromatography the mobile phase is a gas.

As the mobile phase moves through the stationary phase, the sample components in the analyte are **adsorbed** onto the stationary phase to varying degrees. **Adsorption** refers to the binding or adhesion of particles to a surface.

Column chromatography

Traditionally this occurs in a column. The rate of movement of the mobile stage components through a chromatography column, and thus their separation, depends on:

- How much each component dissolves in the mobile stage.
- How strongly each component of the mixture adheres to the stationary phase. If it is not strongly adsorbed, it moves through rapidly.

What comes out of the chromatography column is referred to as the eluate. Evaporating the mobile phase solvents from the eluate leaves us with components of the original sample. Using different solvents, we can extract different components of the original sample.

The time taken for a substance to pass through the chromatography column is called the **retention time** (R_t). The retention time for each component of a mixture being analysed is compared to retention times already measured for pure substances, to determine the identity of the component present.

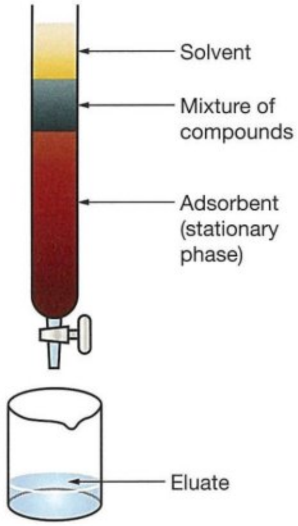


Figure 79.1 Column chromatography.

The eluate which exits the chromatography column is passed through a detector such as **UV light**. Any organic compounds present absorb this UV light, the amount absorbed depending on the quantity of the substance present in the mixture.

The chromatogram

The UV light can be recorded as a **chromatogram** which consists of a series of peaks. Each peak identifies a different substance and the **area under each peak** shows the amount of that substance present in the mixture being analysed.

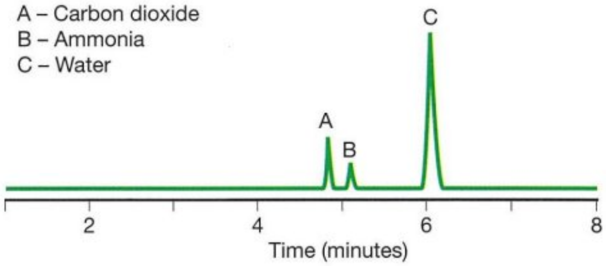


Figure 79.2 A chromatogram of carbon dioxide and ammonia in water.

High pressure liquid chromatography (HPLC)

HPLC is an improved form of column chromatography. In HPLC, the solid phase consists of tiny particles which allows for better adsorption and separation of the mixture components. However, this would slow down flow, so the mobile phase is pushed through the column and adsorption material under a high pressure of up to 400 atmospheres. The methods used to detect the components are **automated and extremely sensitive** making it a **fast and very accurate method of analysis**.

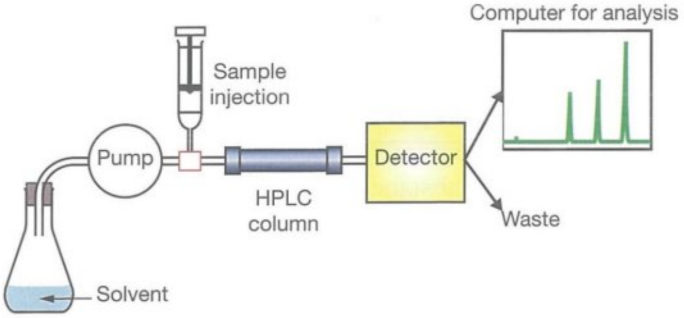


Figure 79.3 High pressure liquid chromatography.

Reversed phase HPLC

Originally the mobile phase was less polar than the stationary phase, but nowadays the most common form of HPLC reverses the phases by using a **polar solvent** (e.g. a mixture of water and alcohol) to produce a **polar mobile stage** and a **non-polar stationary phase** such as a C18 polymer. This results in any polar molecules travelling through the column most quickly.

Uses of HPLC

HPLC is very important in pharmaceutical and industrial analysis. It can be used to test purity of foods, and industrial raw materials and products, to determine the structure of chemicals such as drugs and their breakdown products including herbal medicine as well as synthetic drugs. Some examples of its use are: to separate chiral molecules and their enantiomers, determine composition of proteins, analyse body fluids, for example blood and urine for the presence of drugs or metabolic chemicals, find poisons in autopsy samples, analyse inks used in forged bank notes, track sources of organic pollution, nutritional labelling of foods. HPLC is rapid as well as accurate, and can cope with heavy workloads, features which are essential in these areas.

Gas liquid chromatography (GLC)

In GLC, the sample being tested is **vaporised** and carried through the column by a **gaseous mobile phase**, **usually helium** and the stationary phase is a liquid adsorbed onto a solid. The separation is carried out at high temperatures. This is different from HPLC as the gas is not under high pressure. The retention time is characteristic for each compound and depends on its boiling point, its solubility in the liquid phase and the temperature of the column. Retention time is reduced by having a low boiling point, being more soluble in the stationary phase and having the column at a high temperature.

This is also a very sensitive technique and can detect tiny amounts of a compound, even as small as 10^{-12} grams or 2 to 3 ppb. It can be used to analyse compounds with a large range of molar masses – from 2 to 800. However, they must be able to be **readily vaporised without decomposing**. It is used to detect performance enhancing drugs used by athletes, to analyse proteins found in cells, to assess purity of food and industrial products, to monitor the environment and to carry out continual analysis during industrial chemical production processes.

Chromatography and the mass spectrometer

Chromotography separates out the components of a mixture. Retention time of each component can be compared to known retention times of substances to determine its identity. Alternatively the chromatograph column can be coupled to a mass spectrometer so that samples from the column can be directed into the mass spectrometer for identification.

Analysis by a **mass spectrometer** can also be used to confirm the identity of the substances present. In this technique, separated compounds are ionised and fragmented by hitting them with a beam of electrons. The fragments are placed in a strong magnetic field and their deflection allows for their identification and concentration to be determined. The identity of the components of the mixture can be found as the fragmentation pattern shown by the mass spectrometer can be compared with the known fragment patterns of a huge number of compounds stored in a database.

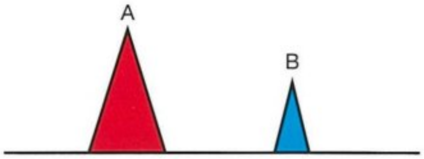
Instruments combining gas chromatography and mass spectrometry have been used to identify hundreds of components present in biological and other systems. For example, they can detect the odour and flavour components of foods, identify water pollutants, analyse components of the breath, study drug metabolites and they are invaluable in medical diagnosis and drug development

Chromatography columns and mass spectrometers can now be produced in much **smaller and more mobile versions** than the machines traditionally used in chemical laboratories. This makes them very useful in areas such as security. For instance, systems are in use at all airports that can detect explosives and chemical warfare agents.

QUESTIONS

1. What is meant by chromatography?
2. During chromatography, components of a mixture being analysed will move through and be adsorbed onto a stationary phase. How does adsorption differ from absorption?
3. (a) What is meant by retention time in chromatography?
   (b) Identify factors that determine the retention time of a compound in chromatography.
   (c) What is the advantage of combining mass spectrometry with chromatography when analysing a mixture?

4. Two peaks in a chromatogram are shown with different areas under each. These are produced by using UV absorption of substances produced in chromatographic analysis of a mixture.



(a) Identify two factors that could determine the sizes of these peaks and the areas under them.

(b) If the peak area for A = 1000 and the peak area for B = 500, what would this tell you about the relative amounts of the two substances in the original mixture?

5. In gas chromatography, the absorbance of each component being analysed is plotted against the retention time.

(a) Explain why a compound with relatively low boiling point will have a shorter retention time than a compound with a relatively high boiling point.

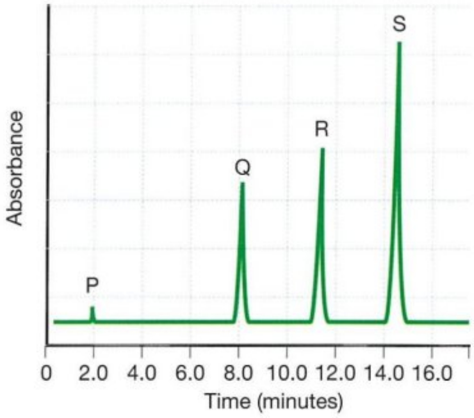
(b) Suggest reasons why a sample may not be suitable to inject into a gas chromatograph.

6. The analysis techniques of chromatography and mass spectrometry are sometimes used together.

(a) Research an example of the use of gas chromatography combined with mass spectrometry.

(b) Research a use of gas chromatography coupled with mass spectrometry in astrochemistry or in medicine.

7. Answer the questions about this gas chromatogram.



(a) How many substances were present in this mixture analysed?

(b) List the substances in order of quantity present, starting from the smallest quantity.

(c) Which substance had the longest retention time?

(d) Which substance had the least affinity for the stationary phase?

(e) In this analysis the stationary phase is non-polar and the solvent is polar. Which compound is most polar?

(f) Is it possible to determine, from this chromatogram, the identity and original amount of each substance in the original sample being analysed?

(g) What effect (if any) could the solubility of a compound in water have on its retention time?

(h) Could the temperature have any effect on retention time?

(i) If the area of peak Q = 500 and the area of peak S is 1000, what does this tell you about the composition of the original sample being analysed?

8. A high pressure liquid chromatography (HPLC) column has a polar solvent and a non-polar stationary phase. Answer the following questions about this column.

(a) What type of attractive forces will form between the solvent particles and any polar molecules in solution?

(b) What type of attractive forces will form between any non-polar molecules in solution and the stationary phase?

(c) Which will travel more slowly through the HPLC column, polar or non-polar molecules?

9. If 0.34×10^{-3} mol of a compound analysed by chromatography produces a peak area of 857 units, what will be the expected peak area produced by the analysis of 0.52×10^{-3} mol of the same compound?

10. Two substances, P and Q are passed through a chromatography column. P adsorbs more strongly onto the stationary phase of the column. Which substance P or Q will have the larger R_f value? Explain.

11. Check your knowledge with this quick quiz.

(a) Which type of chromatography column cannot be used to analyse substance that do not readily vaporise or which decomposes when heated?

(b) The time it takes a chemical to pass through a chromatography column is called the

....

(c) The chemical being analysed is called an

....

(d) What do we call the mobile stage that comes out of a chromatography column?

(e) How does GLC differ from HPLC?

(f) Reversed stage HPLC has a (polar/non-polar) mobile phase.

(g) In chromatography, the amount of a particular chemical present in the sample being analysed is shown by the .... on the chromatogram.

80 Calibration Curves For Chromatography

Calibration is the process of evaluating and adjusting the precision and accuracy of measurement equipment so that you know it is producing accurate data. For example, you would calibrate a pH probe to make sure it produces accurate pH readings. This is also necessary when using techniques such as chromatography.

A **calibration curve** is a graph which shows how the signal produced in a chromatographer changes with the concentration of the substance being measured (the analyte). It provides an accurate way to find the concentration of a substance of unknown concentration (a target analyte) by comparing it to a set of standard samples for which the concentration is known. A calibration curve is sometimes called a **standard curve**.

In chromatography:

- A series of solutions is made up using different concentrations of a compound. These are called **standards**.
- Each solution undergoes chromatography.
- The results are graphed, using a line of best fit to produce a calibration curve.
- Unknown samples then undergo chromatography and their results compared to the calibration curve.

In chromatography, the chromatogram produced shows retention time on the *x*-axis and the *y*-axis gives the intensity of response produced – this could be abundance or intensity. The calibration curve changes the *y*-axis values to conventional concentration units such as mg mL^{-1} or ppm.

The zero line produced when there are no analytes in the instrument is called the baseline. As the analyte enters the chromatographer, peaks are produced which are proportional to the concentration of the analyte present.

Figure 80.1 is an example of a calibration curve for a hypothetical compound Q. To make this curve, five solutions of compound Q, containing concentrations of 3, 6, 9, 12 and 15 mg/mL, were each analysed in a chromatographer. Each concentration produced a different sized peak. The area under the peak for each standard solution was then plotted against the concentration of the solution that produced that peak to make the calibration curve. The area under the peak for samples of Q can then be read off in concentration units (e.g. mg mL^{-1}). Sometimes the height of the peak rather than area is used.

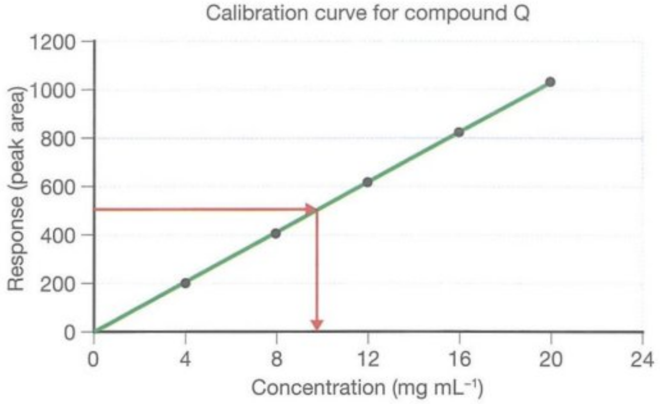


Figure 80.1 Calibration curve for compound Q.

Once the curve is constructed we then analyse compound Q. In this example it shows a peak area of 300 (as shown by the red arrow on the calibration curve) which you can see from the graph corresponds to a concentration of 10 mg mL^{-1}.

Each compound produces its own unique calibration curve. So this procedure is carried out for every substance being analysed.

Importance of calibration curves

The calibration curve also allows for calculations of the uncertainty of the results obtained. The results obtained may be affected by a number of factors including the solvents used, presence of any impurities and external factors such as temperature and pressure. Changing the operating conditions for HPLC could produce changes in the chromatogram produced. For example, if the pressure or temperature of the mobile stage is decreased, this would slow down its movement through the stationary phase and lead to higher retention times. On the other hand, using a less tightly packed column would reduce the interaction between the mobile and stationary phases and this would allow the mobile phase to move through more quickly, resulting in lower retention times.

Figure 80.2 shows the effect on a chromatogram when using a less tightly packed column reduces retention time (R_t) for a compound.

