

1. Much of the work of chemists involves monitoring the reactants and products of reactions and managing reaction conditions

outline the role of a chemist employed in a named industry or enterprise, identifying the branch of chemistry undertaken by the chemist and explaining a chemical principle that the chemist uses

Area of chemistry: Analytical Chemistry - Inorganic chemistry in environmental monitoring

Employer: Government agency - Department of Mines and Energy

Qualifications: BA(Hons), M.Sc(Hons), M.Env.Sc. - 8 years full time study.

Duties

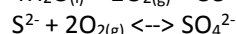
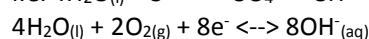
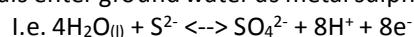
- Fieldwork collection of water and soil samples from mining sites and mine rehabilitation areas.
- Coordinate the duties of technicians within the laboratory.
- Maintain analytical standards of the laboratory to Australian standards specifications so that results can be compared between laboratories.
- Preparing reports on samples for both private groups and other government agencies (e.g. EPA, Dept. Land and Water Conservation) and making recommendations.
- Liaise with community groups, local Councils and mine managers on managing contamination of soil by runoff and groundwater near mine sites.

Analytical methods used:

Flame Atomic Absorption Spectroscopy for heavy metal analysis

Chemical principle:

Many ores contain metal sulphides. The metal sulphides are very insoluble and in this form do not pose a problem. When exposed to air and water the metal sulphides oxidise to sulphates. The solubility of sulphates is much greater than for sulphides. Heavy metals enter ground water as metal sulphate salts.



If acidity were to suddenly decrease, then by Le Chatelier's principle, in eq1, the equilibrium shifts to the right, increasing sulphates in soils.

Maintaining acidity of mullock and slag heaps help prevent mobilisation of heavy metals into ground water.

identify the need for collaboration between chemists as they collect and analyse data

Roles of chemistry are becoming increasingly important and diverse, with different chemists specialising in different fields. Universities, research institutions and industry encounter chemical problems in the world today which often require more than one field of specialisation.

For instance, for environmental monitoring, knowledge of chemical analysis (separation techniques and spectrometry), is very different to knowledge required as a chemical engineer with background in chemical and engineering concepts such as equilibrium, reaction rates and mechanisms, catalysts and energy use.

Many chemists solving complex problems via collaboration, exchanging and discussing different viewpoints about the problems as they collect and analyse data. Ability to communicate all aspects of their particular disciplines skilfully and concisely (without excessive technical jargon) allows teams to work together with little misunderstanding.

gather, process and present information from secondary sources about the work of practising scientists identifying:

- the variety of chemical occupations
- a specific chemical occupation for a more

Practising chemists contribute to society in a wide variety of chemical occupations such as:

- Environmental monitoring
- Research and development
 - Paint

This career requires development of new paints to meet changing market needs. Working as a member in a team.

- Good knowledge of organic chemistry, particularly interest in

occupations

- a specific chemical occupation for a more detailed study

Paint

This career requires development of new paints to meet changing market needs. Working as a member in a team.

- Good knowledge of organic chemistry, particularly interest in solvents, colloids and polymers.

○ Surfactant

This role requires research in surfactants which reduce surface tension, enhance surface tension, enhancing solubility or emulsification of organic substances in water. Application in agricultural or cleaning products requires meeting strict environmental standards as well as development of large scale production. Working with a team of research chemists.

- Knowledge of surface chemistry, solvents, organic chemistry, chemical synthesis and analysis.

- Organic chemist (drugs)

Development of new pharmaceuticals to improve treatment of diseases and medical conditions. Working as a member of a team, developing and testing.

- Bachelor of Science, PhD in organic chemistry, underlying knowledge of computer-aided molecular design and chemical synthesis.

- Nuclear chemist

- Chemical engineer

Environmental Monitoring

This career undertakes scientific study of natural chemical and biochemical phenomena, examining sources, transport, reaction and effect of chemical species in abiotic environments (air, water, soil); particularly the effect of human activity on natural cycles which sustain our water supplies and atmosphere.

We face changing atmospheric composition from combustion of fossil fuels while various fertilisers and industrial wastes are washed into waterways. However, collection of data about our environments and the interpretation of these data can provide enhanced understanding of human impacts.

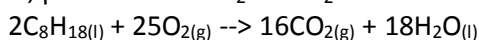
Society now appreciates the importance of environmental sustainability and at the EPA, this career can result in formulation of government policies regarding ecologically sustainable development, providing policy advice to statutory authorities.

Environmental chemists work as a member of a team, drawing on a range of concepts from chemistry and environmental sciences to assist the study of chemical species in the environment. They would ideally have a Bachelor of Science with a good underlying knowledge of sampling and analytical chemistry (separation techniques and spectrometry), with post-graduate qualification in scientific communication or management.

describe an example of a chemical reaction such as combustion, where reactants form different products under different conditions and thus would need monitoring

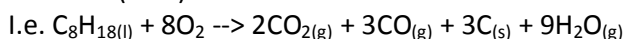
Combustion forms different products under different conditions and it's important for the reaction to be carefully monitored to ensure maximum energy output and reducing harmful waste products.

For instance, the combustion of octane in petrol used in internal combustion engines produce a combination of products which can be formed due to varying amounts of available oxygen. When burnt in plentiful supply of oxygen, products are CO₂ and H₂O:



Although CO₂ is a greenhouse gas, it doesn't present an acute local pollution problem.

However, if oxygen supply is limited or the engine is poorly tuned, incomplete combustion may take place, resulting in any combination of H₂O, CO₂, CO and C (soot).



Is it water vapour in incomplete combustion?
Or is it H₂O_(l)?

Carbon monoxide is a pollutant that's particularly dangerous as it's odourless and extremely poisonous. High carbon monoxide levels can lead to death and so it is crucial that they are monitored in cities with large traffic volumes. Levels can exceed 100ppm, which is a concern for drivers who spend long periods in traffic.

Automobile manufacturers also collaborate with environmental and atmospheric chemists to constantly monitor output of the combustion process in the engine and the impact on engine efficiency and wear. Subsequently, new technologies to develop efficient and clean engines can assist in reducing harmful waste products. By reducing toxic products (i.e. CO, and soot), negative impacts of octane combustion can be minimised.

2. Chemical Processes in industry require monitoring and management to maximise production

■ identify and describe the industrial uses of ammonia

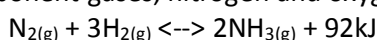
Most of the ammonia produced is used industrially as a raw material from which a substance or industrial process is derived (i.e. feedstock).

- Used for fertilisers, which are used to grow plants in soils which may be nitrogen deficient. (fertilisers include ammonium sulphate, ammonium nitrate, ammonium hydrogenphosphate and urea). *To make solid fertiliser, ammonia reacts with sulphuric acid to form ammonium sulphate fertiliser, or react with nitric acid to form ammonium nitrate.*
- Manufacture of explosives derived from nitric acid such as TNT, nitroglycerine, and nitrocellulose.
- Production of cyanide, used in plastics manufacturing and gold extraction.

Ammonia also has important uses in manufacture of synthetic fibres (e.g. Nylon), effluent treatment, manufacture of some pharmaceuticals (e.g. sulphonamides), and refrigeration.

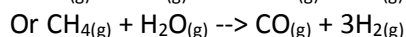
■ identify that ammonia can be synthesised from its component gases, nitrogen and hydrogen

The Haber process is the industrial process of ammonia synthesis from its component gases, nitrogen and oxygen.



N_2 can be collected by distillation of liquid air, while H_2 can come from sources depending on where

- i.e. Risdon Tasmania, using hydroelectricity to electrolyse water
- Kwinana WA, Natural gas from NW Shelf supply is brought in contact with steam: $\text{CH}_4(g) + \text{H}_2\text{O}(g) \xrightarrow{\text{Ni}} \text{H}_2(g) + \text{CO}(g) + \text{CO}_2(g)$



Note that as CO poisons the iron catalyst used in the Haber process, it must be removed by forming CO_2 : $\text{CO}(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}_2(g) + \text{H}_2(g)$

This produces more $\text{H}_2(g)$ as well.

$\text{O}_{2(g)}$ must also be removed to prevent explosion with the H_2 and methane is used to remove it by combustion to produce CO_2 and steam. CO_2 is removed by reaction with a base, and a 3:1 mixture of hydrogen to nitrogen can enter the Haber process reaction.

■ describe that synthesis of ammonia occurs as a reversible reaction that will reach equilibrium

AND

■ identify the reaction of hydrogen with nitrogen as exothermic



The synthesis of ammonia is a reversible reaction, and with all reversible reactions in a closed system, it will reach equilibrium after a time (when forward and reverse reaction rates are equal).

At standard temperature and pressure, the equilibrium lies well to the left, and very little ammonia is present. To make it commercially viable, the Haber process involves the circulation of hydrogen and nitrogen gases over an iron catalyst (magnetite Fe_3O_4) at, ideally, temperatures of about 500°C and pressure of 35000kPa . (Though Haber and Bosch originally used $15000\text{--}20000\text{kPa}$).