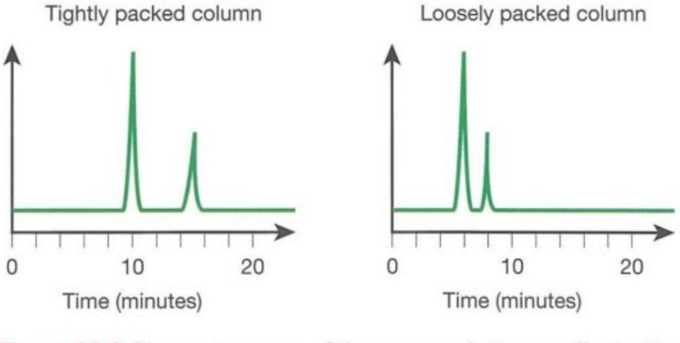
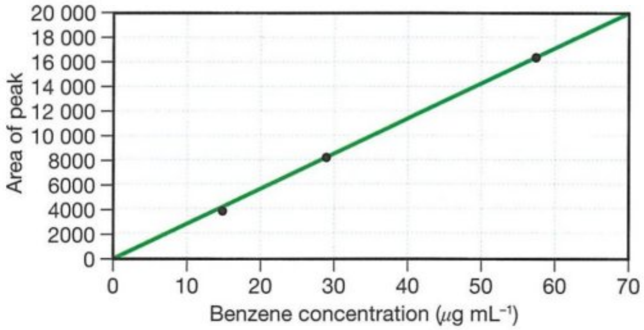


Figure 80.2 Chromatograms of the same substance affected by how tightly the column is packed.

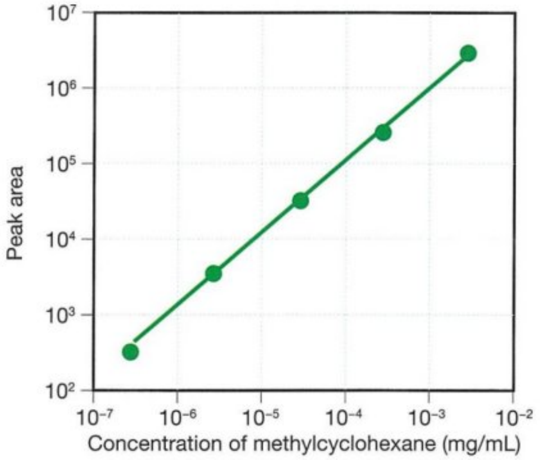
Running standards through the HPLC and comparing calibration curves taken at different times allows the effect of such factors to be detected.

QUESTIONS

1. (a) What is a calibration curve?
   (b) Identify the main steps in the construction of a calibration curve for use with chromatography.
   (c) Identify any analysis techniques you have studied during this course that use a calibration curve.
2. Benzene is a toxic compound. Exposure can cause damage to the central nervous system, an increased incidence of cancer and in high concentrations it can cause death. Any exposure to this chemical must be carefully monitored.
   A calibration curve is shown for gas chromatography of benzene.



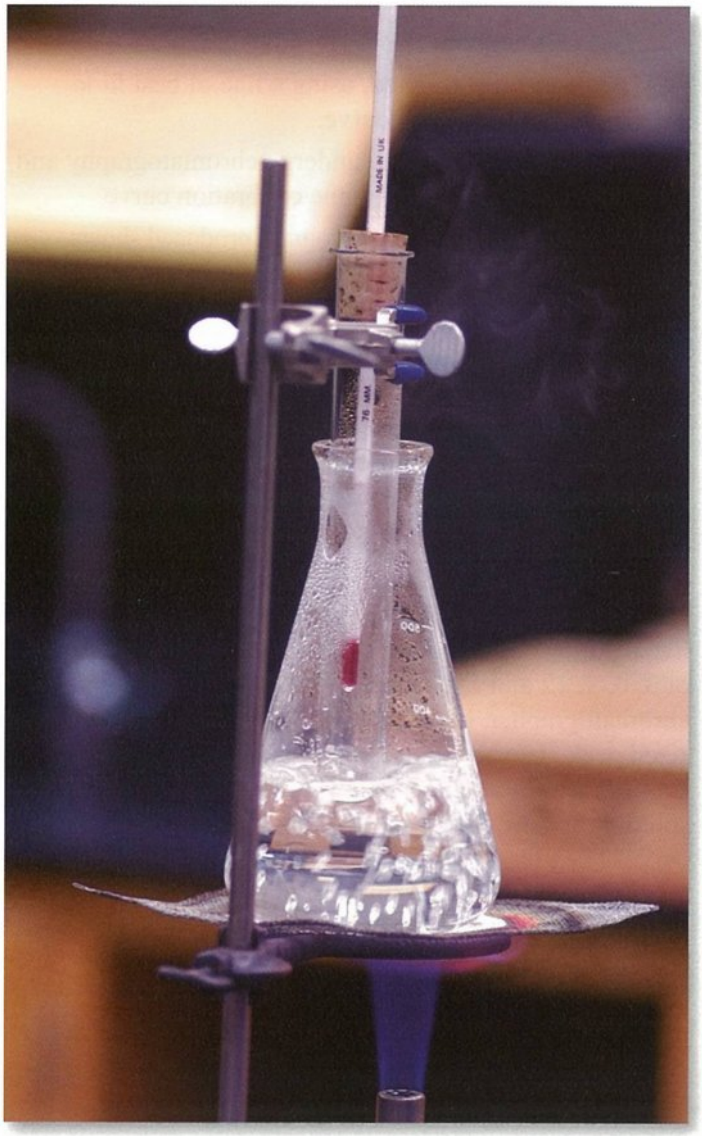
   Based on this curve, determine the concentration of benzene if the area under the peak is:
   (a) 6000
   (b) 14 000
3. The calibration curve is shown for methylcyclohexane injected into a gas chromatograph.



   A sample of unknown concentration is analysed using a gas chromatograph. If the area under the peak using a gas chromatograph is found to be 0.5×10^5, what would be the concentration of the sample?
4. Formaldehyde (methanal) is a toxic chemical which occurs naturally. It is used as an antifungal agent and also in the manufacture of products such as resins, polymers and construction materials. Because of its many uses and its toxicity it needs to be extensively monitored in products and the environment and HPLC may be used to do this.
   (a) Standard solutions of formaldehyde undergo HPLC and the following results are obtained.

Concentration (ppm)	100	250	500	750
Area under the curve	8	15	25	35

   Use these results to construct a standard curve.
   (b) A sample of contaminated water is diluted 1 in 2 and 1 in 5. Each dilution is analysed three times using HPLC under the same conditions.
   The 1 in 2 dilution samples gave the area under the curve as 30, 28 and 31 units.
   The 1 in 5 dilution samples gave results of 9, 15 and 17 units.
   Calculate the concentration of formaldehyde in the original sample in ppm and g L^{-1}.



81 Combining Analytical Methods

In laboratories, to determine the structure of organic compounds evidence may be needed from more than one analysis technique. Researchers use a combination of techniques including mass spectrometry, infra-red spectrometry and proton and carbon-13 nuclear magnetic resonance.

Mass spectrometry looks at charge to mass ratio and provides information about the molecular mass of the substance and the differences in mass of fragments of the molecule. A mass spectrum can be used to determine the molecular mass (from the largest fragment). The difference in mass between fragment ions can provide information about the structure of the molecule which can help to find the molecular formula. It also provides information about the presence of any isotopes of elements.

Infra-red spectroscopy looks at absorption of infra-red radiation by electrons and provides information about the types of bonds present in a molecule as well as atoms and groups of atoms present. It is very useful for determining the functional groups present in the compound being analysed.

Nuclear magnetic resonance (NMR) is also used to determine the structure of a compound. It uses information about the absorption of radio waves by atomic nuclei in a magnetic field to provide information about the chemical environment of every H or C atom in the molecule. To determine the structure of an organic molecule it is useful to look at either ^{1}H NMR and mass spectrometry or ^{1}H NMR and ^{13}C NMR.

Chromatography is a technique that uses retention time to separate components of a mixture, identify them and determine the quantity present.

High pressure liquid chromatography (HPLC) uses a liquid mobile phase under high pressure and is used to separate and quantify medium to high molecular weight organic compounds that can be dissolved in a solvent. It can record automatically and continuously which is an advantage in industrial processes.

Gas chromatography (GC) is useful for smaller molecular weight organic compounds (less than 800 amu) that can be readily vaporised without decomposing. This technique is extremely sensitive.

For example:

An organic compound is found to have a molecular formula of $C_6H_{12}O_2$. The **IR spectrum** indicates that it contains C–H bonds, a C=O bond and a C–O bond, indicating it could be a carboxylic acid or an ester. Further inspection shows that it does not have an O–H bond, so it is not an acid and is most likely an ester.

This compound undergoes **^{1}H NMR analysis** to determine its structure and the spectrum shown in Figure 81.1 is produced.

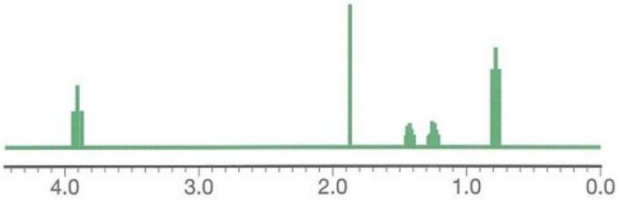
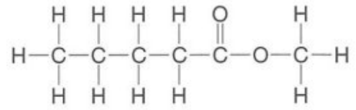


Figure 81.1 ^{1}H NMR spectrum of unknown ester.

The spectrum shows five hydrogen environments, in order, from left to right these are:

- A triplet (there will be 2 H's on the next C).
- A tall singlet (probably there will be a CH_3 group on its own).
- Two small sextets (probably two CH_2 groups surrounded by 5 nearby H's).
- A triplet (probably a CH_3 group at the end of a molecule with the next C having 2 H's).

The structure of the molecule is:



$CH_3CH_2CH_2CH_2COOCH_3$

QUESTIONS

1. The basic function of chromatography, both GC and HPLC, is to separate components of a mixture, identify them and determine the quantity present.
   (a) Identify some similarities.
   (b) Complete the table to show differences between GC and HPLC.

Factor	GC	HPLC
State of analyte		
Mobile phase		
Stationary phase		
Introduction of sample		
Particularly useful for:		

2. Of the analysis techniques studied here, identify any which:
   (a) Involve the absorption of electromagnetic radiation to change the behaviour of bonds.
   (b) Separate and distinguish between fragments of a molecule which have different mass.
   (c) Involve the use of a calibration curve.
   (d) Involve exciting nucleons to higher energy levels.

82 Revision Of Analysis Of Organic Substances

In this section you have revised some laboratory tests for functional groups of organic homologous series and you have also looked at instrumental analysis of substances.

If you have any problems with these multiple choice questions, consult your teacher.

QUESTIONS

1. To test for the presence of –C=C– double bonds you would use:
(A) Indicators.
(B) Sodium metal.
(C) A carbonate.
(D) Bromine water.

2. Which substance would decolourise bromine water in the absence of UV light?
(A) Ethane.
(B) Cyclohexene.
(C) Cyclohexane.
(D) Chloroethanol.

3. Which substance would produce carbon dioxide gas when added to sodium carbonate?
(A) Ethene.
(B) Ethane.
(C) Ethanoic acid.
(D) Ethanol.

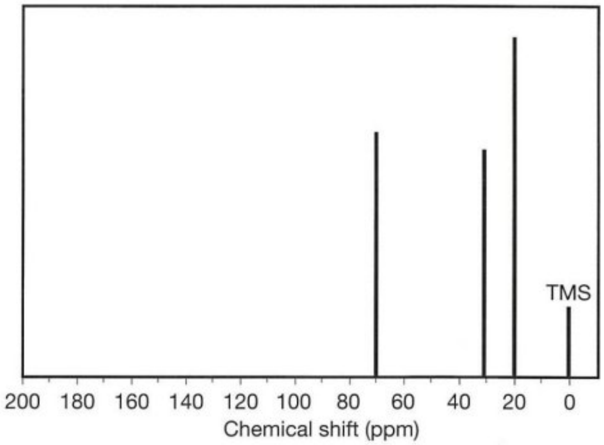
4. Which substance would react with sodium to produce hydrogen gas and an alkaline solution?
(A) Ethanol.
(B) Ethanoic acid.
(C) Ethene.
(D) Cyclohexene.

5. A chemical which would oxidise a primary or secondary alcohol could be:
(A) A tertiary alcohol.
(B) Acidified potassium dichromate.
(C) The ester, ethyl ethanoate.
(D) Calcium bicarbonate.

6. Calcium bicarbonate is the same substance as:
(A) Carboxylic acid
(B) Sodium hydrogen carbonate.
(C) Calcium hydrogen carbonate.
(D) Calcium hydroxyl ester.

7. To test for carbon dioxide gas you would:
(A) Bubble the gas through limewater.
(B) Carry out a 'pop' test.
(C) Bubble the gas through bromine water.
(D) React the gas with an ester or an alcohol.

8. The diagram shows a ^{13}C NMR spectrum for an organic compound.



Identify which one of the following compounds could have produced this ^{13}C NMR spectrum.
(A) Propane.
(B) 2,2-Dimethylpropane.
(C) 2-Methylpropan-1-ol.
(D) Butan-2-ol.

9. In gas chromatography, which of the following gases would not be used as a carrier gas?
(A) Argon.
(B) Helium.
(C) Hydrogen.
(D) Neon.

10. If gas chromatography is carried out at a higher temperature, you would expect to observe:
(A) All molecules having lower retention times.
(B) All molecules having higher retention times.
(C) Retention times unchanged.
(D) Some retention times increased and others decreased.

11. Using a HPLC column, with a non-polar stationary phase and a polar mobile phase, which of the following molecules would you expect to show the shortest retention time on the column?
(A) 2-Bromo-2-methylpropane.
(B) 2-Bromo-2-methylbutane.
(C) 2-Bromo-2-methypentane.
(D) 2-Bromo-2-methylheptane.

12. One of the following factors has no effect on the retention time in a gas chromatography column. That one is:
(A) Temperature of the column.
(B) The rate at which the carrier gas flows.
(C) The solubility of components in the mobile phase.
(D) The concentration of the compound moving through the column.

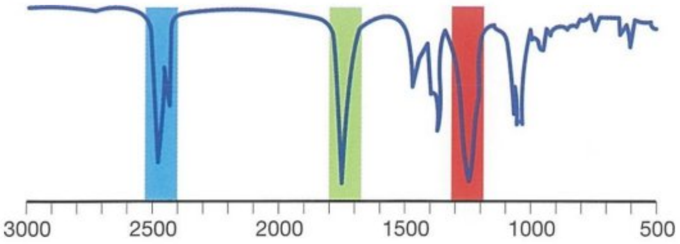
13. Which one of the following statements relates to NMR spectroscopy?

(A) Valence electrons in metal atoms absorb energy and become excited, moving to higher energy levels.
(B) The energy absorbed depends on the mass of the atoms which form the bond.
(C) Bonds present in a molecule absorb energy of specific wavelengths which makes them stretch or bend.
(D) Nuclear particles absorb radio waves and move to higher energy spin states.

14. Which one of the following statements relates to IR spectroscopy?

(A) Valence electrons in metal atoms absorb energy and become excited, moving to higher energy levels.
(B) The energy absorbed is independent of the mass of the atoms which form the bond.
(C) Bonds present in a molecule absorb energy of specific wavelengths which makes them stretch or bend.
(D) Nuclear particles absorb radio waves and move to higher energy spin states.

15. Three areas of interest are noted on an IR spectrum of an organic compound as shown. (Refer to data tables at the back of the book.)



The presence of a C=O bond would be indicated by absorption of infra-red radiation in the band coloured:

(A) Blue.
(B) Green.
(C) Red.
(D) Green and red.

16. Which would be the most appropriate technique to use for determining the number of isotopes of copper?

(A) Infra-red spectrometry.
(B) High pressure liquid chromatography.
(C) Nuclear magnetic resonance.
(D) Mass spectrometry.

17. A sample of the compound 2-methylpentane is analysed using a mass spectrometer. What maximum m/z value would be shown by peaks on the mass spectrum?

(A) 86 (B) 71 (C) 57 (D) 43

18. Pentan-3-one has the molecular formula $CH_3CH_2COCH_2CH_3$. During mass spectrometry it is likely to form ions with a positive charge and containing the C=O group.
Mass spectrometry of pentan-3-one would produce a mass spectrum with a strong line at the following position(s):

(A) $m/z = 43$
(B) $m/z = 57$
(C) $m/z = 71$
(D) $m/z = 43$ and 71

19. Which one of the following analysis techniques involves the destruction of the sample being studied?

(A) Mass spectroscopy.
(B) Infra-red spectroscopy.
(C) High pressure liquid spectroscopy.
(D) Nuclear magnetic resonance.

20. One thing that NMR cannot be used for is:

(A) Research.
(B) Analysis of mixtures.
(C) Determining 3-D structure.
(D) Determining purity of a sample.

21. One of the following is not a quantitative analytical technique. That one is:

(A) Gravimetric analysis.
(B) Atomic absorption spectroscopy.
(C) High pressure liquid chromatography.
(D) Flame test.

22. The adhesion of particles to a surface of a solid is called:

(A) Cohesion.
(B) Surface tension.
(C) Absorption.
(D) Adsorption.

23. Which one of the following could not be analysed using a chromatographic technique?

(A) Different coloured dyes in inks.
(B) The concentrations of chemicals in foods.
(C) Performance enhancing drugs in urine.
(D) The concentration of metal ions in blood.

24. A characteristic feature of chromatography is the use of:

(A) A mobile and a stationary phase.
(B) A spectroscope.
(C) Ultraviolet radiation.
(D) A strong magnetic field.

25. Advantages of HPLC include:

(A) It is a fast process.
(B) It can be used to monitor a process continuously.
(C) It is a sensitive, accurate technique.
(D) All of the above.

26. Which of the following would consist of more than one phase?
    (A) Froth on the top of milk.
    (B) A bottle of unopened soft drink.
    (C) An emulsion such as mayonnaise.
    (D) Homogenised milk.
27. A component of a mixture that has a short retention time in the HPLC column would:
    (A) Have only very weak attraction to the stationary phase.
    (B) Be soluble in the mobile phase.
    (C) Have a high affinity for the stationary phase.
    (D) Be soluble in both the stationary and mobile phases.
28. Which statement about the stationary phase in the HPLC column is correct?
    (A) The stationary phase must be an absorbent material.
    (B) The stationary phase should be fine particles of a stable, inert solid.
    (C) The stationary phase should have ionic charges on its surface.
    (D) All of the above.
29. Organic pollutants are of concern because many of them:
    (A) Are toxic.
    (B) Persist in the environment.
    (C) Can be absorbed by fatty tissue in the body and persist there.
    (D) All of the above.

INQUIRY QUESTION

1. Identify three functional groups that can be identified by relatively simple laboratory tests and outline how these tests are carried out.
2. Summarise what you have learned about the different ways in which nuclear magnetic resonance spectroscopy, mass spectroscopy and infra-red spectroscopy obtain information about the structure and reactivity of organic compounds.
3. Can instrumental analytical methods be used to help reduce the pollution of our atmosphere and water?

83 Chemical Resources

Natural products become a **resource** when we develop a way to use them. For example, petroleum was known for thousands of years before the Industrial Revolution but, at that stage, was not considered useful.

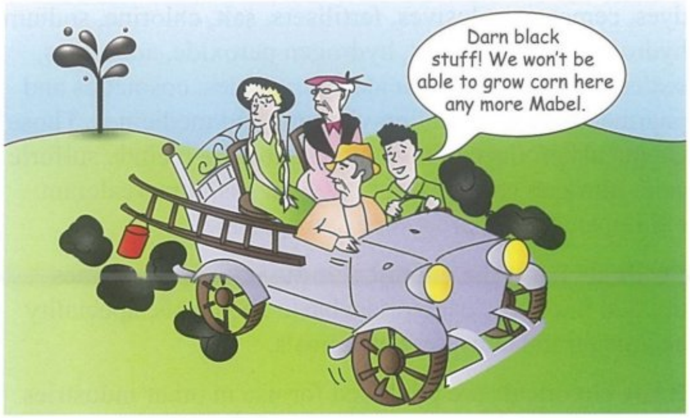


Figure 83.1 What is this black stuff?

The more uses we find for a resource, the more valuable it becomes. This pushes up its price, which in turn leads to more technological advances so that we can extract and use that resource more economically.

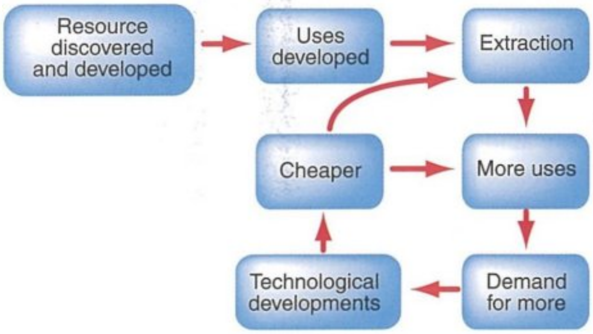


Figure 83.2 Resource flow chart.

We need to constantly increase our production of resources, such as metals and fossil fuels, to cater for new uses, increases in our population and improvements in living standards. However, these resources are finite, so we will eventually run out. As these resources become scarce, their costs escalate and this stimulates the search for replacement substances and new techniques to make them more cheaply and in larger quantities.

Throughout recorded history, the imagination and inventiveness of humans has repeatedly led us to new ideas, new processes and the development of an increasing variety of resources. For example, with the discovery of metals we soon found many ways to use them. Once we realised how useful metals could be, we set out to mine them more quickly and efficiently. Today, increasing demand has led to some metals being in short supply, which has led to the development of replacements. So we see the following trends.

- Improving the accessibility of ores by technological developments in mining equipment and bulk transport.
- Improving extraction techniques and thus increasing the ability of low grade ores to be mined profitably.
- Replacement of non-renewable resources with other substances, for example copper water pipes have largely been replaced by polymer pipes.
- More recycling (especially aluminium and copper), made possible by technological developments that have made this economic.

Many other resources have been manufactured **synthetically** in large quantities, for example:

- Synthetic detergents, needed due to the shortage of supplies of the fats needed to make soap.
- Polymers developed to supplement or replace natural products such as cotton, wool and rubber.
- Artificial timbers and other surface materials to partly replace wood as supplies are used up.
- Pharmaceutical products such as aspirin, penicillin and insulin which were initially made from plants and animals and are now synthesised artificially in much larger quantities.

Chemical synthesis has been essential to the search for new uses for resources and replacements for natural products as they become scarce or unable to be used and it is likely to continue in this role.

QUESTIONS

1. Define the following terms.
   (a) Resource. (b) Industrial Revolution.
   (c) Technology. (d) Finite.
2. Identify three reasons why we may need to increase our supplies of a resource.
3. Why do we sometimes need to develop replacements for resources?
4. Research the following.
   (a) Discuss the issues and problems associated with shrinking world resources with regard to one identified natural product.
   (b) Identify the replacement materials used or outline current research for a replacement for this named product.
   (c) Evaluate the progress made in solving the problems you have identified.

84 Industrial Chemistry

Industrial chemistry is the branch of chemistry which uses chemical reactions and processes to convert raw materials into useful products on a commercial scale. It is an **applied science**.

Industrial chemistry involves the design, setting up and operation of large scale equipment. It also involves obtaining the raw materials needed, setting the production process in operation, monitoring the process, checking the efficiency of the process and optimising yields, carrying out quality control, ensuring the safety of all steps in the manufacturing process, and also the marketing of products. The study of industrial chemistry involves not only chemistry, but also chemical engineering, mathematics, economics, and business management.

Most industrial chemical processes are designed in a laboratory and produced in large **chemical plants** which are built especially for the purpose and can be very expensive. Trials may first be carried out on a smaller scale using a pilot plant.

The **chemical reactions** involved may be dangerous if not carefully controlled, especially as they often take place in large containers, at high temperatures and pressures, so chemists and engineers must constantly monitor the process. Catalysts are frequently used to increase the reaction rate and/or allow the reactions to take place at lower temperatures and under lower pressures.

The products are separated out **using processes** that you have already learned about in the laboratory such as filtration, fractional distillation, crystallisation and precipitation. Control laboratories are set up to test products and make sure they are being made to specifications, including purity.

Figure 84.1 Workers in a chemical plant.

Industrial chemistry **affects society** by providing necessary chemicals and jobs for people and by its effects on the environment and the economy. It is a very important contributor to the wealth of a country.

The chemical industry uses a diverse range of **raw materials** including petroleum, natural gas, the air, water, plants, salt, metal ores, sand and various minerals. Raw materials must be available in good quantities and good quality.

The chemical industry produces a diverse **range of products** – almost 100 000 different products. These include polymers and plastics, textiles, paper, metals, dyes, cement, explosives, fertilisers, salt, chlorine, sodium hydroxide, sulfuric acid, hydrogen peroxide, adhesives, sealers, catalysts, insecticides, fungicides, cosmetics and pharmaceuticals including vitamins and medicines. Those chemicals produced in the largest volume include sulfuric acid, nitrogen gas, ethylene, oxygen gas, lime (calcium oxide), ammonia, propylene and chlorine.

Products from the chemical industry are sometimes divided into three categories: basic chemicals, speciality chemicals and consumer chemicals.

Basic chemicals are produced for use in other industries and they include the following.

- Chemicals derived from petroleum (called petrochemicals), e.g. ethene, methanol, styrene.
- Polymers (which may be derived from oil and gas or biomass), e.g. polyethene (polyethylene).
- Basic inorganics such as chlorine, sulfuric acid and nitric acid which are produced fairly cheaply and in large amounts.

A large percentage of the basic chemicals made are then used to make other chemical products. For example, ethanoic acid is used to make esters, some of which are used to make paints.

Speciality chemicals include paints, pigments, fertiliser for crops, and ink for printers.

Consumer chemicals are sold direct to the public for their use, e.g. detergents, soaps, cosmetics.

The **global distribution of industrial chemical plants and companies** is changing. In the past, most were centred in Europe, the United States and Japan. However, Asia, especially China, is taking over as the main centre for chemical manufacture. Half the world's population live in Asia and urbanisation there is occurring rapidly. China is overtaking the United States as the largest chemical producer in the world.

With the present awareness of **environmental issues** and the potential for damage by industrial chemical plants, regulations are becoming tougher, and markets are changing. For example, the cost of reducing the emission of carbon dioxide and other greenhouse gases, has led to renewable energy sources such as solar and wind energy being developed.

To compete in **today's markets**, chemical industries need to operate economically using sustainable processes and technologies that reduce environmental pollution while still optimising yield. Chemical industries also need to be involved in research and development to find new products that appeal to, and meet the needs of the consumer and they need to market their products well.

Other **challenges** today include reducing our dependence on non-renewable resources, ensuring that any new technologies, such as the use of nanomaterials, do not introduce risks to health and the environment, and introducing safety measures to minimise the effects of political unrest. It is important that chemicals be produced and used safely and used for legitimate purposes as many are toxic and/or explosive.

Safety issues must be taken very seriously in chemical plants. This is essential as frequently workers are dealing with chemicals which are potentially hazardous. Procedures must be implemented to minimise the risk of fire, spillage of chemicals, pollution of air and water, pollution by noise, heat and dust. Protective apparel must be provided where necessary, and workers must be trained in safety precautions and what to do in the event of an accident.

Chemists worldwide have collaborated under the United Nations (UN) to develop a uniform system of classifying and labelling chemicals to indicate if they are hazardous. This system is called the **GHS** – the **Globally Harmonised System of Classification and Labelling of Chemicals** and it is being promoted in Australia by the government and Safe Work Australia. The GHS includes the use of specific labels on chemicals as shown in the following diagram.

Explosive

Flammable

Oxidising

Gases under pressure

Acute toxicity

Health hazards

Corrosive

Chronic health hazards

Environmental

Figure 84.2 Labels for chemicals.

QUESTIONS

1. Define industrial chemistry.
2. Research an industrial chemical company in your area. For this company, find information about one of their products and its uses.
   You should research the raw materials used, their sources and reserves. Consider whether there would be a problem if the resource became limited or unavailable and if any replacements are possible. Also look at environmental issues including any waste products released during production.
3. What do the following signs tell you about the contents present in the container they label?