As seen in the above equation, the forward process is exothermic. It can also be expressed as: $\text{H}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$, $\Delta H = -92\text{kJ/mol}$. Noting that ΔH is negative, hence the process is exothermic and heat is given out. *Bonds are formed and 92kJ of energy is released, three moles of nitrogen gas produces two moles of ammonia.*

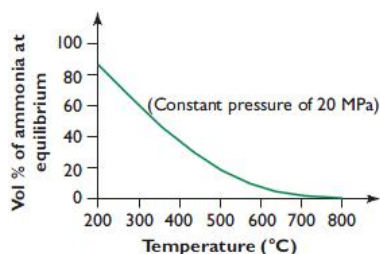
■ explain why the rate of reaction is increased by higher temperatures

Kinetic factors, particularly due to change in temperature (and pressure), affects rates of reaction. The kinetic theory of gases predict the rate of

explain why the rate of reaction is increased by higher temperatures

AND

explain why the yield of product in the Haber process is reduced at higher temperatures using Le Chatelier's principle



Kinetic factors, particularly due to change in temperature (and pressure), affects rates of reaction. The kinetic theory of gases predict the rate of reaction increases when more successful collisions occur in the shortest time.

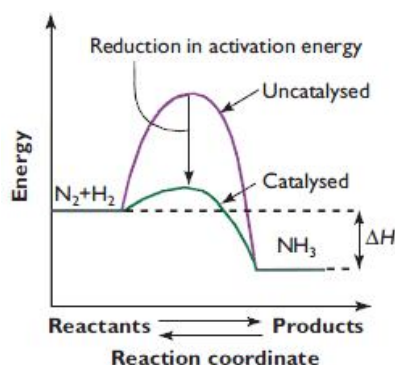
- High temperatures gives reactant particles higher kinetic energy to overcome the activation energy for the reaction. There is greater chance for successful collisions hence reaction rate is increased with greater temperatures. Reaction rate speeds up in both directions, but equilibrium position is reached sooner.
- The reverse is true for lower temperatures and ammonia cannot be produced at a reasonable rate.

However, yield from the Haber process is adversely affected by increased temperatures. The formation of ammonia is exothermic, so as temperature increases, by Le Chatelier's principle, the equilibrium will shift so as to partially counteract the change, i.e. favouring the endothermic reaction (i.e. reverse reaction decomposing NH_3 into its elements), reducing yield. Hence, as the forward reaction is exothermic, high yield is favoured by low temperatures.

But low temperatures don't allow the reaction to proceed at a reasonable rate, therefore a compromise between high yield and rapid reaction rate is required to maintain reasonable yield obtained at a satisfactory rate. In practice, temperatures of about 400-550°C are used. (ideally approx. 500°C)

Left, Yield of ammonia decreases as temperature increases.

explain that the use of a catalyst will lower the reaction temperature required and identify the catalyst(s) used in the Haber process



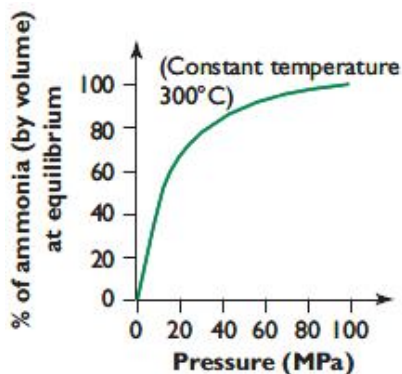
The Haber process uses catalysts which are a mix of metals and oxides. Magnetite (Fe_3O_4) is combined small amounts of K_2O , Al_2O_3 and CaO and then reduced to porous iron. This is finely ground and powdered to increase the surface area available for reactants (N_2 and O_2 gas) to adsorb more readily onto the solid catalyst surface, and consequent bond rearrangement results in ammonia molecules.

A suitable catalyst lowers the activation energy required for a reaction by providing an alternate pathway for the reaction to proceed.

For a reversible reaction, a catalyst equally increases both forward and reverse reaction rates such that the equilibrium position isn't changed. Hence, yield is not affected and a catalyst simply decreases the time taken for the system to reach equilibrium.

As the activation energy is lowered, less temperature is required to attain a high reaction rate. Lower temperatures allows the equilibrium to favour more products in the Haber process, whereas higher temperatures without catalyst to attain an equivalent rate of reaction would drastically reduce the yield.

analyse the impact of increased pressure on the system involved in the Haber process

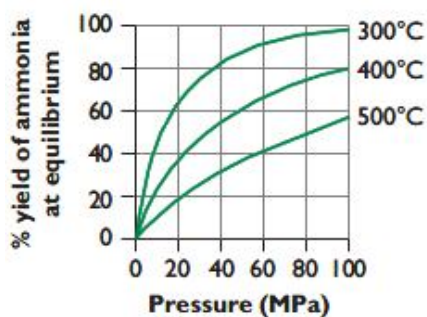


Higher pressure favours increased frequency of successful molecular collisions as the same number of molecules are in a smaller space, having higher concentration. And note that for the Haber process, kinetically the rate of reaction is given by the concentration: $K_f = k_1 [\text{H}_2][\text{N}_2]^3$. Therefore, as pressure increases, the forward rate of reaction increases while the backward reaction increases but to a lesser extent.

And Since all reactants and products are gas, changes in pressure will effect the equilibrium position. ammonia production (forward reaction) is accompanied by a decrease in the number of gaseous molecules, by Le Chatelier's principle, increasing pressure also causes the equilibrium to shift to partially counteract the change, i.e. in favour of the reaction which produces less moles of gas. Thus, the forward reaction is favoured, and increasing yields of ammonia with higher pressure.

From these two factors, increasing the pressure increases the amount of

explain why the Haber process is based on a delicate balancing act involving reaction energy, reaction rate and equilibrium



Graph summarising effect of pressure and temperature on yield of ammonia.

ammonia in the equilibrium mixture. Modern ammonia process plants operate at high pressures of 35000 kPa.

Like many other industrial processes, the manufacture of ammonia in the Haber process requires the compromise between reaction rate, equilibrium yield and economic factors.

High temperature is favoured for fast rate of reaction. Equilibrium factors predict that the forward reaction is favoured under low temperatures. This is because ammonia synthesis is exothermic, and by Le Chatelier's principle, increased temperatures would cause the system to partially counteract the change by favouring the endothermic (i.e. reverse) reaction, decreasing yield. Thus low temperatures favours high yield, and is also cost efficient. Therefore, the compromise between fast rate of reaction and reasonable yield must be maintained with modern plants at around 500°C.

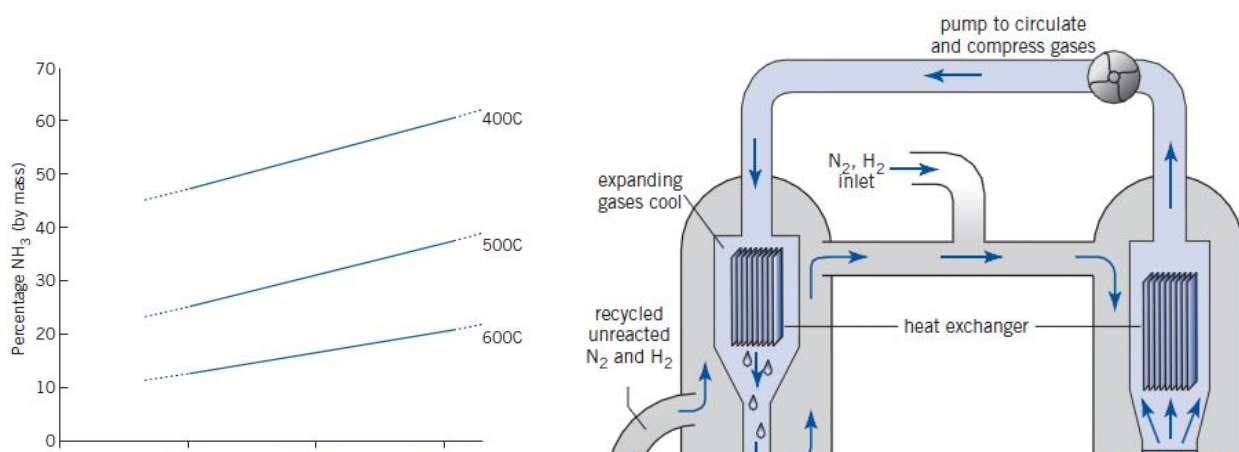
High pressure would increase yield of the reaction, as by Le Chatelier's principle, to partially counteract the increase in pressure, the reaction which produces less moles is favoured, i.e. forward reaction. Furthermore, higher pressure increases collisions, and increases the rate of reaction. Although ideally, the pressure is as high as possible, but economic and safety considerations prevent this. Hence pressure in modern plants is around 35000 kPa to lower running costs, ensure longer lifetime of reaction vessel and improve safety.