(a)


(b)


(c)


(d)


(e)


(f)


4. Distinguish between organic and inorganic chemicals and give three examples of each.
5. Why is it considered necessary to use a uniform system of classifying and labelling chemicals?
6. Illustrate the following information about the chemical industry, using two different types of graph.
   (a) A typical breakdown of products from the chemical industry would be basic chemicals 60%, specialty chemicals 25%, and consumer chemicals 15%. Basic chemicals can be subdivided into polymers 17%, petrochemicals 25% and basic inorganics 18%.
   (b) In Australia, of the people employed in industrial chemistry, approximately 53% are involved in the manufacture of polymers, 3% in natural rubber production, 22% in basic chemical and product manufacturing, 5% in the manufacture of fertilisers and 17% in the manufacture of cleaning and toiletry products.
7. Research the names of three chemicals manufactured in Australia. Identify a use for each of these three chemicals and a site where there is a chemical plant manufacturing each of these chemicals in Australia. Tabulate your answer.
8. Research and discuss what is meant by quality control and the need for quality control in the chemical industry.

85 Chemical Synthesis

Chemical synthesis is the process of making chemical compounds from other chemicals.

Synthesis occurs when existing bonds are broken and new bonds are formed, such as when:

- Two or more elements are reacted together to make a compound, for example when sodium combines with chlorine to form sodium chloride.
  $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$
- Compounds are broken down and then recombined to make a new compound, for example the synthesis of a polymer such as poly(ethylene).
  $nC_2H_4 \rightarrow -[-C_2H_4-]-_n$

The synthesis process may be quite complex and involve a number of chemical reactions as well as physical processes such as filtering. Intermediate products may be formed during the process.

Synthesis is of particular importance in organic chemistry and the term was first used by the organic chemist **Hermann Kolbe** (1818-1884) from Germany. In the 19th century scientists believed that organic chemicals found in our bodies could not be made in the laboratory. They believed that such chemicals could not exist without some sort of 'life force'. Hermann Kolbe was one of the chemists who showed that this was not correct and organic chemicals such as acetic acid could be made in the laboratory.

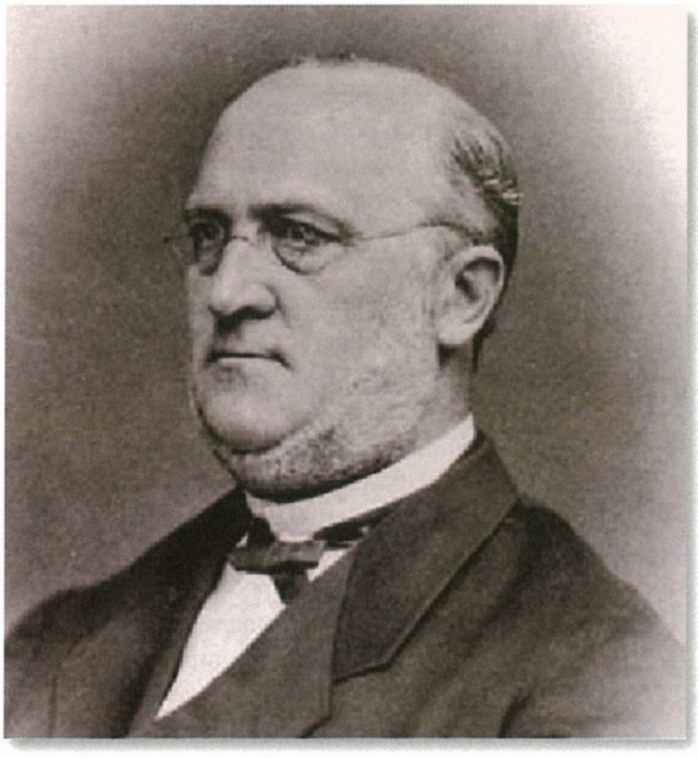


Figure 85.1 Adolph Wilhelm Hermann Kolbe.

Uses of chemical synthesis

Synthesis is used to **make new products** for use by consumers and to **improve** on substances already in use. Compounds may be synthesised to **test a theory**, or to **confirm the structure** of a compound. Drugs such as insulin are synthesised to **supplement supplies** which were initially obtained, with difficulty, from natural sources. Chemical synthesis can be used to make large quantities of many useful substances such as pharmaceuticals, polymers, dyes, herbicides, cosmetics and cleaning products.

Both inorganic compounds and organic compounds can be synthesised. Table 85.1 lists some examples of a few substances which are synthesised.

Table 85.1 Synthesised chemicals and their uses.

Type of chemical	Example	Use
Pigments	Titanium oxide	Make white paint.
Pharmaceuticals	Aspirin (salicylic acid) and insulin	Relieve pain. Treat diabetics.
Fertilisers	Ammonium sulfate	Improve crop yield.
Food additives	Aspartame	Sweeten food.
Insecticides	Organophosphates, organochlorides and pyrethroids	Prevent malaria by killing mosquitoes.
Cosmetics	Glycerol	Skin creams.
Inorganic compounds	Ammonia and sodium bicarbonate	Cleaning products, as food additives, to neutralise environmental spills.

Over recent years the number and variety of chemicals being synthesised has increased enormously and there is a big market for custom synthesis – the manufacture of products which have been designed and synthesised for specific purposes.

One area which uses a huge range of synthesised chemicals is that of **cosmetics**. The chemicals used in cosmetics include emulsifiers, solvents, thickeners, pigments, antimicrobials, preservatives, antioxidants and moisturisers. These chemicals must all be synthesised and then combined as required to make each product.

Chemical synthesis of **pharmaceuticals** can produce large volumes of products rapidly and chemical modifications can be used to enhance the activity of the active ingredient. Generally a pharmaceutical plant will produce many different products, and care must be taken to keep these separate and prevent cross-contamination of products.

Before a synthesis process is undertaken, **research** should be carried out to determine any risks associated not only with its production but also with its use. Sometimes products are developed and synthesised which serve a current need but which are later found to have **negative effects**, which are often unforseen. For example, with the increased use of refrigeration and air conditioning during the 20th century, gases called CFCs (chlorofluorocarbons) were manufactured in increasing quantities to replace the ammonia used at that time. These compounds were considered stable and inert. However, as they rose into the upper atmosphere they reacted with ozone, breaking it down and thus allowing increased amounts of UV radiation to reach the Earth's surface, resulting in undesirable effects such as an increase in skin cancer. Eventually, by international agreement, these gases were banned from manufacture.

The process of synthesis

There are many things to consider when synthesising chemicals. Some of the most important are as follows.

- **Reagents** (reactants) must be chosen that are readily available and as cheap as possible.
- The **quantities** of reactants needed must be calculated. It they are added in **stoichiometric** proportions, there will be minimal waste.
- The **method** to be used must be considered and chemical engineers may be needed to design and construct suitable **equipment** on an industrial scale.
- **Conditions of operation**, such as temperature and pressure, must be carefully considered so as to control the rate of synthesis. These are designed with safety and costs in mind. For instance using high pressure may produce a high yield quickly, but this increases the cost of construction and increases the risk of accidents, so a compromise often has to be reached. An exothermic process produces heat, so the reaction vessel may need to be cooled during the synthesis process. Catalysts may be designed to allow a reaction to take place at a lower temperature and/or pressure. Nanotechnology is proving very useful in chemical synthesis.
- The **rate of reaction** is carefully monitored using techniques such as ultraviolet (UV) spectroscopy, infra-red (IR) spectroscopy or nuclear magnetic resonance (NMR).
- A **risk assessment** is needed so as to keep any risks to the minimum. Industrial processes, as for any chemical reaction in the laboratory, must be carried out safely and precautions must be in place in case of accidents. Workers may need to wear special clothing to protect against spills, breathing apparatus may need to be handy as well as easy to operate showers.
- As the reaction proceeds, a method is needed to remove any **product** and by-products from the reaction mix. Processes such as precipitation, filtration and distillation are often used.
- **Monitoring** must take place to ensure the environment is not polluted.
- The **purity of the product** must be monitored and **percentage yield** calculated.

The aim in a synthesis process is to produce the **highest yield** possible of a useful product, in the **shortest time** possible, under **safe** conditions, with **minimal costs** and **minimal or nil pollution**.

QUESTIONS

1. The following steps have been identified as essential in the synthesis of a chemical. Outline the importance of each step.
   (a) Choose the reaction pathway to use.
   (b) Do a risk assessment.
   (c) Calculate the amounts of reactants needed.
   (d) React the chemicals using suitable equipment under the best conditions.
   (e) Separate the product needed from the reaction mixture.
   (f) Purify the product.
   (g) Measure the yield and purity of product.
2. Chemists often need to synthesise a naturally occurring substance which has a complex structure and which may have important medicinal use. This occurs when synthesis allows faster, more cost effective production and/or increased supplies. Identify an example of this.
3. Economic considerations are important in any industrial process. Outline factors that need to be considered for cost effectiveness.
4. (a) Define a catalyst.
   (b) Explain why catalysts are often used in industrial processes.
   (c) Research the names of some catalysts used and the process they catalyse.
   (d) Research the influence of nanotechnology on the use of catalysts.
5. Research a product which was initially made from a naturally occurring substance and which is now synthesised in a chemical laboratory.

86 Reactants, Products and Reaction Conditions

In any synthesis reaction, three very important factors in the reaction pathway are the reagents used, any by-products formed and how they can be either used or disposed of, and the conditions under which the reaction will take place.

Reagents

The term reagent includes the reactants in a chemical reaction and any chemicals needed to make this reaction occur as efficiently as possible. These often include catalysts which lower the activation energy of the reaction, do not actually take part in the reaction, and can be recovered and re-used. The choice of reagents to use in any synthesis process is influenced by factors such as suitability to produce the product, cost, availability and safety considerations.

Products

The product is what the industrial manufacturer is trying to make as efficiently, cheaply and rapidly as is safely possible. In the next chapter we will look at how the yield of a product is controlled.

If more than one product is produced during a synthesis reaction, then they will have to be separated. Products also have to be separated from any remaining reactants in the reaction vessel. Various techniques are possible for **product separation** depending on the properties of the reactants and products. For instance, the desired product may be soluble in a solvent that will not dissolve any other reactants or products involved. An example of this is in the production of an ester, the ester itself may be separated out by adding an aqueous solution. The ester is insoluble and will form a layer on top of the mixture.

By-products

A by-product refers to any product of a chemical reaction other than the product that is intended to be made. For example, in the manufacture of sodium carbonate, a by-product is **calcium chloride**. This has few uses so most is discarded as waste and this has had harmful environmental effects.

$$CaCO_3(s) + 2NaCl(aq) \rightarrow Na_2CO_3(aq) + CaCl_2(aq)$$

However, many by-products can also be valuable if they are commercially useful – that is, if they can be separated out easily and sold for a profit. An example is **carbon dioxide**, a by-product of fermentation, which is collected for use in soft drinks and in the production of dry ice.

Glycerol is a by-product of saponification. It is collected and used in other industries such as the manufacture of cosmetics.

Reaction conditions

The conditions under which a chemical reaction is carried out are designed by chemists to maximise the yield of the desired product so as to produce the product with the minimum production of unwanted by-products.

Heat and pressure may be used to increase reaction rate, but maintaining high temperatures and pressures is costly and may have associated safety risks, so another pathway may be chosen which uses lower temperatures and pressures.

Catalysts can be used to change the rate of a chemical reaction without taking part in the reaction or being used up by the reaction. Most catalysts with which we are familiar are used to increase the rate of reactions, but there are also catalysts called inhibitors available which can slow down reactions. Industrial synthesis reactions use catalysts to increase the rate of reactions. Concentrated sulfuric acid is used as a catalyst in some organic reactions, for example esterification.

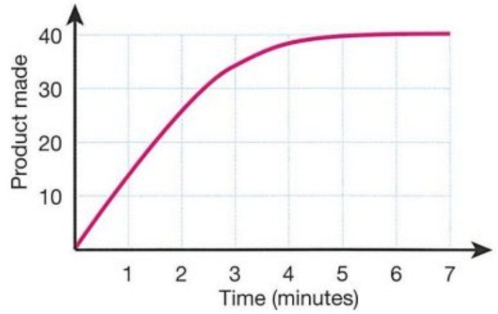
Transition metals such as platinum can also be used to catalyse hydrogenation reactions.

Ethene $C_2H_4 \xrightarrow{Pt}$ ethane C_2H_6

Catalysts can be expensive to purchase, so their use must be justified by producing considerable savings. Recovery and re-use of catalysts can help reduce the cost of using them. Also, many catalysts are now being used as nanoparticles. This decreases their cost as well as increasing their effectiveness. The higher surface area of nanoparticles increases catalytic activity. One example of this is the use of nanoparticle catalysts in hydrogen/oxygen fuel cells.

QUESTIONS

1. Suggest reasons why it is important to maximise the yield of a product in an industrial process.
2. (a) Recall the factors that affect rates of reactions.
   (b) The graph shows reaction rate during a reaction. Account for the slope of the graph.



3. Identify techniques that can be used to maintain a continuous yield of a product from an industrial process.
4. (a) Distinguish between a product and a by-product.
   (b) Identify two by-products and the reaction in which they are produced.

87 Stoichiometry and Yield

Stoichiometry and limiting reagents

Throughout this course you have seen a number of examples, in both organic and inorganic chemistry, of how the reactants used and the conditions under which they react can both help to determine the yield of the desired product and its purity. However, before we look at calculations of yield, we should first revise the ideas of **stoichiometry and limiting reagents**.

To maximise yield, reactants are often introduced to the reaction vessel in **stoichiometric** proportions, using exactly the right amounts so that all of each reactant is used up and there is no wastage. For example, if methane reacts with chlorine, to form chloromethane:

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

Then 1 mole of chlorine could react with 1 mole of methane. If the two chemicals are mixed in this 1 : 1 mole ratio, then they are said to be in stoichiometric proportions.

Mixing chemicals in stoichiometric proportions will help to minimise waste. However, sometimes it is more important to add excess of one reactant, for example when this will push an equilibrium reaction to the right to increase the yield.

The concept of limiting reagent is also important in figuring out the yield of a reaction. In the example:

$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$

If the reactants are present in a ratio of 1 : 1, that is 1 mole of ethene and 1 mole of bromine (stoichiometric proportions), then all of each reactant will be used up.

However, if 1 mole of ethene were mixed with 2 moles of bromine, there would be excess bromine and the ethene would limit the reaction. When that mole of ethene was used up, the reaction would stop – even though there is still bromine left. In that case ethene would be called the **limiting reagent**.

However, notice that sometimes having excess of a reactant will result in a different product being formed. For example:

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

$CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$

With limited chlorine, chloromethane is produced. With more chlorine a series of substitution reactions can occur and products such as tetrachloromethane can be formed.