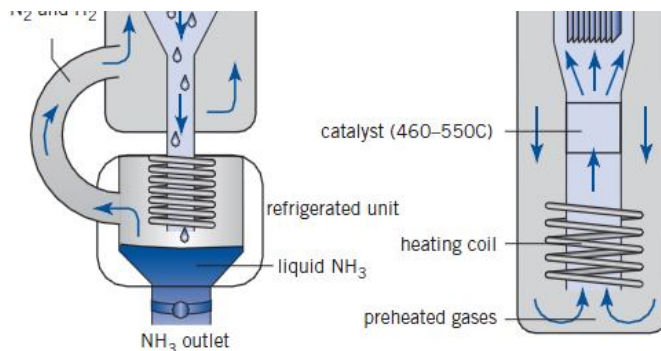
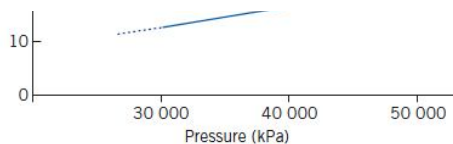
Although catalysts are usually expensive, an iron oxide (Fe_3O_4) catalyst fused with other metal oxides (K_2O , Al_2O_3 , CaO) are ideally used to increase rate of reaction. Being ground into fine powder, this porous catalyst provides high surface area for reactants to adsorb onto the solid catalyst surface, providing an alternate pathway and decreasing the activation energy and increasing the rate of reaction of both forward and reverse reactions, allowing equilibrium to be reached faster.

However, the reaction is prevented from reaching equilibrium as the product is continually removed. Ammonia is constantly removed from unreacted N_2 and H_2 by liquefying it under pressure. By Le Chatelier's principle, this shifts the equilibrium to the right, favouring products and increasing yield. Unreacted nitrogen and hydrogen are recirculated into the reaction chamber to be used again, improving efficiency of the process. However, this is done whilst maintaining the stoichiometric mixture H_2 and N_2 (3:1). Since the reaction is exothermic, heat released in the reaction is removed, and temperatures maintained around 500°C. The heat can be recycled to heat up the gas mixture entering the reaction chamber.

Under suitable conditions of 35000 kPa, 500°C, reasonable yield of 30-40% is achieved at a satisfactory rate and moderate cost.

WHY?:: Jacaranda says 15-20%??





explain why monitoring of the reaction vessel used in the Haber process is crucial and discuss the monitoring required

A range of monitoring activities are performed by industrial chemists and chemical engineers to ensure quality control of ammonia manufacturing.

- Temperature monitoring ensures it's within optimal range. Too high and ammonia yield is reduced, too low and rate of reaction reduces below the satisfactory level. Various temperature sensors measure temperature inside the reaction vessel. Excess temperatures can also damage the catalyst.
- Continuous monitoring of pressure ensures ammonia production occurs under safe conditions (pressure not too high), and yield isn't compromised (pressure not too low). Various sensors electronically monitor pressure within the high pressure reaction vessel.
- The particle size of the catalyst is also monitored to ensure it provides sufficient surface area. Generally, it has the lifetime of 5-10 years.
- The hydrogen and nitrogen feedstocks must be monitored to maintain them in **correct ratios (3:1)** and keep them free of contamination.

Sensors detect information about the gas stream.

- O_2 must be removed as it is explosive with H_2 .
- CO and sulphur compounds need to be removed as it can poison the catalyst, reducing adsorption and hence rate of reaction.
- Build up of methane must be avoided to ensure conversion efficiency.
- Ammonia liquefaction process is also monitored to ensure optimal yield.

All this data is conveyed to a monitoring computer allowing all this data to be displayed and interpreted centrally.

New catalysts and production line efficiencies are continually researched by research chemists in the ammonia industry.

gather and process information from secondary sources to describe the conditions under which Haber developed the industrial synthesis of ammonia and evaluate its significance at that time in world history

The Haber process was developed by Fritz Haber in a crucial time when Germany was about to enter WWI. Haber was interested in the effect of heat on the chemistry of gases, and in 1905, he published his work, reporting that the reaction between gaseous nitrogen and hydrogen at $1000^\circ C$ using an iron catalyst produced small amounts of ammonia.

At that time, Germany was heavily dependent on overseas supplies of nitrate salts for agriculture and explosives manufacturing. During the war, blockades prevented import of ammonia to Germany and without the Haber process, explosives and fertiliser for food would have run out by 1916. Haber's contributions overcame Germany's supply problems and effectively prolonged the war.

The Haber process allowed cheap production of ammonia on a large scale. Carl Bosch developed the necessary chemical engineering and ammonia can be readily converted into usable compounds for fertilisers and explosives. However, this effectively prolonged the war by solving Germany's supply shortages.

Although the Haber process supported the war effort, in the long run, it benefited mankind. Without fertilisers, crop rotation was essential to

regenerate adequate levels of inorganic nitrogen in the soil to support crop growth. However, with increased population, traditional farming techniques were insufficient. Greater quantities of food was required and this required use of nitrogenous fertilisers derived from natural deposits (saltpetre and guano).

Global demand for these natural reserves soon exceeded supply, but the Haber process overcame world wide shortages. Industrial synthesis of ammonia facilitated manufacture of fertilisers for food production so nitrogenous fertilisers no longer need to be derived from natural deposits. Consequently, Haber was awarded the Nobel prize in chemistry in 1918.

Today, more than 100 million tonnes of nitrogenous fertiliser are produced (primarily in the form of anhydrous ammonia, ammonium nitrate and urea), and is responsible for sustaining more than one third of the Earth's population

3. Manufactured Products, including food, drugs, household chemicals, are analysed to determine or ensure their chemical composition

deduce the ions present in a sample from the results of tests

Qualitative analysis of unknown chemicals such as precipitation tests and flame tests can identify many soluble ions.

Ion testing

Generally, a series of elimination procedures are carried out in order to identify the cation/anion. The **series of sequenced elimination tests** lead to identification of ions present in an unknown sample. Although there are various methods, it must be **performed in a strict order** as different ions can react with the same reagent to produce similar results. Then **confirmatory tests** can be performed to verify the observation.

This process of elimination and confirmation is straightforward if we restrict ourselves to one ion. Generally, each sample is 1-2mL of 0.1M solution for accurate results in each test.

We need to understand basic solubility rules before proceeding:

- All nitrate salts are soluble (won't cause precipitation of cations)
- Group 1 salts are soluble (won't cause precipitation of anions)

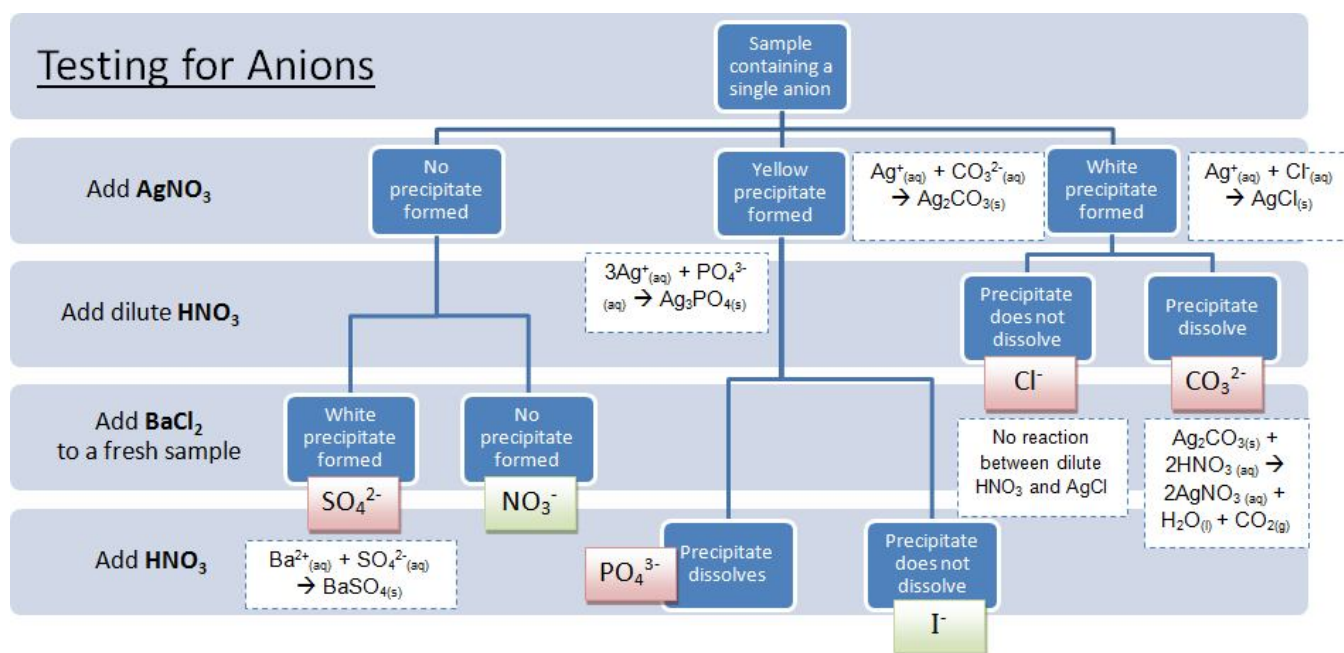
Anion	Soluble	Slightly soluble	Insoluble
CO_3^{2-}	$\text{Na}^+, \text{K}^+, \text{NH}_4^+$	—	most
Cl^-	most	Pb^{2+}	Ag^+
OH^-	$\text{Na}^+, \text{K}^+, \text{NH}_4^+, \text{Ba}^{2+}$	Ca^{2+}	most
PO_4^{3-}	$\text{Na}^+, \text{K}^+, \text{NH}_4^+$	—	most
SO_4^{2-}	most	$\text{Ca}^{2+}, \text{Ag}^+$	$\text{Ba}^{2+}, \text{Pb}^{2+}$

Solubility rules and colour of precipitates help us identify the presence of specific ions.

Anion Analysis

CO_3^{2-} , Cl^- , PO_4^{3-} , SO_4^{2-}

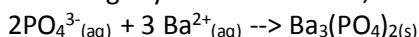
From a series of qualitative tests involving the formation of gases or precipitates can be used to determine anions in solution.



Note that CO_3^{2-} can be immediately identified by adding 2mol/L nitric acid drop wise into the original unknown solution, creating an effervescence of a colourless gas (CO_2). Use limewater to

confirm that CO₂ gas is evolved.

To test for PO₄³⁻, make original unknown solution (or filtered solution) slightly alkaline (pH=10) with drops of ammonia solution. Add barium nitrate dropwise. A white precipitate should form in the slightly alkaline solution, indicating presence of phosphate ions:



An alternative method:

1. Add 2mol/L nitric acid **dropwise** and observe whether there's effervescence (CO₃²⁻)

$$\text{CO}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$$
2. **Acidify** new sample of unknown solution (remove carbonate from previous steps), add drops of dilute solution of barium nitrate. White precipitate of barium sulphate indicates sulphate ions present (SO₄²⁻)

$$\text{SO}_4^{2-}(\text{aq}) + \text{Ba}^{2+}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$$
3. Use nitric acid to **acidify** original solution (or filtered solution from previous step), and add drops of silver nitrate solution. White precipitate of silver chloride indicates chloride ions are present.

$$\text{Cl}^-(\text{aq}) + \text{Ag}^+(\text{aq}) \rightarrow \text{AgCl}(\text{s})$$
4. Make original unknown solution, or previous filtered solution, slightly **alkaline** (pH approx. 10), using drops of ammonia. Add dropwise a solution of barium nitrate. White precipitate forms in slightly alkaline solution indicates presence of phosphate ions.

$$2\text{PO}_4^{3-}(\text{aq}) + 3\text{Ba}^{2+}(\text{aq}) \rightarrow \text{Ba}_3(\text{PO}_4)_2(\text{s})$$

Confirmation tests

Anion	Procedure	Observation and Equation
CO ₃ ²⁻	Test original solution with universal indicator	Solution should have a pH in the alkaline range (8-11): $\text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq})$
SO ₄ ²⁻	To the acidified solution, add drops of lead (II) nitrate solution.	White lead (II) sulphate precipitate forms: $\text{SO}_4^{2-}(\text{aq}) + \text{Pb}^{2+}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s})$
Cl ⁻	Add 1-2mL of 10% ammonia solution to the suspension, and heat in water bath.	White precipitate should dissolve to form a colourless silver complex: $\text{AgCl}(\text{s}) + 2\text{NH}_3 \rightarrow \text{Ag}(\text{NH}_3)_2^+(\text{aq}) + \text{Cl}^-$ <i>Note silver chloride should turn brown/purple in sunlight, another confirmatory test.</i>
PO ₄ ³⁻	<ol style="list-style-type: none"> 1. Add ammonium molybdate [NH₄MoO₄] solution to acidified unknown solution. Warm mixture gently 2. Acidify solution with 5mol/L sulphuric acid. Add ammonium molybdate and ascorbic acid. Heat to 90°C in water bath. 3. Add AgNO₃ 	<ol style="list-style-type: none"> 1. A pale yellow precipitate of ammonium phosphomolybdate forms: $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 3\text{H}_2\text{O}$ 2. When ascorbic acid is added instead, a blue complex (molybdenum blue) forms. The more concentrated the solution, the more intense the blue. 3. A yellow precipitate forms.

*Example: How to show experimentally that both chloride ions and sulphate ions are present in solution? Take sample of solution in test tube and acidify it, creating an environment where only certain compounds precipitate. Now add excess barium **nitrate** until no further precipitation. The heavy white precipitate indicates no sulphate ions are present.*

Now, filter the mixture from first reaction, and keep the acidic filtrate. Now add drops of silver nitrate solution. A white precipitate of silver chloride should form. This indicates chloride ions are present. Tests are done in this order to avoid possibility of precipitation of sparingly soluble silver sulphate.

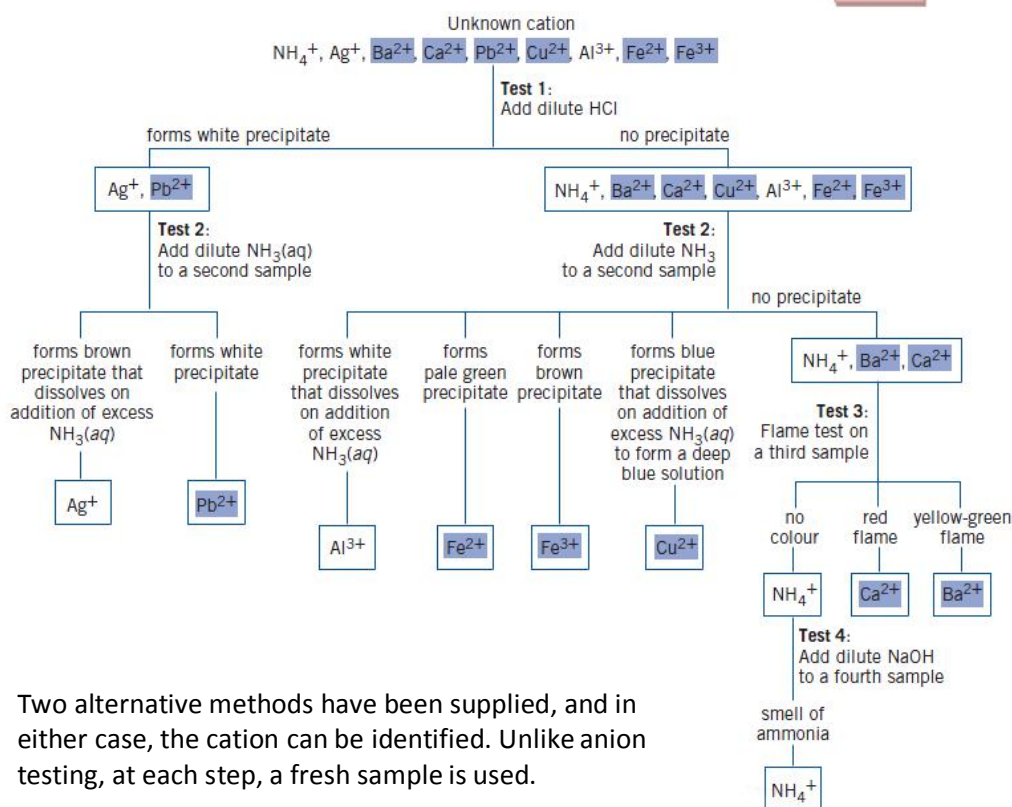
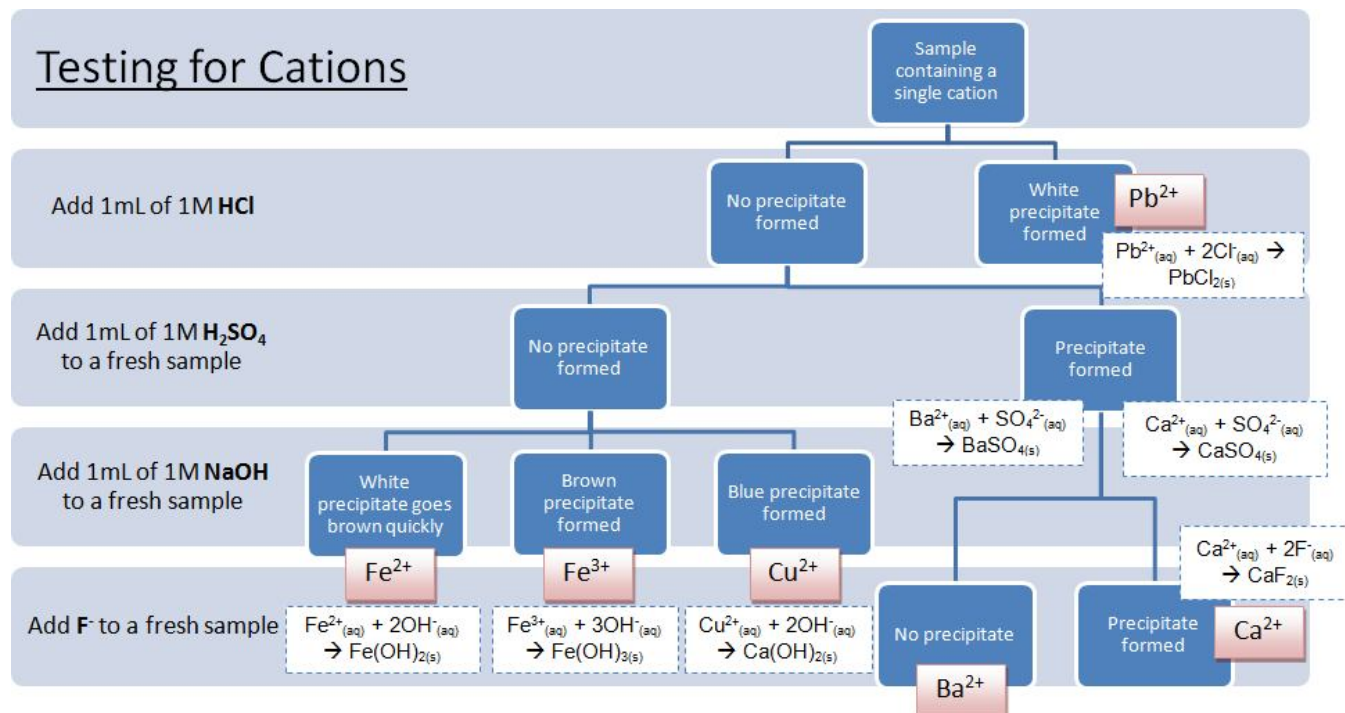
Cation Analysis