Another example would be the combustion of carbon compounds where, in excess oxygen, carbon dioxide forms, whereas in limited oxygen, carbon monoxide forms.

Example:

Iron(II) sulfide can be synthesised by heating a mixture of iron and sulfur in the absence of air.

(a) Write an equation for this reaction.
(b) 3.0 grams of iron is mixed with 1.4 grams of sulfur. How many moles of each element is present in the mixture?
(c) Are these elements present in stoichiometric proportions?
(d) Identify which element is present in excess and which will limit the reaction.
(e) How much sulfur would be needed to use up all of the iron?

Answer:

(a) $Fe(s) + S(s) \rightarrow FeS(s)$

(b) No. of moles $= \dfrac{\text{mass}}{\text{molar mass}}$

$\text{Mol Fe} = \dfrac{3.0}{55.8} = 0.05376 \text{ mol}$

$\text{Mol S} = \dfrac{1.4}{32.1} = 0.04361 \text{ mol}$

(c) No, according to the equation, Fe and S react in the ratio of 1 : 1. In this case, Fe and S are present in the ratio 0.05376 : 0.04361 which is approximately 5 : 4.

(d) Iron is present in excess. Sulfur is the limiting reagent – when the sulfur runs out, there will still be some iron left.

(e) There is 0.05376 mol Fe.
This will react with 0.05376 mol S.
Mass of 0.05376 mol S
= no. of mol × molar mass
= 0.05376 × 32.1
= 1.7 grams of sulfur.

Yields of chemical reactions

The **yield** of a chemical reaction is a measure of the chemical efficiency of converting reactants into pure products. Yield is usually expressed as a percentage of the maximum amount of purified product that could be produced if all of the reactants used were converted into the desired product.

In industrial synthesis, the aim is to **produce a high yield of a very pure product in as short a time as possible**. Chemical reactions do not typically produce 100% yield.

All of the starting material does not get converted to the product for a number of reasons.

- The reaction may be incomplete – e.g. the reactants not mixed or not given time to completely react.
- Some may be converted to unwanted by-products.

- Some of a chemical may be lost in separation or purification processes, during transferring or heating.
- Impurities may be present that do not react or the product may be wet.
- The more reactions there are involved in a reaction pathway, the lower the yield is likely to be.

The percentage of starting material that gets converted to product is called the percentage yield. Calculations can be made using moles or grams.

$$\text{Per cent yield} = \frac{\text{actual yield of purified product}}{\text{theoretical yield}} \times 100\%$$

The theoretical yield is the amount predicted based on a stoichiometric calculation.

If a reaction pathway involves two reactions, with an 80% yield for the first reaction and 70% yield for the second reaction, then the overall yield is calculated as follows.

$$\frac{80}{100} \times \frac{70}{100} \times 100 = 56\% \text{ yield}$$

Factors to consider when deciding acceptable yield levels include the following.

- Economics – low costs and high yields will maximise profits.
- Amount of waste, energy use and environmental damage. If chemicals are added in stoichiometric proportions, there will be less waste and reduced energy use. If there are no excess chemicals to be discarded then environmental damage will be reduced.
- Safety of workers. It is not acceptable to use conditions that produce a higher yield, e.g. higher temperatures and pressures, if this increases the risk to employees.
- Purity and quality of product should not be compromised, even if this means accepting a slightly lower yield. This is particularly important with pharmaceutical and food products. Continuous monitoring, using the analytical techniques you have been studying, is essential to ensure consistent purity of products.
- By-products produced need to be minimised unless there is a good market available for their use. If useless by-products have to be disposed of this can cause environmental damage and also add to increased costs.

QUESTIONS

1. Methane reacts with chlorine in a series of substitution reactions forming tetrachloromethane, as shown by the equation:
   $CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$
   (a) How many moles of chlorine would be needed to convert 1 mole of methane to tetrachloromethane.
   (b) If 2.3 mol methane is reacted with 10 mol chlorine, which reactant would be in excess and which would be the limiting reagent?
2. In a chemical laboratory, 15.0 grams of an organic compound was produced. The calculated theoretical yield suggested that 18.5 grams should have been produced.
   Calculate the percentage yield.
3. Propanoic acid reacts with propanol to produce propyl propanoate.
   (a) Write an equation for this reaction using molecular formulas.
   (b) 4 mol propanoic acid reacts with 10 mol propanol. Which reactant is the limiting reagent?
   (c) Calculate the theoretical yield.
   (d) 3 mol of propyl propanoate is produced. Calculate the percentage yield.
4. A synthesis reaction requires three steps: $A \rightarrow B \rightarrow C \rightarrow D$. The percentage yield for each step is shown in the table. Calculate the percentage yield for the whole synthesis process.

Process	Yield (%)
$A \rightarrow B$	80
$B \rightarrow C$	60
$C \rightarrow D$	75

5. Glucose is fermented to produce ethanol according to the following equation.
   $C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH(aq) + 2CO_2(g)$
   The yield is 15%. What mass of ethanol would be produced from 1.0 kg of glucose?
6. The Haber process is used for the production of ammonia from nitrogen and hydrogen gases.
   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   (a) If 100 mol hydrogen is reacted with 100 mol nitrogen, which chemical is the limiting reagent?
   (b) If 50 g hydrogen is reacted with nitrogen:
      (i) Calculate the moles of hydrogen reacted.
      (ii) What mass of nitrogen will be needed for complete reaction?
      (iii) Calculate the mass of ammonia that will be produced from 112 g nitrogen and excess hydrogen if the process is 95% efficient.
7. The Solvay process to produce sodium carbonate takes place in a number of steps, but the overall reaction can be shown by the following equation.
   $CaCO_3(s) + 2NaCl(aq) \rightarrow Na_2CO_3(aq) + CaCl_2(aq)$
   53 kg of calcium carbonate is treated with 30.0 kg of sodium chloride.
   (a) Calculate the molar masses of calcium carbonate and sodium chloride.
   (b) Which reactant will be the limiting reagent? Show your working.
   (c) Calculate the yield of sodium carbonate in kg, assuming 100% efficiency.

88 Atom Economy

Producing a high **yield** for reaction pathways is very desirable, but it is not the only way of assessing their efficiency. The calculation of yield has a drawback. It only considers **one product**, the chemical that the reaction is designed to produce.

However, in many reactions more than one product is formed. Sometimes a by-product can also be collected and sold. But at other times by-products have no use and have to be disposed of.

An example from inorganic chemistry is the reaction in the Solvay process that is used to produce sodium carbonate on an industrial scale.

$$CaCO_3(s) + 2NaCl(aq) \rightarrow Na_2CO_3(aq) + CaCl_2(aq)$$

The product wanted is sodium carbonate. Calcium chloride is a by-product. It has very little use, and has to be discarded in large quantities. The disposal of large amounts of calcium chloride has caused the silting up of waterways and also ecological damage due to its salinity.

Table 88.1 shows the atoms (and their masses) used to make the product sodium carbonate in blue and those that will be wasted are in red.

Table 88.1 Production of sodium carbonate.

	Reactants		Products	
Formulas	$CaCO_3$	2(NaCl)	Na_2CO_3	$CaCl_2$
Masses (g)	40.1 + 60	46 + 71	106	111
Total	217		217	

You can see that 217 grams of reactants are being used in the reaction. But only 106 grams of this is used to synthesise the required product (sodium carbonate).

You can see at a glance that a lot of the reactant mass is wasted. It would be better if a reaction pathway could be found that only produced one product – with all reactant atoms going to make up the product. This idea of **atom economy** is one of the principles of green chemistry (see Chapter 89).

Atom economy provides a measure of the efficiency of a chemical reaction – it compares how many atoms from the reactants make it into the final product and how many are wasted. Atom economy can be calculated for this reaction using the figures in Table 88.1.

Percentage atom economy

$$= \frac{\textbf{formula weight of atoms used}}{\textbf{formula weight of all reactants}} \times \mathbf{100}$$

$$= \frac{106}{217} \times 100 = 48.8\%$$

Even if this reaction is carried out in such a way that it has a high yield. It will still have low atom economy because it makes waste.

Another way of expressing the equation for the calculation of atom economy is:

Percentage atom economy

$$= \frac{\textbf{mass of wanted products}}{\textbf{total mass of products}} \times \mathbf{100}$$

As an example, look at two reaction pathways to produce ethanol from ethene.

Reaction 1 – Hydrolysis of ethene – a one-step reaction pathway.

$$C_2H_4 + HOH \rightarrow CH_3CH_2OH$$

$$\text{Atom economy} = \frac{\text{mass of wanted products}}{\text{total mass of products}} \times 100$$

This reaction has only one product, so these values are equal and atom economy = 100%

Reaction 2 – a two-step reaction pathway involving the **addition of HCl** to make chloroalkane and then the **substitution of an hydroxyl group** into the chloroalkane.

$$C_2H_4 + HCl \rightarrow CH_2ClCH_3$$

$$CH_2ClCH_3 + NaOH \rightarrow CH_3CH_2OH + NaCl$$

$$\text{Atom economy} = \frac{\text{mass of wanted products}}{\text{total mass of products}} \times 100$$

$$= \frac{\text{mass } CH_3CH_2OH}{\text{mass } CH_3CH_2OH + NaCl} \times 100$$

$$= \frac{46}{46 + 58.5} \times 100 = 44\%$$

The first method has a much higher atom economy (100%) than the second method (44%), so the first method would be the preferred method based on atom economy. A low atom economy indicates an inefficient way to synthesise a product.

Addition and rearrangement reactions have a higher atom economy than substitution and elimination reactions.

QUESTIONS

1. The Haber process to produce ammonia involves the following reaction. $N_2 + 3H_2 \rightleftharpoons 2NH_3$
   What is the atom economy for this reaction?
2. You are in charge of an industrial laboratory and you find that the reaction pathway being used to manufacture your main product has a very low atom economy.
   (a) What does this mean?
   (b) What could you do to address this situation?
3. Calculate the atom economy for the following reactions.
   (a) Esterification to synthesise ethyl propanoate.
   (b) Production of butan-1-ol from butene.
   (c) Production of butan-1-ol from butane using a two-step process starting with the substitution of:
      (i) Chlorine. (ii) Bromine.

89 Green Chemistry

Green chemistry involves the design, development and and implementation of chemical products and chemical processes which reduce, and hopefully will eliminate, the use and manufacture of hazardous substances that could harm people and the environment.

The idea is to use sustainable processes that carry out chemical reactions and produce chemical products in ways that do not produce pollution and thus prevent environmental pollution before it occurs – to stop it at its source.

Chemical synthesis using the principles of green chemistry, aims to use renewable raw materials, limit the use of potentially harmful solvents and minimise the amount of unwanted products.

Green chemistry can be applied to both small laboratories and large industries. At all levels, it encourages chemists to look for processes which are sustainable, produce less waste, use safer practices and do not use or produce hazardous substances.

Two American chemists, **Paul Anastas** and **John Warner** have developed twelve principles of green chemistry which illustrate its aims.

Figure 89 .1 Paul Anastas and John Warner.

Principles of green chemistry

1. **Prevent waste**

Cleaning up after a chemical discharge and disposing of waste can be difficult and also very costly. Preventing waste is better than treating or cleaning up waste after it is formed. This ties in with the idea of atom economy.

2. **Atom economy**

Another American scientist, Barry Trost, is credited with suggesting the principle of atom economy in the 1990s. This is a way of describing the efficiency of a chemical reaction numerically – by dividing the molecular mass of the required product(s) by the combined molecular mass of all the reactants. The idea is that synthetic processes should be designed so that all materials used are incorporated into the final product. As much as possible of the mass of all the reactants should be included in the mass of the products.

An example is the anti-inflammatory drug ibuprofen, which was initially synthesised using a six-step process with low atom economy of 40.1%, and the formation of waste inorganic salt (sodium sulfite). Only 40.1% of the mass of the reactants ended up in the desired product. A greener, three-stage process was developed with an atom economy of 77.4%. This new process uses catalysts and there is no waste produced.

3. **Less hazardous chemical synthesis**

Wherever practicable, substances used and produced should have little or no toxicity to humans and the environment.

An example is the development of insecticides that target an insect's own hormones. The structure of the insect's hormone receptor is studied and then synthetic molecules are developed to interact with these receptors. This is an example of biomimicry, and in this case it can make the insect moult prematurely and die. Advantages are that only a small amount of the chemical is needed, the insect will not develop resistance, and the insecticide is only toxic to the target species of insect.

Another example involves the use of chemicals to destroy plants and animals growing on the hulls of ships. These need to be removed as the drag generated increases fuel costs. Early antifouling chemicals were toxic for marine animals and persisted in the environment. These have been replaced by toxins which exist for only a few hours in water and sediment, so they do not accumulate in shellfish or the environment.

4. **Design safer chemicals**

Chemical products should be designed to be as efficient as possible and have the least toxicity possible.

Chemicals such as tetrachloroethylene were used as dry cleaning fluids, however this is toxic and flammable. Perchlorethylene is still used extensively, although it is reputed to be carcinogenic and is being phased out. Siloxane may be safer, or else glycol ether may be used to wash garments which are then rinsed with liquid carbon dioxide.

Another example is the production of paints. Some companies are making resins and solvents from a mixture of soya oil and sugar instead of from fossil fuels.

5. Use safer auxiliaries

Auxiliary substances, such as solvents and separation agents should be used as little as possible and if needed they should be non-toxic. Solvents make up 50% or more of the total chemicals used in most processing plants and they are of concern because they are flammable, volatile and sometimes explosive. They also contribute to energy costs. A green solvent should be non-toxic, inexpensive, readily available and work well in the context.

Many of the solvents, e.g. chlorinated hydrocarbons, previously used in the synthesis of organic compounds are now considered too toxic and have been replaced by more environmentally friendly alternatives such as ethanol, supercritical carbon dioxide, ionic liquids and water.

6. Energy efficiency

Energy requirements should be minimised so as to have as little impact as possible on the environment and economy.

Energy is used during production for processes such as heating, cooling, separations such as isolating solvents and removing impurities, electrochemistry, pumping. Only about 2% of the energy in fossil fuels actually gets used usefully – the rest is lost in conversion. Also a lot of energy is lost in transportation. Wherever possible, synthesis should take place at ambient temperature and pressure to prevent the use of energy in maintaining high temperatures and pressures.

7. Use renewable feedstocks

A raw material (feedstock) should be renewable wherever this is technically and economically practicable. This will help prevent the depletion of finite resources such as fossil fuels.