Pb²⁺, Ba²⁺, Ca²⁺, Cu²⁺, Fe²⁺, Fe³⁺

Firstly, the colour of the solutions can identify the cation:

Cation	Fe ²⁺	Fe ³⁺	Cu ²⁺
Colour	Yellow-orange to pale yellow	Pale green to colourless	Blue to green-blue

Testing for Cations



Two alternative methods have been supplied, and in either case, the cation can be identified. Unlike anion testing, at each step, a fresh sample is used.

Confirmation tests

Cation	Procedure	Observation and Equation
Pb ²⁺	Add drops of dilute sodium iodide solution to the original solution	A yellow precipitate confirms lead ions are present: $\text{Pb}^{2+}_{(\text{aq})} + 2\text{I}^{-}_{(\text{aq})} \rightarrow \text{PbI}_{2(\text{s})}$
Ba ²⁺ , Ca ²⁺	1. Add dropwise, a solution of sodium fluoride 2. Use original solid or solution to conduct a flame test	1. A white precipitate confirms calcium $\text{Ca}^{2+}_{(\text{aq})} + 2\text{F}^{-}_{(\text{aq})} \rightarrow \text{CaF}_{2(\text{s})}$ However, since barium fluoride is sparingly soluble, no precipitate occurs (unless excess fluorine is added) 2. Brick red flame indicates calcium ions. Yellow-green flame indicates barium ions.

Cu^{2+}	1. Add NH_3 to copper (II) hydroxide precipitate 2. Use original solid or solution to conduct flame test	1. In excess ammonia, the precipitate decolourises and dissolves before forming copper complex ion (Cuprammonium) $\text{Cu}(\text{OH})_2(\text{s}) + 4\text{NH}_3(\text{aq}) \rightarrow \text{Cu}(\text{NH}_3)_4^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$ 2. Green flame indicates copper ions
Fe^{2+}	1. Add a few drops of 2M HNO_3 to acidify solution, then add 1mL of 1M KMnO_4 2. Add 10 drops of 4mol/L HCl solution to acidify solution. Remove 2 drops of this solution to a white tile and add a drop of potassium hexacyanoferrate (III) reagent.	1. Decolourises purple potassium permanganate solution to colourless $5\text{Fe}^{2+}(\text{aq}) + 8\text{H}^+(\text{aq}) + \text{MnO}_4^-(\text{aq}) \rightarrow 5\text{Fe}^{3+}(\text{aq}) + \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$ 2. A dark Prussian blue colour indicates Fe^{2+} $3\text{Fe}^{2+}(\text{aq}) + 2\text{Fe}(\text{CN})_6^{3-}(\text{aq}) \rightarrow \text{Fe}_3(\text{Fe}(\text{CN})_6)_2(\text{s})$
Fe^{3+}	Add 10 drops of 4mol/L HCl solution. Remove 2 drops of this to a white tile and add a drop of potassium thiocyanate reagent.	A deep blood-red colour indicates Fe^{3+} $\text{Fe}^{3+}(\text{aq}) + \text{SCN}^-(\text{aq}) \rightarrow \text{FeSCN}^{2+}(\text{aq})$

Cation	Colour of ion in solution	Flame test	Dilute $\text{HCl}(\text{aq})$	Dilute $\text{NaOH}(\text{aq})$	Dilute $\text{NH}_3(\text{aq})$	Useful confirmatory test
Barium Ba^{2+}	colourless	yellow-green	soluble no reaction	soluble no reaction	soluble no reaction	H_2SO_4 solution forms white ppt BaSO_4
Calcium Ca^{2+}	colourless	red	soluble no reaction	slightly soluble (may form white ppt of $\text{Ca}(\text{OH})_2$)	soluble no reaction	forms white ppt with NaF
Lead(II) Pb^{2+}	colourless		white ppt PbCl_2	white ppt of $\text{Pb}(\text{OH})_2$ dissolves in excess $\text{NaOH}(\text{aq})$ to form colourless solution of $\text{Pb}(\text{OH})_4^{2-}$	white ppt of $\text{Pb}(\text{OH})_2$	forms bright yellow ppt with KI
Copper(II) Cu^{2+}	blue	green	soluble no reaction	blue ppt $\text{Cu}(\text{OH})_2$	blue ppt $\text{Cu}(\text{OH})_2$, in excess $\text{NH}_3(\text{aq})$ dissolves to form dark blue solution of $\text{Cu}(\text{NH}_3)_4^{2+}$	
Iron(II) Fe^{2+}	pale green	no characteristic colour	soluble no reaction	green ppt $\text{Fe}(\text{OH})_2$	pale green ppt $\text{Fe}(\text{OH})_2$	If left for a day will change to orange brown solution (oxidises to Fe^{3+}) or will decolourise acidified $\text{KMnO}_4(\text{aq})$ $\text{K}_3\text{Fe}(\text{CN})_6$ will form blue ppt
Iron(III) Fe^{3+}	orange-brown	no characteristic colour	soluble no reaction	brown ppt $\text{Fe}(\text{OH})_3$	brown ppt $\text{Fe}(\text{OH})_3$	solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ forms blue ppt of $\text{KFe}[\text{Fe}(\text{CN})_6]$

Note that PbCl_2 and CaSO_4 are slightly soluble. Hence, if HCl , H_2SO_4 AND NaOH have been used, and there's still no precipitate, then it must be either Pb or Ca , of which, their specific confirmatory tests are used.

Flame Tests

Metal	Flame colour
barium	yellow-green
calcium	red
copper	green
lithium	crimson
potassium	lilac
sodium	yellow-orange

Many metal ions emit a distinctive colour if their compound is heated in a flame or their vapours are exposed to an electric discharge (identified in table on left). But some elements don't produce a distinctive colour (i.e. iron, aluminium, zinc, tin, etc.)

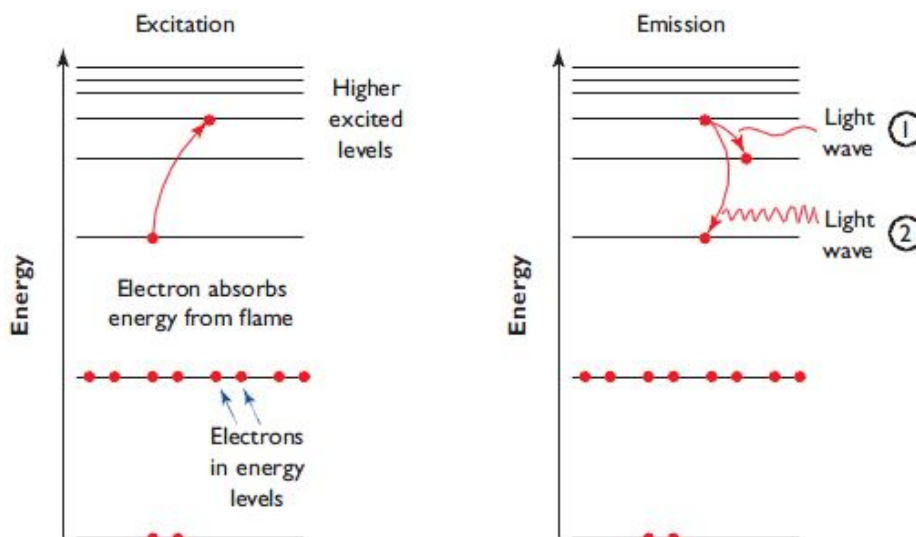
When an electron absorbs exactly the difference in energy level between shells, it occupies a higher 'excited' energy level instantaneously, then falls back instantaneously with release of energy. The released energy in the form of a photon of a characteristic

potassium	lilac
sodium	yellow-orange
strontium	scarlet

occupies a higher excited energy level, then falls back instantaneously, then falls back instantaneously with release of energy. The released energy in the form of a photon of a characteristic frequency (that may not be in the visible range). This jump up and down results in the process of excitation and emission and occurs so frequently that colour is seen.

Generally, spectra emissions from cations are seen, but not from anions.

The flame test involves placing a small sample of the compound on a platinum wire and placing this in a non-luminous (blue) bunsen flame. The colour observed is strong evidence for the presence of a particular metal.



perform first-hand investigations to carry out a range of tests, including flame tests, to identify the following ions:

- phosphate
- sulfate
- carbonate
- chloride
- barium
- calcium
- lead
- copper
- iron

Ion Testing Validity

- Purity of solutions, whether there has been contamination
 - Use of clean equipment
- Using solutions of sufficiently high concentration to produce visible precipitates
- Including confirmation tests in the method makes the test fairer and improves validity

Reliability

- Repeating the experiment many times, each time with clean equipment to avoid potential contamination factors.

Accuracy

- If the equipment is clean, then it must be accurate

gather, process and present information to describe and explain evidence for the need to monitor levels of one of the above ions in substances used in society

Lead

Lead levels must be continually monitored has severe implications on human health even at low contaminations as it is a toxic, heavy metal.

Lead additives to petrol increases lead accumulation in air, further causing it to accumulate in soils. Main source of poisoning is from direct ingestion of lead contaminated soil (i.e. clinging to leaves, fruits), though less of a problem in developed countries. Furthermore, some crops (carrots, potatoes, etc.) accumulate lead in contaminated soil.

Use of lead paints, esp. in decades prior, is a problem as deteriorating lead-based paints are likely to chip and is sweet tasting. But can also powder and be inhaled.

Plumbing and fixtures of lead or trace lead causes contaminated drinking water.
Some lead can also be found in imported cosmetics or toys.

Chronic lead poisoning entails accumulation of lead ions which are difficult to extract, resulting in:

- Neurological problems (esp. in children - stunts growth), cognitive impairment, irritability, insomnia, greater risk of miscarriage etc. Even seizure and comas.
- Especially damages brain, kidney and disrupts enzyme function.
- Inhibits haemoglobin formation, resulting in anaemia.

It is toxic as it mimics other biologically important metals (Ca, Fe, Zn, etc.), used in many enzymic reactions. Binding and interacting with the same enzymes as these metals, but due to different chemistry, interferes with enzyme catalysis as it doesn't function properly.

Health and environmental implications of lead necessitates monitoring of lead ion levels in the atmosphere, water, food and soil.

The IATL utilises AAS in measuring lead concentration of paint (mg/kg, mg/cm², ppm), water (µg/L, ppb), and soils (mg/kg or µg/m²). Sample wipes of surface lead is analysed using AAS, reported in µg/m². Lead in air is measured with AAS in the lab via NIOSH 7082 protocols, measured in (µg/m³).

K-fluorescent X-ray metering measures bone-lead, while portable x-ray fluorescence (XRF) equipment measures lead concentrations and exposures in the field, able to test lead paints, toys, etc. Inexpensive test kits are also available showing small colour changes based on chemical reactions, though it is inexact.

describe the use of atomic absorption spectroscopy (AAS) in detecting concentrations of metal ions in solutions and assess its impact on scientific understanding of the effects of trace elements

Atomic Absorption Spectroscopy (developed by Alan Walsh - CSIRO 1952) is a versatile technique to detect concentration of metal ions in solution. AAS is very sensitive and can detect concentrations of elements at ppm or even ppb levels, where other typical techniques are not possible.

It works under the principle of atom absorbance spectra as elements absorb radiation of specific wavelengths characteristic of the element.

Using a cathode of the element being measured, a cathode lamp generates light of specific wavelengths characteristic of the element being analysed. (i.e. lead cathode used for finding lead concentration in water).

A series of diluted standard solutions of the metal to be analysed are sprayed/aspirated on the flame. As the light beam passes through the atomised aspirated sample, certain wavelengths from the transmitted light is absorbed by electrons of the ions in the sample as they are excited. After passing through a monochromator, intensity of the resultant beam is measured.

The diluted standard solutions tested produces a calibration curve. Now, the unknown sample can be aspirated and interpolated on a curve to give very accurate results.

The most common detectors for AAS are photomultiplier tubes.

Traditional methods were unable to determine existence of trace elements due to interference from other ions in the sample. But being able to detect extremely low concentrations of elements using AAS, scientists are becoming aware that very small amounts of certain elements may have a large impact within a biological system, especially in agriculture where trace elements in soil can affect plant growth. Agricultural productivity can be limited by absence of trace levels of some elements (zinc, copper, iron, manganese, etc.), having a major implication for sufficient food production.

Also, elements required for specific biochemical pathways and body function have been determined. Prior to this, deficiency diseases could not be explained.

- Iron required for functioning haemoglobin.
- Iodine for proper functioning thyroid gland
- Zinc required for amino acid production, metabolism and energy production.

Other applications for AAS include:

- Monitoring pollutants in air, water and soil (particularly heavy metals)
- Testing blood/urine samples for excess/deficiency of particular elements, allowing diagnosis of certain conditions in humans and animals.
- Detecting metal content in mineral samples to determine economic viability of mining

and metal extraction processes.

- Analysis of metal pollutants (mercury, lead) in water and food samples.
- Checking metals in engine oil, determining amount of wear and predict engine failure.

identify data, plan, select equipment and perform first-hand investigations to measure the sulfate content of lawn fertiliser and explain the chemistry involved

analyse information to evaluate the reliability of the results of the above investigation and to propose solutions to problems encountered in the procedure

Many assumptions:

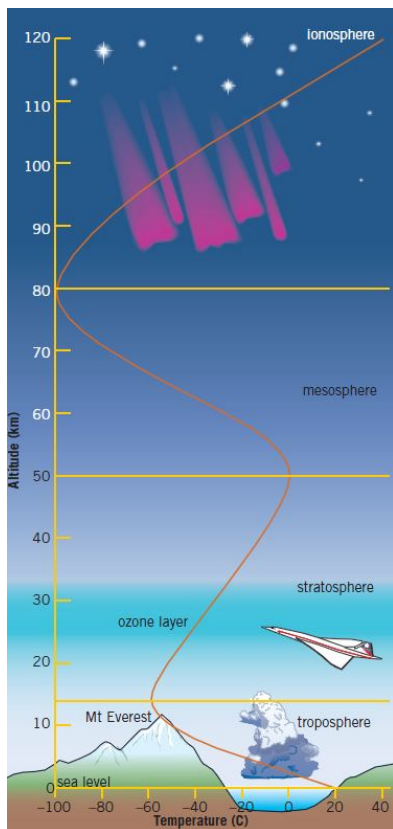
Added BaCl_2 reagent only precipitated sulphate and not anything else, in reality all the precipitate is not sulphate.

Also assumed that filtrand only has precipitate of BaSO_4 and was free of impurities (particles?)

Assumed that filtrate was devoid of precipitate (i.e. all BaSO_4 was filtered by filter paper, in reality, some must go through and is lost unless it is filtered again using finer equipment.

4. Human activity has caused changes in the composition and the structure of the atmosphere. Chemists monitor these changes so that further damage can be limited.

describe the composition and layered structure of the atmosphere



The atmosphere is a relatively thin layer of gases surrounding the earth. Atmospheric composition is not uniform, but consists of four major layers marked by abrupt temperature changes that occur with altitude. These four layers include the troposphere, stratosphere, mesosphere, thermosphere:

- **Troposphere** - This region is the closest to the surface (region of altitude 0-15km) and contain 75% of gases. Gases are well mixed, and include:
 - N_2 , O_2 , H_2O , Ar, CO_2 .
 - Temperature decreases with increasing altitude.
- **Stratosphere** - From 15-50km altitude, this region has much lower pressure with greater spacing between particles. Besides N_2 and O_2 , another significant species is O_3 . The ozone layer is located within this layer at approximately 25km altitude.
 - The troposphere and stratosphere contain 99% of the Earth's gases.
 - Temperature increases with increasing altitude in this layer.
- **Mesosphere** - Extending from 50-85km altitude, this layer has sparse particles and sees the decrease in temperature with altitude to about $-100^\circ C$.
- **Thermosphere** - From 85km up, the temperature of this layer rises steadily. Gas species include ions (such as O_2^+ , NO^+) together with atoms (i.e. O) and free electrons which would otherwise be unstable at low altitudes are found here.
 - It contains the ionosphere which is essential for reflecting radio waves for long distance communication.
 - Very high frequency radiation is absorbed here.