Green chemistry supports the use of renewable feedstocks to produce not only chemicals but also fuels. Examples of fuels include biodiesel from plants and algae, as well as bioethanol and butanol from sugars and lignocelluloses. Examples of products from feedstocks include plastics, foams and thermoset plastics from lignin and plant oils and electronic materials including computer chips from the protein keratin in chicken feathers.

Polylactic acid polymers (PLAs) are recyclable, biodegradable polymers which are synthesised from lactic acid which can be largely derived from renewable sources. Their production also reduces the need for hazardous materials such as organic solvents, and catalysts are used to achieve high yields using less energy.

Scientists have also produced a biodegradable composite material of renewable resources – flax yarn embedded in a soy polymer resin. This product has tensile properties similar to steel and is suitable for some building applications.

8. Reduce derivatives

Avoid the unnecessary production of derivatives wherever possible. For example, in early production methods for penicillin a number of different stages were produced during its manufacture. The influence of green chemistry has led to a production process that is more direct, with fewer stages. This process is possible because of the use of an enzyme. Enzymes are biocatalysts; they are biodegradable and environmentally compatible. Using such catalysts, reactions can occur in water under mild conditions of temperature and pressure.

9. Using catalysts

You will recall that catalysts are substances that speed up chemical reactions by providing an alternate pathway for the breaking and making of bonds: a pathway with lower activation energy.

Catalysts are generally preferable to reagents such as oxidants and reductants as catalysts can be used in small amounts and can be collected, cleaned and re-used. They help to maximise atom economy, increase energy efficiency, allow the use of safer reaction conditions and reduce the production of by-products and waste. Thus they help to reduce pollution. Catalysts are often specific to one reaction, or one type of reaction. **Biocatalysts** are being used to replace metal catalysts in some processes such as the synthesis of drugs for diabetes.

During this course you have seen quite a few examples of the use of catalysts, and many are summarised in Table 89.1.

Table 89.1 Some industrial catalysts.

Industrial process	Catalyst used
Production of polyethylene	Ziegler-Natta catalysts – transition metals.
Hydrogenation processes	Transition metals such as platinum.
Haber process to make ammonia.	Iron
Manufacture of sulfuric acid.	Vanadium(V) oxide, V_2O_5
Manufacture of nitric acid.	Platinum and rhodium
Production of medicinal drugs and in catalytic cracking of petroleum into fractions.	Zeolites – crystalline inorganic polymers.
Manufacture of esters	Concentrated sulfuric acid

10. **Design products that degrade**

Chemical products should be designed so that at the end of their function they break down (degrade) rather than persist in the environment. This reduces the time they are available in the environment to cause damage. An example is the biodegradable bags now being made from cassava starch and calcium carbonate.

11. **Real time analysis and monitoring**

Analytical methodologies need to be further developed to allow for real time monitoring and control, during a chemical process, before hazardous substances are formed. Any changes, such as in pH, temperature or the poisoning of catalysts, needs to be detected immediately, before any serious damage occurs.

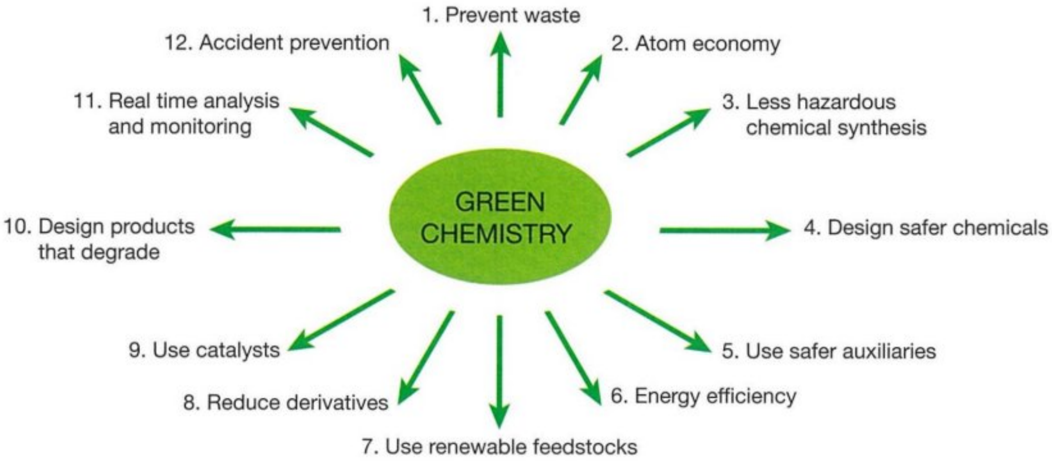
Technological developments that help in this area include the ability to analyse using increasingly small samples, and the ability to analyse quickly and accurately using instrumental methods, such as spectroscopy, rather than the slower conventional methods of 'wet chemistry'. Such techniques not only promote the principles of green chemistry but also improve the safety and efficiency of chemical plants.

12. **Accident prevention**

Substances and the form of a substance used in a chemical process should be chosen to minimise potential for chemical **accidents**, including releases, explosions, and fires. We already have in place engineering controls, administrative and work practice controls, and the use of personal protective equipment by workers, to reduce the likelihood of an accident involving hazardous substances. Green chemistry goes further. It asks for the elimination of hazardous substances from the workplace wherever possible.

QUESTIONS

1. What is meant by green chemistry?
2. Why is green chemistry sometimes referred to as sustainable chemistry?
3. Green chemistry is sometimes classified into four main areas of action.
   (a) Efficient use of energy and chemicals.
   (b) Hazard reduction.
   (c) Waste minimisation.
   (d) Use of renewable resources.
   For each of these four areas, research an example of how green chemists are introducing practices to accommodate these aims.
4. Green chemistry has been criticised in a number of ways.
   (a) It has been said that green chemistry is not new. Discuss this statement.
   (b) Green chemistry is not economically viable. Evaluate this claim.
5. The 2005 Nobel Prize for Chemistry was awarded to Yves Chauvin, Robert Grubbs and Richard Schrock for developing a chemical process called metathesis in organic chemistry.
   Metathesis is a reaction mechanism in organic chemistry which uses specially designed catalysts to rearrange fragments of the carbon chains and hence make new products.
   Research the importance of this process.
6. Research the significance of each of the following developments in synthesis.
   (a) In 1929 Wohler synthesised urea from a compound called ammonium isocyanate.
   (b) In 1856, the chemist Perkin produced a synthetic purple dye.
7. Find out about awards given in countries such as Australia and the United States to encourage the development of green chemistry. Describe two innovations that have received such an award.



90 Synthesis Of Soap

Throughout this course you have studied a number of synthesis processes, including the synthesis of addition polymers and condensation polymers, the synthesis of ammonia by the Haber process, and the synthesis of biofuels. Here we will look at the synthesis of soap.

You will recall that soap is the salt of a long chain fatty acid with an alkali metal ion attached. Fatty acids are carboxylic acids with more than 10 carbon atoms in their hydrocarbon chains, for example stearic acid is $CH_3(CH_2)_{16}COOH$.

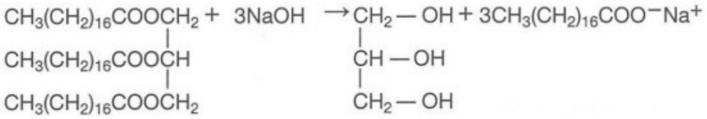
The synthesis of soap is called saponification.

Saponification

The chemical reaction occurring in saponification is the hydrolysis, in basic solution, of fats and oils (triglycerides). The products formed are glycerol and the salts of fatty acids (soaps).

When the fat glycerol tristearate is heated with a concentrated base such as sodium hydroxide, hydrolysis takes place, producing sodium stearate (soap) and glycerol.

Fat/oil, e.g. glyceryl tristearate + Base, e.g. sodium hydroxide → Glycerol + Salt (soap), e.g sodium stearate



$$\begin{array}{ll} CH_3(CH_2)_{16}COOCH_2 + 3NaOH & \rightarrow CH_2-OH + 3CH_3(CH_2)_{16}COO^-Na^+ \\ CH_3(CH_2)_{16}COOCH & \quad\; CH-OH \\ CH_3(CH_2)_{16}COOCH_2 & \quad\; CH_2-OH \end{array}$$

We can write a general equation for this reaction as:

$$(RCOO)_3C_3H_5 + 3NaOH \rightarrow C_3H_8O_3 + 3RCOO^-Na^+$$

Most soap is made from vegetable oils, especially olive oil, palm oil and coconut oil. Some soap is made from animal fats, called tallows. A number of internet sites give details about the types of fats and oils that can be used as well as instructions on how to make your own soap if you are interested. The Sydney University website on polymers also has excellent information on the production of soap and related topics.

Industrial production of soap

The main steps in the industrial production of soap are as follows.

- Fats and oils are blended.
- These fats and oils are boiled with an hydroxide solution such as sodium hydroxide, potassium hydroxide or ammonium hydroxide.
- Concentrated sodium chloride solution (brine) is added to this soapy mixture in order to dissolve the glycerol and separate it from the soap. Glycerol will dissolve in salt water but the soap will not dissolve, so the soap precipitates out, forming a surface layer.
- The soap is separated and washed to remove any remaining hydroxide or brine. Any unused fatty acids left in the brine will separate out as an oily layer which solidifies on cooling and can be removed. Glycerol is recovered by vacuum distillation of the remaining solution.

Perfume and colour can be added to the soap, and translucent soaps can be made by adding alcohol, sugar and glycerol to slow down the growth of soap crystals as it solidifies.

QUESTIONS

1. Define saponification.
2. If you carried out an experiment on saponification in the laboratory,
    (a) Describe the method you used.
    (b) Explain any safety measures needed.
3. Using the Sydney University website on polymers, or other similar information source, compare your laboratory method of saponification with the industrial process of saponification. Tabulate your answer.
4. In the saponification reaction, if glyceryl trioleate were used instead of glyceryl tristearate, the salt produced would be sodium oleate instead of sodium stearate.
    (a) Name and show the structure of the other product of this reaction.
    (b) Name the salt produced if the fat used is glyceryl trilaurate.
5. Use a flow diagram to show the steps in the industrial production of soap.
6. Check your knowledge with this quick quiz.
    (a) Name the process of making soap.
    (b) Identify the systematic name for glycerol.
    (c) Identify three fats or oils used to make soap.
    (d) Identify a base commonly used in saponification.
    (e) In the industrial manufacture of soap, the process used to separate salt water from glycerol is called
    (f) In making liquid soaps, the sodium hydroxide is usually replaced with ....
    (g) Identify the solution used to precipitate soap from solution.
    (h) Identify the salt formed when sodium hydroxide is reacted with lauric acid.
7. Tabulate a comparison between soaps and detergents.

91 Carbohydrates

Carbohydrates are important organic chemicals. Although they are not mentioned in the syllabus content, they are mentioned in the content focus for Module 7 and could perhaps be used in process questions on synthesis or instrumental analysis. Consequently this chapter on carbohydrates has been included to provide some basic background information about them.

Carbohydrates are organic compounds made of carbon, hydrogen and oxygen in the ratio 1 : 2 : 1. They have the **general formula** $C_x(H_2O)_y$.

Carbohydrates are a regular part of our diet in the form of sugars and starches and provide us with a source of energy. Plants make the carbohydrate glucose during photosynthesis. They use carbohydrates as structural materials (cellulose) and to store energy (starch).

Carbohydrates are classified as monosaccharides, disaccharides and polysaccharides.

Monosaccharides

Monosaccharides are the simplest carbohydrates and have a general formula of $(CH_2O)_n$ where n can be 3 to 7. They are usually colourless, crystalline solids which are soluble in water. Most taste sweet and they cannot be broken down into a simpler sugar by hydrolysis.

Examples of monosaccharides are glucose, fructose, galactose, xylose and ribose. Notice that the names of sugars all end in -ose.

Glucose is the main fuel in our bodies – it is converted into carbon dioxide and water, during respiration in our cells, releasing energy in the process. Fructose (called fruit sugar) is found in plants, often joined with glucose to make the disaccharide sucrose. Fructose and glucose are found in honey made by bees.

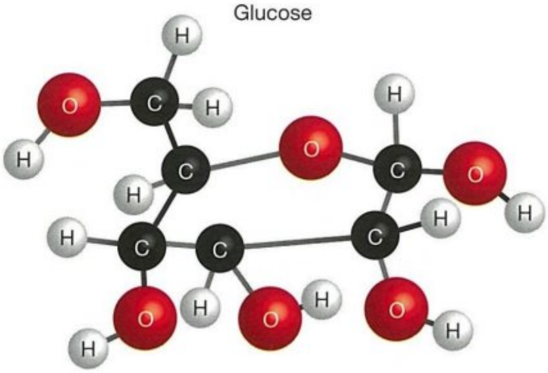


Figure 91.1 A model of glucose.

Glucose ($C_6H_{12}O_6$) exists mainly as a **ring structure**, as shown in the model above, but the ring form can also open to form a **straight chain**. In the ring form, the hydroxyl group (–OH) on C1 can be below or above the ring, forming alpha glucose and beta glucose respectively. In a glucose solution all three forms shown in Figure 91.2 are present in equilibrium.

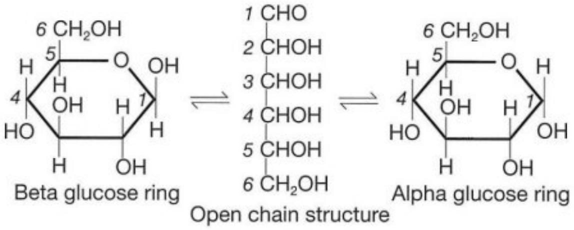


Figure 91.2 Forms of glucose.

The other monosaccharide sugars vary in the number of carbon atoms and the orientation of their hydroxyl (–OH) groups on the carbons – they can be above or below the ring.

Notice that all monosaccharide molecules contain a **carbonyl (C=O) group** which can be on the C1 or C2. This is easiest to see when you look at the straight chain forms.

Hydrogen bonds occur between sugar molecules, making them solids at room temperature. Hydrogen bonds also occur between sugar molecules and water, which is why they are soluble in water.

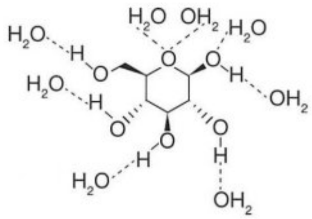


Figure 91.3 Hydrogen bonding between a glucose molecule and water.