Note that gases in the troposphere can't move to the stratosphere as temperature of stratosphere gases are higher. Tropospheric gases are also more dense. Hence there is little mixing between the two layers. (i.e. CFCs take a long time to rise) The atmosphere also maintains Earth's heat balance by absorbing IR radiation emitted by the earth and provides air pressure, which is an important physical factor for living organisms.

Earth's weather events (clouds and storms) occur within the troposphere.

identify the main pollutants found in the lower atmosphere and their sources

Human activities have resulted in the increase in pollutants in the troposphere which can have an impact on the natural environment with sufficient concentration. Concentration of pollutants vary depending on location, and are generally measured in ppm. Their occurrence is generally the highest in regions of higher population density.

Pollutant	Source	Effect
Lead	Vehicle using leaded fuel, some metal extraction, recovering old houses containing lead paint, electric wire covering	Direct poison, neurological problems (especially children)
Sulphur Oxides	Burning fossil fuels, some metal extraction processes (mineral smelters)	Smog, acid rain
Nitrogen oxides	High temperature environments usually involving combustion (e.g. power stations, internal combustion engines, or lightning)	Acid rain, photochemical smog
Methane	Anaerobic decomposition of organic matter,	Greenhouse effect

	natural gas seepage, ruminants	
Volatile organic compounds - (Hydrocarbons)	Vehicles using hydrocarbon fuels. Solvents and unburnt fuels.	Photochemical smog
Carbon monoxide	Incomplete combustion, particularly of fossil fuels in motor vehicles.	Direct poison
Carbon dioxide	Burning fossil fuels	Greenhouse effect
Chlorofluorocarbons (CFCs)	Formerly in spray cans, refrigerant - air conditioner coolant, foaming agent	Ozone depletion in stratosphere
Particulates	Incomplete combustion, earthmoving dust storms, some agricultural and industrial processes	Aggravates asthma, reduces lung capacity, increases susceptibility to respiratory illnesses

describe ozone as a molecule able to act both as an upper atmosphere UV radiation shield and a lower atmosphere pollutant

90% of ozone is in the stratosphere, while the rest is in the troposphere.

Note that ozone is also a greenhouse gas and heats up the stratosphere, absorbing and emitting infra-red radiation.

Ozone exists in the upper and lower atmosphere. It is formed mainly by UV acting upon oxygen in the stratosphere. *But its peak concentration is small at about 10ppm at altitudes of about 32km in the stratosphere.*

Ozone is a toxic gas and lower atmosphere, tropospheric pollutant, being a component of photochemical smogs due to by-product of sunlight on NO_x and hydrocarbons. It is poisonous at concentrations greater than 20ppm sustained over several hours. Being a strong oxidant, it is a respiratory irritant and attacks organic tissues easily, disrupting biochemical processes in the body. It also attacks rubber and plastics.

However, it only occurs naturally in the troposphere to a limited extent due to its high reactivity and instability relative to oxygen.

In the upper atmosphere, stratosphere, it exists vitally as a thin layer, and is beneficial to humans and living organisms by absorbing UV-C and a majority of UV-B radiation. Some UV is necessary to produce vitamin D and maintain levels of Ca and P. However, without ozone, excessive UV levels (particularly of shorter wavelengths) can lead to sunburns, skin cancer, cataracts, etc.

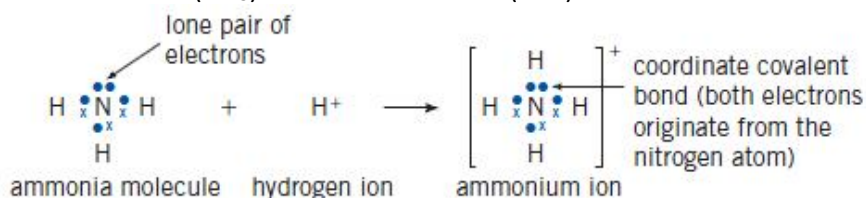
describe the formation of a coordinate covalent bond

AND

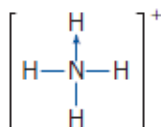
demonstrate the formation of coordinate covalent bonds using Lewis electron dot structures

Exam: Use dots, keep electron notation identical, do not differentiate.

A coordinate bond is a bond where both electrons in the bonding pair of electrons originate from one of the bonding atoms. Often elements in groups V, VI, and VII retain non-bonding pairs of electrons after forming molecules, and may form a coordinate covalent bond when an electropositive atom nears. (i.e. highly charged H⁺ ion can force a coordinate covalent bond as it nears ammonia (NH₃) to form ammonium (NH₄))



Once a coordinate covalent bond is formed, it is indistinguishable from a normal covalent bond. NH₄ is alternatively: (remembering that all four N-H bonds are identical and the arrow points to the atom being donated to).

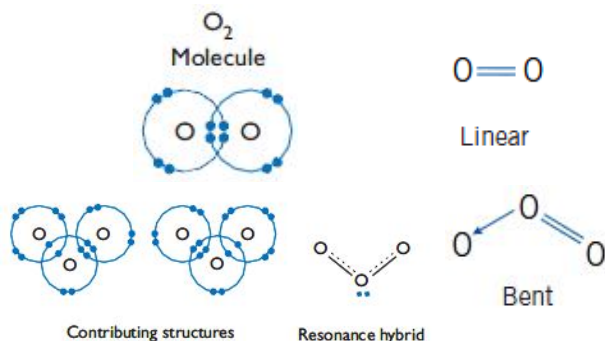


compare the properties of the oxygen allotropes O₂ and O₃ and account for them on the basis of molecular

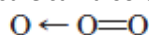
Oxygen exists as two allotropes, diatomic oxygen (O₂) and triatomic oxygen (O₃). Allotropes are different forms of the

compare the properties of the oxygen allotropes O_2 and O_3 and account for them on the basis of molecular structure and bonding

When asked to draw, draw a Lewis dot formula one, showing only one form.



The bonding in an ozone molecule can also be written as:



Oxygen exists as two allotropes, diatomic oxygen (O_2) and triatomic oxygen (O_3). Allotropes are different forms of the same element existing in the same state, having different properties, molecular structure and bonding.

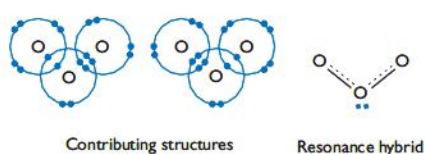
Diatomic oxygen consists of two oxygen atoms linked very strongly by a double covalent bond, having a high bond energy of 498 kJ/mol. Whereas ozone consists of three oxygen atoms, the third bonded together with a coordinate covalent bond, hence ozone is more reactive than diatomic oxygen, having a lower bond energy of 445 kJ/mol.

However, the melting and boiling points of ozone (-193°C/-111°C) are higher than that of oxygen (-219°C/-183°C). This is due to ozone's higher molecular mass, having more dispersion forces between molecules. Furthermore, while O_2 only has dispersion forces, O_3 is polar due to the bent structure and coordinate bond, hence it has dipole-dipole interaction between molecules.

O_3 has a lone pair of electrons on the central atom. The bent structure minimises repulsion between bonding and non-bonding valence electrons. Due to this asymmetrical arrangement the ozone molecule is polar due to uneven distribution of negative charge.

The polar nature of ozone also means it has greater solubility than oxygen, due to dipole-dipole interaction with water.

Property	Oxygen (O_2)	Ozone (O_3)
Melting and Boiling point	-219°C/-193°C	-183°C/-111°C
Odour	Odourless	Sharp irritating electric odour, poisonous at >20 ppm
Colour	Colourless	Pale blue
Density	Slightly denser than air	About 1.5 times denser than air
Stability	Stable	Unstable - disassociates to form O_2
Reactivity	Moderately high reactivity (oxidising agent): <ul style="list-style-type: none"> Metals: $2Mg + O_2 \rightarrow 2MgO$ Non-metals: $S + O_2 \rightarrow SO_2$ 	Highly reactive (oxidises all common metals except Au and Pt), e.g. $Zn + O_3 \rightarrow ZnO + O_2$ Attacks double bonds in alkenes, deteriorates textiles and rubber.
Water Solubility	Sparingly	Slight
Uses	Sustain life in eco-systems, life support, combustion, rocket fuel (liquid O_2)	Sterilisation of water supplies and swimming pools (kills bacteria and viruses) Sterilises stagnant air in animal slaughter rooms and underground railways.
Preparation	Industry: Distillation of liquid air Lab: Decompose $H_2O_{2(aq)}$ catalysed by $MnO_{2(s)}$ $2H_2O_2 \rightarrow 2O_2 + 2H_2O$	Electric discharge or UV radiation through O_2 gas
Test	Glowing splint test	Characteristic odour, IR spectrometry



It was determined that both bond links in O_3 are identical. So a single diagram is not the actual representation of the bonding (hence a limitation of the Lewis dot model).