Disaccharides

Disaccharides are sugar carbohydrates formed by a condensation reaction between two monosaccharides. A molecule of water is released.

$$2C_6H_{12}O_6(aq) \rightarrow C_{12}H_{22}O_{11}(aq) + H_2O(l)$$

Examples of disaccharides are sucrose, lactose and maltose, as shown in Table 91.1.

Table 91.1 Some disaccharides.

Disaccharide	Made from	Found in
Sucrose (cane sugar)	Glucose and fructose	Plants
Lactose (milk sugar)	Galactose and glucose	Milk
Maltose	Glucose and glucose	Grains such as barley

Sucrose is used in large quantities as a sweetener in foods and drinks. It is broken down in our intestines to glucose and fructose by the enzyme called sucrase. Notice that enzymes that act on sugars have names that end in -ase. If you warm sucrose with the enzyme sucrase present, sucrose breaks up into glucose and fructose. Boiling with acid has the same effect.

Other properties

Melting points. Monosaccharides and disaccharides are **solids at room temperature** due to the strong hydrogen bonds which hold their molecules together in a crystalline lattice structure. They do not have sharp melting points as many decompose around their melting points.

Action with concentrated acids. When concentrated sulfuric acid is added to sucrose it becomes dehydrated and reduced to carbon (see Figure 91.4).

$C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O$

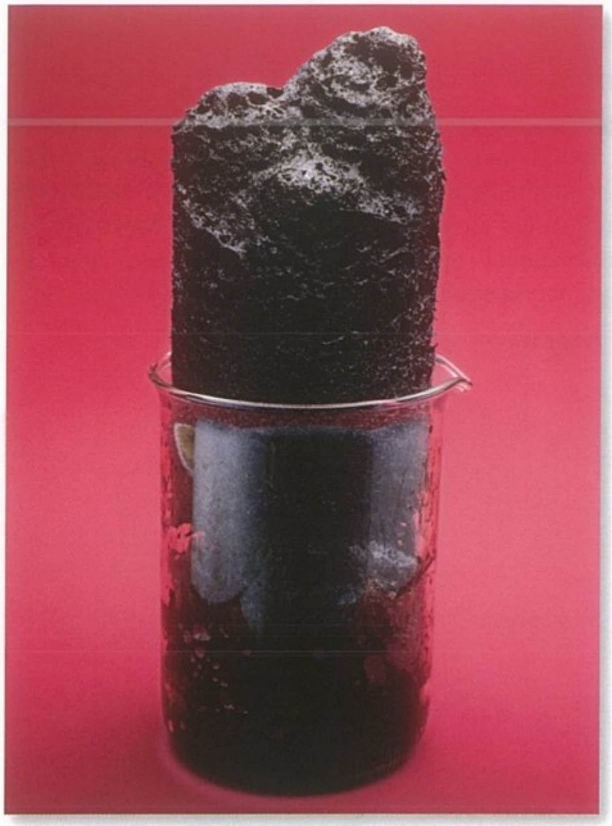


Figure 91.4 Carbonisation of sucrose.

Combustion. When sugars such as sucrose and glucose are heated they will burn producing carbon dioxide and water.

$C_6H_{12}O_6 + 6O_2(g) \rightarrow 6CO_2 + 6H_2O$

Figure 91.5 Burning glucose.

Glycosidic links

A glycosidic link consists of covalent bonds that join a carbohydrate molecule to another molecule.

Disaccharides consist of two monomer molecules held together by a glycosidic link which consists of two covalent bonds which share an oxygen atom.

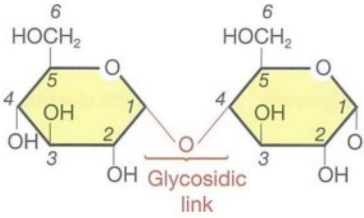


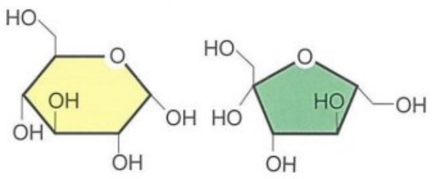
Figure 91.6 The disaccharide maltose consists of two glucose molecules joined by a glycosidic link.

Glycosidic links are named according to the position of the connected C atoms. For example, Figure 91.6 shows a 1-4 linkage between two glucose molecules.

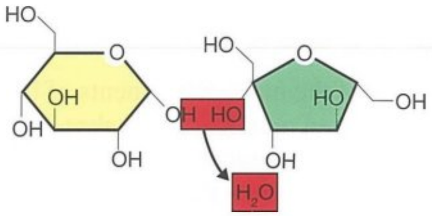
They can also form between C atoms in other positions such as C1 and C6.

Glycosidic links are formed when a **condensation reaction** occurs between two molecules and water is eliminated.

(a) Two molecules come close together.



(b) A water molecule is eliminated.



(c) A 1-2 glycosidic link forms.

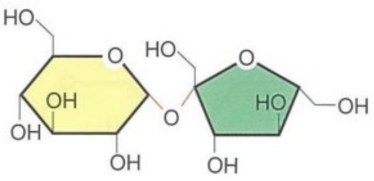
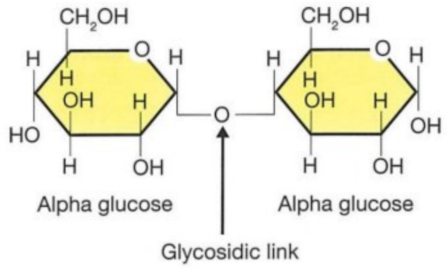


Figure 91.7 Steps in the formation of sucrose from a glucose molecule and a fructose molecule.

Figure 91.8 shows the glycosidic links between two alpha glucose molecules to form maltose and between beta glucose and beta galactose to form lactose.

Maltose



Lactose

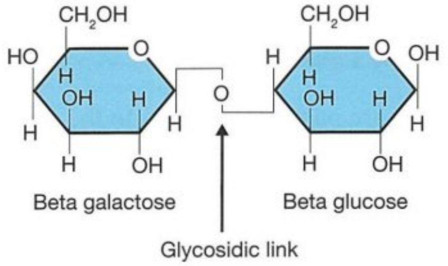


Figure 91.8 Glycosidic links.

Polysaccharides

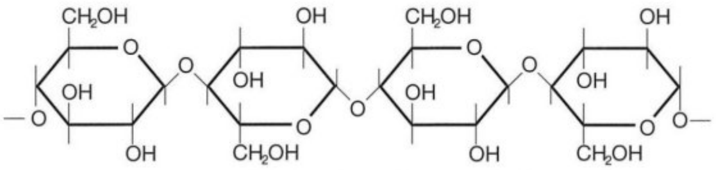
Polysaccharides are carbohydrates which are polymers. They are formed by **condensation reactions** involving many monosaccharide molecules (mainly glucose) joined together by covalent bonds.

$$n(C_6H_{12}O_6) \rightarrow \left[C_6H_{10}O_5 \right]_n + nH_2O$$

Polysaccharides are used to build structure and for storage in plants and animals. Three common polysaccharides are cellulose, starch and glycogen.

Cellulose

Cellulose is one of the main components of biomass (organic matter based on plants). It makes up the cell walls of plants and is the most abundant structural carbohydrate on Earth, even though it is only found in plants. Cellulose consists of very long chains composed of 4000 to 8000 beta glucose units. In cellulose, alternate glucose units are inverted relative to each other.



Section of a cellulose molecule

Figure 91.9 Small section of a cellulose molecule.

Hydrogen bonding between parallel chains binds them close together in a regular lattice, which makes cellulose dense, fibrous, rigid, strong, insoluble and resistant to chemicals.

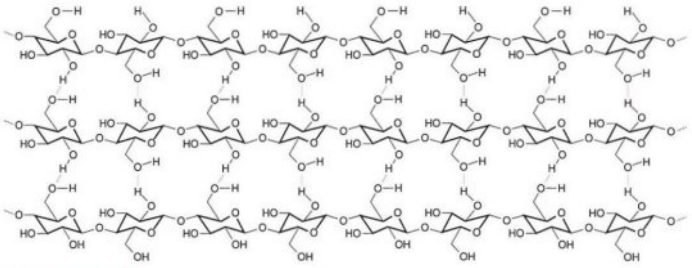
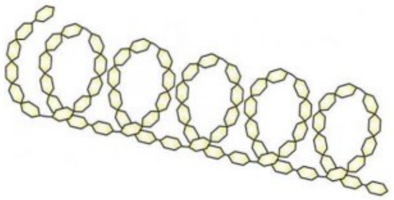


Figure 91.10 Hydrogen bonding between cellulose chains.

Starch

Starch occurs as a natural polymer in green plant tissues, e.g. rice, potato, wheat, maize, corn and tapioca, where it is the main storage material. There are two components of starch called amylose and amylopectin. Amylose consists of unbranched, spiral chains of glucose units, whereas amylopectin consists of a branched chain of glucose units.

(a) Amylose.



(b) Amylopectin – a branched starch.

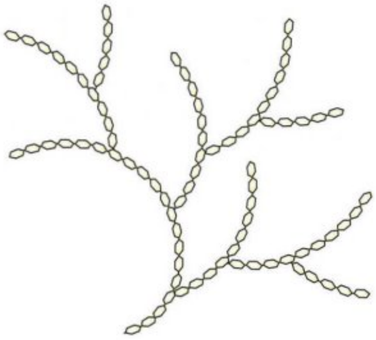


Figure 91.11 Small section of starch molecules.

Due to the branching and spiral structure of the chains in starch, its molecules cannot pack so closely together, making starch soft and powdery and globular. Hydrogen bonds hold the granules of starch together.

Glycogen

Glycogen is a multi-branched polysaccharide of glucose. It is similar to starch except that the side branches are more frequent and longer. It forms small compact globules.

Glycogen is the form in which carbohydrate is stored in the liver and muscles of animals. Glycogen granules form in the liver when blood glucose levels are high. Athletes eat a high carbohydrate diet in the days before an endurance event in order to build levels of muscle glycogen.

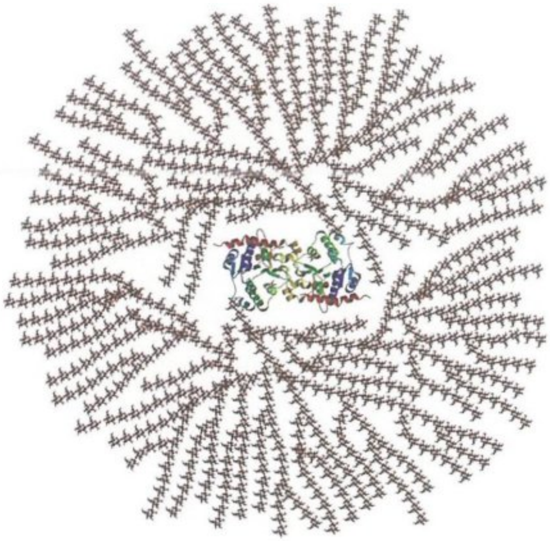


Figure 91.12 Glycogen with a protein at its core.

Biodegradability

Polysaccharides, like proteins, are broken down by enzymes in the digestive tracts of animals and by decomposers (bacteria and fungi) in the environment. However cellulose, unlike starch and glycogen, is dense, strong and insoluble so it can only be biodegraded by bacteria, fungi and some termites. In herbivores such as cows and rabbits, micro-organisms in the digestive system decompose cellulose.

Tests for carbohydrates

Reducing sugars. Some sugars such as glucose and lactose, can be identified by adding Fehling's or Benedict's solutions as they produce a brick-red colour when heated. This test is based on the ability of these sugars to reduce the chemicals in Fehling's and Benedict's solutions. They have a carbonyl group (C=O) at the end of a carbon chain (like aldehydes) and this carbonyl group can be oxidised.

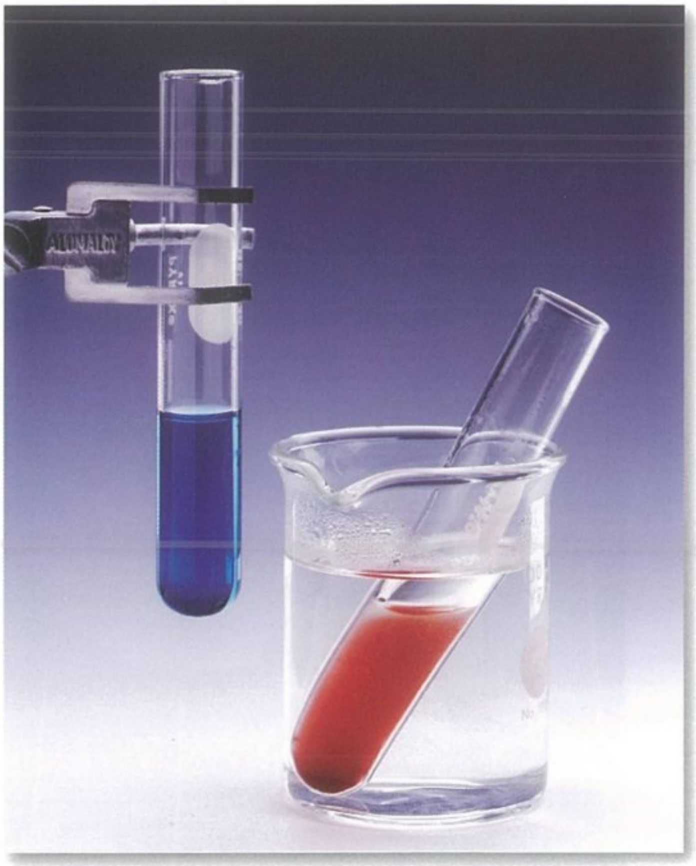


Figure 91.13 Fehling's solution with a reducing sugar, before and after heating.

Non-reducing sugars such as sucrose, do not have this end carbonyl group, so they cannot produce the characteristic brick-red colour on testing with Fehling's or Benedict's solutions.

However, they can be hydrolysed, to break them down to simpler sugars which will give a positive result when tested.

Polysaccharides. Iodine can be used to test for polysaccharides. Starch will turn a blue-black colour with iodine solution, and glycogen goes purple-red.

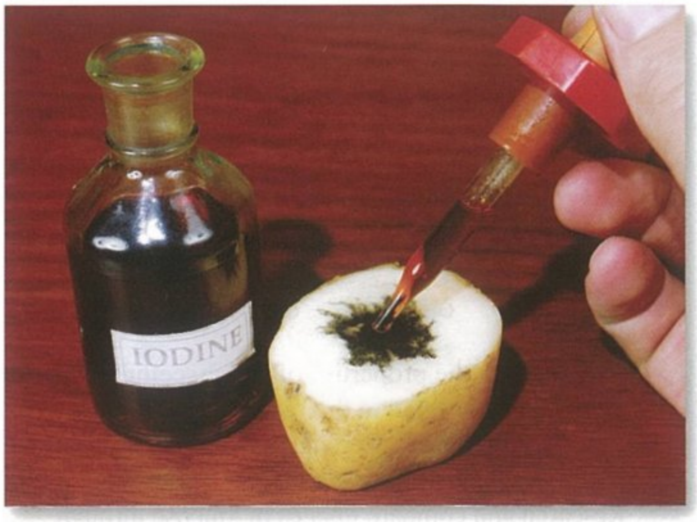


Figure 91.14 Testing for starch with iodine solution.

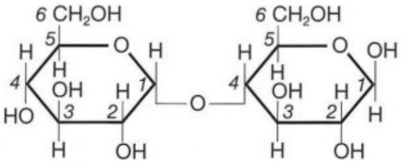
QUESTIONS

1. (a) Name three different types of carbohydrates.
   (b) State the general formula for carbohydrates.
   (c) Name three monosaccharides and three disaccharides.
2. Outline the importance of glucose in living things.
3. Sodium chloride melts at 804°C and sucrose begins to char and decompose at 160°C as shown in the photograph.

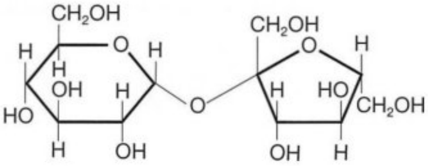
Explain this difference in terms of bonding.

4. (a) What is a meant by a condensation reaction?
   (b) Give an example of a condensation reaction between two monosaccharides.
5. Comment on the biodegradability of sugars.
6. What is meant by a glycosidic link and how is it formed?
7. For each of the following diagrams, circle any glycosidic bonds, name the molecules and name the disaccharide produced.

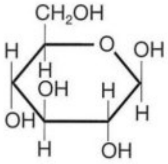
(a)

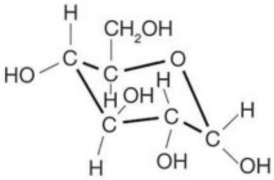


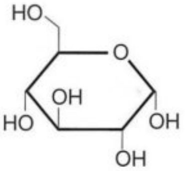
(b)



8. Explain how the properties of starch, cellulose and glycogen are related to their structure and uses.
9. You have seen that different spectroscopy processes provide different information about molecules. Research and compare images of glucose through NMR, mass spectroscopy and infra-red spectroscopy.
10. What do these molecules all have in common?

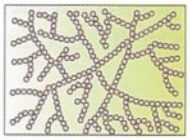




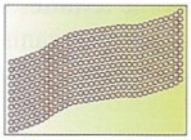


11. Starch and cellulose are both polysaccharides.
    (a) These two substances are similar in that both are made of many .... molecules joined together.
    (b) Because they are made of a chain of repeating units, these substances are called ....
    (c) Which of these polymers has branched chains?
    (d) Starch is soft and powdery whereas cellulose is strong and fibrous. Account for these differences in property.
    (e) Name the type of reaction used to make a polysaccharide.
    (f) Identify the small molecule produced during the formation of polysaccharides.
12. Identify which of the following diagrams represents cellulose, starch and glycogen. Justify your classification.

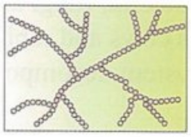
(a)



(b)



(c)



13. Check your knowledge by naming the following carbohydrates.
    (a) The sugar called fruit sugar.
    (b) The disaccharide called milk sugar.
    (c) The sugar which is our main source of metabolic energy.
    (d) The sugar made from barley.
    (e) State the molecular formula of glucose.
    (f) Name three polysaccharides.
    (g) Name the three elements that constitute carbohydrates.
    (h) In the formation of a condensation polymer, which small molecule is released?

92 Revision Of Synthesis and Design

You now have just this one last area to revise. You need to consider what you have learned about chemical synthesis and design, and its implications for society. This is a big topic, you are really just starting to scratch the surface here, and it is an area that will continue to develop over time with new discoveries in materials and methods of synthesis.

Here are a few multiple choice questions on the work you have covered.

QUESTIONS

1. When setting up a chemical plant, procedures are implemented to minimise the risk of:
   (A) Fire and accidents.
   (B) Spillage of chemicals.
   (C) Dust and noise pollution.
   (D) All of the above.
2. The 12 principles of green chemistry were developed by:
   (A) Rudolf Diesel and Humphry Davy.
   (B) Frederick Sanger and Hermann Kolbe.
   (C) August Kekulé and Archibald Couper.
   (D) Paul Anastas and John Warner.
3. Of the following chemicals, which would be the preferred solvent in a green chemistry project?
   (A) Ethanol.
   (B) Benzene.
   (C) Water.
   (D) Acetone.
4. Green chemistry principles prefer an industrial chemical process to take place:
   (A) Without using a catalyst.
   (B) At normal temperatures and pressures.
   (C) Using up toxic chemicals so there will be none left to pollute.
   (D) Using as many simple stages as possible.
5. One of the green chemistry principles can be paraphrased as:
   (A) Clean up all waste produced, especially toxic by-products.
   (B) Use solvents and separating agents wherever possible.
   (C) Wherever possible use fossil fuels as feedstocks.
   (D) Analyse and monitor continually during chemical synthesis.
6. Which of the following is not a synthetic product?
   (A) PVC.
   (B) Petroleum.
   (C) Soap.
   (D) Detergent.
7. In industrial chemistry water is used as:
   (A) A solvent.
   (B) A coolant.
   (C) To reduce airborne dust.
   (D) All of the above.
8. A by-product of saponification is:
   (A) Glycerol.
   (B) Soap.
   (C) Long chain fatty acids.
   (D) Anionic surfactants.
9. Which of the following is not an example of a catalyst?
   (A) Platinum used in hydrogenation reactions.
   (B) Iron used in the Haber process.
   (C) Concentrated sulfuric acid used in esterification.
   (D) Triglycerides used in soap production.
10. The efficiency of converting reactants into products is referred to as the:
   (A) Purity of the product.
   (B) By-product.
   (C) Yield.
   (D) Limiting reagent.

INQUIRY QUESTION

What are the implications for society of chemical synthesis and design?

93 Revision Of Applying Chemical Ideas

You have completed this course in chemistry. Congratulations! We hope that you have enjoyed your studies in Chemistry and that this course has helped you be more aware of and to further understand the chemical world that you are part of, that includes and surrounds you. Best wishes for your future.

To finish with, here are some questions to help you check that you understand and remember the concepts covered in this module and find any areas of weakness. If you are unsure of any areas you should, as always, consult your teacher.

QUESTIONS

Analysis Of Inorganic Substances

1. The branch of chemistry that deals with the separation, identification and quantification of the chemical components of materials is called ....
2. Tests which detect but do not measure components are called ....
3. Name three qualitative tests.
4. Tests which both detect and measure the amounts of components present are called ....
5. Name three quantitative tests.
6. List four examples of the needs for chemical analysis in our society.
7. Identify six techniques used in analysis of inorganic substances.
8. Identify the most common anion and cation in water.
9. Name two trace elements that may be found in water or soil.
10. Identify four possible sources of ions present in waterways.
11. What do we call the pollution of a body of water that is stagnant with dead algae and contains a high nitrogen : phosphorus ratio?
12. Why is rising salinity of our soil a problem?
13. Identify the main cause of acidic rain.
14. Name the gas which is useful in the stratosphere but harmful to health in the troposphere.
15. Identify three gases that cause global warming.
16. In a flame test, which ions cause a lilac flame and an apple-green flame?
17. Solubility rules are useful in analysis. Name the colour of the following precipitates.
    - (a) Lead iodide.
    - (b) Lead hydroxide.
    - (c) Iron(II) hydroxide.
    - (d) Copper(II) hydroxide.
    - (e) Iron(III) hydroxide.
    - (f) Barium, calcium and magnesium sulfates.
    - (g) Silver chloride.
    - (h) Silver bromide and silver iodide.
18. Which anion can be identified by the release of carbon dioxide gas when dilute acid is added?
19. The ammonium molybdate test is used to identify which ion?
20. What is the name and colour of the complex ion with formula $[Cu(OH_2)]_6^{2+}$?
21. What is the colour of the tetraamminediaquacopper(II) complex ion?
22. Name a green complex ion.
23. The quantitative analytical technique that depends on separating out components and weighing them is called ....
24. What could you use as a precipitating agent if you were to analyse for halide ions in solution?
25. Colorimetry is used to identify or measure the concentration of a coloured substance by measuring the light of a particular wavelength that is (reflected/absorbed) as it is passed through the substance being analysed.
26. Identify three advantages of colorimetry.
27. What is analysis of spectra using the absorbance of light in the visible and ultraviolet ranges of the electromagnetic spectrum called?
28. Atomic absorption spectroscopy is used to detect and measure the concentration of what sort of substances?
29. Identify three advantages of AAS analysis.

Analysis Of Organic Substances

1. Name two organic pollutants that need to be monitored in air or water.
2. Which is the less toxic pesticide, an organophosphate or pyrethrum?
3. Why are organic pollutants such as oil spills of concern?
4. Identify the test for the −C=C− double bond.
5. Identify the distinguishing test for an alcohol.
6. Write a equation for the action of ethanol on sodium metal.
7. Identify a simple test to distinguish between an alcohol and a carboxylic acid.
8. You add an unknown organic compound to an alcohol and an ester is formed. What was the unknown substance?

9. The effect of a magnetic or electric field on a moving charged particle is used in which analytical technique?
10. Identify three uses of mass spectrometry.
11. What do we call the strongest signal on a mass spectrogram?
12. An instrument that measures the mass-to-charge ratio of charged particles in a sample is called a ....
13. Identify two factors which affect the amount of deflection of ions in a mass spectrometer.
14. Identify three uses of infra-red spectrometry.
15. What do we call the part of an infra-red spectrum which is unique for every organic compound?
16. An instrument that analyses the structure of molecules and identifies chemicals by measuring the absorption of infra-red radiation is called an ....
17. Infra-red radiation causes covalent bonds to .... and ....
18. The higher the frequency of infra-red radiation absorbed, the (weaker/stronger) is the bond.
19. Can molecules which are non-polar, such as hydrogen molecules (H_2) absorb infra-red radiation?
20. Infra-red spectrometry makes use of the way in which different types of bonds vibrate at different frequencies and thus they will absorb infra-red light of different ....
21. Identify the method of analysis that uses the magnetic properties of some atomic nuclei to determine physical and chemical properties of atoms in molecules.
22. Name three isotopes used in NMR analysis.
23. Which part of the electromagnetic spectrum is used in NMR analysis?
24. Identify the two influences applied to samples during NMR spectroscopy.
25. Which chemical is used as a standard in NMR analysis?
26. In NMR, what does the chemical environment refer to?
27. Why is the environment important?
28. In NMR, what do we call the position in the spectrum where absorption occurs for each hydrogen or carbon atom in the molecule being studied?
29. Which isotope is used to determine the type and number of carbon atoms in a molecule and their environments.
30. In an ^{1}H NMR spectrum, the relative heights of the peaks and the relative area under each peak tells us about the ratio of .... atoms in different environments within the molecule being studied.
31. State the the $n + 1$ rule used in ^{1}H NMR spectrometry.
32. Name the two phases used in chromatography.
33. The retention time is the time it takes a chemical to pass through a ....
34. What is the analyte in chromatography?
35. Copy and complete the table to summarise and compare analysis techniques.

Factor	IR	MS	NMR
Quantitative or qualitative			
Sample			
Sample destroyed or not?			
Calibration curve?			
Basic concept			

Chemical Synthesis and Design

1. List four important activities involved in an industrial chemistry plant.
2. Name four physical or chemical processes you have carried out in the laboratory, that could be involved in an industrial operation.
3. The process of making chemical compounds from other chemicals is called chemical ....
4. List four reasons to synthesise chemicals.
5. Name four chemicals you have studied which are produced by chemical synthesis.
6. When reactants are added in the ratio in which they will combine, this is referred to as being in ....
7. The synthesis of soap is called ....
8. Saponification is the ...., in (acidic/basic) solution, of ....
9. Complete the word equation.
   Glycerol tristearate + conc. sodium hydroxide → sodium stearate + ...
10. Most soap is made from (vegetable oils/animal fats).
11. Designing, developing and using chemicals and processes without using or producing hazardous substances is referred to as .... chemistry.
12. Name two chemists who have been instrumental in the development of green chemistry.
13. Very briefly identify four principles of green chemistry.
14. Identify four synthesis processes you have studied during this course.
15. Name three substances used as catalysts during synthesis processes.

Extended answer questions

This section provides extra practice in answering extended response questions that can refer to any topic covered during this whole course.

You should answer some using essay style answers with headings and subheadings. However, it is also important to be able to answer questions concisely, while still including all the relevant facts and ideas, so you should try answering some questions in summary form, with the minimum number of words, employing formats such as flow charts and tables.

We know time is limited, so discuss with your teacher which questions you should answer first and also how long your answer should be. Answers are not provided for these questions as they can vary considerably. Show your answers to your teacher for feedback.

1. Discuss ways in which information and communications technology (ICT) has changed the work of chemists and/or the understanding of chemistry by students.
2. Describe an advance in one aspect of chemistry that you have studied and show how this has had an effect on the development of technology.
3. Chemical theories are contested and changed when there is new evidence that challenges the existing theories and/or has greater explanatory power. Discuss this with reference to a theory about a named chemical concept.
4. Society, economics and culture can influence the acceptance of chemical knowledge. Discuss the influence of society, economics or culture on one named area of scientific knowledge.
5. Knowledge and techniques of chemistry can be used to monitor, assess and evaluate risk. Outline one example of this.
6. Chemical knowledge cannot always provide answers to issues of concern to the public. Suggest reasons for this.
7. Outline an example of a project in the field of chemistry where international collaboration is occurring.
8. Write a play, poem or short story, or make a short film, about some aspect of chemistry you have studied this year.
9. Find three articles in the media about a topic studied in chemistry this year and discuss the accuracy of information provided to the public by the media.