Having two contributing structures doesn't mean the O_3 structure oscillates between the two representations, but it is

somewhere in between. Therefore, there is only one type of O_3 depicted through resonance structure due to limitation of the electron model.

compare the properties of the gaseous forms of oxygen and the oxygen free radical

Describe reactivity
Highly reactive
Due to two unpaired electrons.

The oxygen free radical is denoted by $O\bullet$, having two paired electrons and two unpaired electrons in their valence shell. The unpaired electrons exist in higher energy states (excited states) than the ground state. Thus they are very reactive, even more than O_3 . Hence, unlike O_2 , oxygen free radicals only occur briefly in the lower layers of the atmosphere before reacting with other radicals or molecules. In the thermosphere, far UV photons cause photodissociation of oxygen molecules to form $O\bullet$.

identify the origins of chlorofluorocarbons (CFCs) and halons in the atmosphere

CFCs and halons are responsible for the decline in ozone levels in the atmosphere. Beneficial properties of chlorofluorocarbons (CFCs) and halons prompted their use:

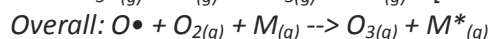
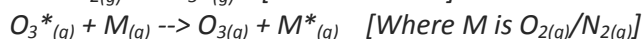
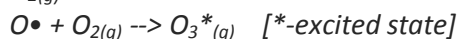
- CFCs were unreactive, non-toxic and readily liquefied on compression. Hence they were manufactured to replace toxic ammonia as a refrigerant gas. Also used in propellants in spray cans, solvents for cleaning and blowing agents to make expanded plastics.
 - These contain carbon, fluorine and chlorine (at least one of each, composed of single bonds).
- Halons have outstanding fire-retardant properties and have been used extensively for fire extinguishers, especially in electrical systems.
 - They contain carbon, fluorine and bromine (all single bonds).

discuss the problems associated with the use of CFCs and assess the effectiveness of steps taken to alleviate these problems

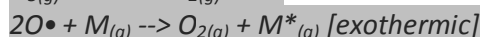
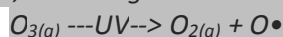
AND

present information from secondary sources to write the equations to show the reactions involving CFCs and ozone to demonstrate the removal of ozone from the atmosphere

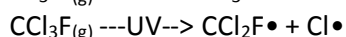
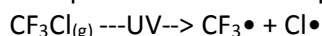
In normal circumstances, an ozone molecule is formed such that:



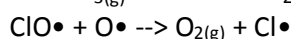
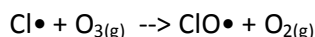
This process is reversed when O_3 absorbs UV light in the **photodissociation of ozone**, occurring at 20-49km altitude:



CFCs and halons are stable enough in the lower atmosphere and have sufficiently long lifetimes to diffuse to the stratosphere. There, stronger UV radiation splits the molecules apart.

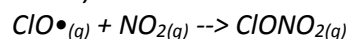
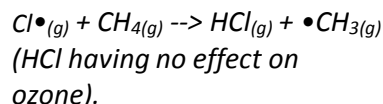


The chlorine radical is a concern as it catalyses the decomposition of ozone.



Therefore: $O_{3(g)} + \bullet O \rightarrow 2O_{2(g)}$. Overall, ozone is destroyed and the Cl radical catalyst is regenerated, capable of destroying thousands more ozone molecules before being removed by other processes (i.e. reaction with CH_4 or NO_2). Halons similarly produce Br radicals which are much more deadly and have greater potential to deplete ozone.

Chlorine is removed by CH_4 and NO_2 :



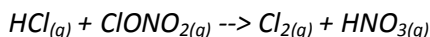
(Chlorine radicals cannot regenerate from $ClONO_2$, chlorine nitrate)

Hence chain reaction involving free radicals stops.

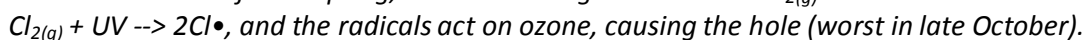
Due to these CFCs, overall ozone levels have declined for many years during the 80's and 90's. It is evident that at the beginning of each spring approximately 70% of O_3 over the south pole disappears.

Both HCl and $ClONO_2$ are inactive but act as a **chlorine reservoir** in the stratosphere, releasing $Cl\bullet$ each spring. During the Antarctic winter, the polar vortex (wind patterns preventing Antarctic air mixing with warmer air) traps air above the south pole. In this cold air, temperatures drop to $-90^\circ C$ and stratospheric clouds form (despite air being very dry). Crystals in the ice remove

NO₂ which stops removal of Cl•, and provides a surface that catalyses a reaction between HCl and HClONO₂:



At the commencement of each spring, UV in the sunlight acts on the Cl_{2(g)}:



As temperatures warm and the polar vortex stops, ozone from surrounding areas move in and the hole disappears (early January).

Emission of CFCs and halons into the atmosphere due to their extensive use prior to first discovering their ozone depleting effects in the 1970s. In the late 1980s, world CFC production was 1.2 million tonnes, almost all this ended up in the atmosphere. Powerful evidence provided by NASA experiments caused scientists to lobby extensively and raised global concerns throughout the world. Initially 0.05ppm in 1971, this exploded to 0.275ppm in 1993.

Although unreactive in the troposphere, CFCs in the air break are broken down by UV radiation releasing chlorine radicals which attack ozone molecules: $\text{CF}_2\text{Cl}_{2(g)} \xrightarrow{\text{UV}} \text{CF}_2\text{Cl}\bullet + \text{Cl}\bullet$. Bromines from halons released in a similar way is even worse.

A series of international agreements, starting with the Montreal Protocol in 1987, have been implemented with the phasing out of ozone-harming chemicals (CFCs, halons, CCl₄) according to a timetable. Schedule was later tightened, but less able nations were provided support.

Subsequent development into CFC alternatives such as HCFCs and HFCs to replace CFCs. I.e. C₂H₂F₄ for refrigerant. These compounds are less damaging as they are more reactive, consequently reacting before reaching the ozone layer.

Due to all these effective actions, we have seen the decline of tropospheric chlorine and bromine since the mid-1990s and ozone levels will return to 1970 levels by 2050. Overall, due to the world's prompt action and implementation, it has been said that "the single most effective agreement to date has been the Montreal protocol".

analyse the information available that indicates changes in atmospheric ozone concentrations, describe the changes observed and explain how this information was obtained

Ground based UV spectrophotometers are a means of measuring ozone layer thickness from the ground. One such device is the Dobson ozone spectrometer, which measures the intensity of light received from the sun at a wavelength which ozone absorbs, then wavelengths on either side which ozone doesn't absorb. Comparing intensity of these wavelengths give a measure of total ozone in the atmosphere per unit area of the Earth's surface at that location. Ozone layer thickness is measured in Dobson Units (DU).

Spectrophotometers can also be used on satellites scanning through the atmosphere. Total ozone mapping spectrophotometers (TOMS) used on NASA satellites (Nimbus-7, Meteor-3), measure "total column ozone" the amount of ozone in a column of air from the Earth's surface to the upper atmosphere. It measures both incoming solar energy directly from the Sun and backscattered UV radiation at six wavelengths. Some backscattered radiation has been absorbed by ozone. The TOMS instrument then compares backscattered radiation to incoming radiation which has not been absorbed, at identical wavelengths, to determine the amount of ozone above the Earth's surface. This operates on a much larger scale of operations than ground based spectrophotometers as satellites can orbit the Earth.

Spectrophotometers can also be carried by helium balloons into the stratosphere to measure concentrations of various substances including ozone as a function of altitude. Ozone sondes are balloon-borne instruments which continuously monitor ozone concentration estimates as they ascend in the atmosphere. A profile of ozone concentration is obtained up to around 30km until the burst point of the balloon.

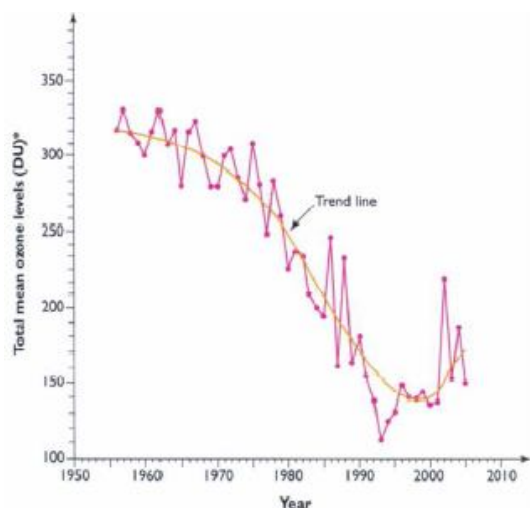
Ozone concentration is measured in Dobson Units (DU).

Due to CFCs (photodissociation) the amount of ozone over Antarctica has dropped. Twenty years ago, ozone levels above Antarctica were 270DU, and have dropped to 230DU in 1990 and 216DU in 1996. This indicates an ozone hole which seasonally occurs in the Antarctic spring due to prolonged winters with a period of continuous darkness. <Polar Vortex explanation - Quote

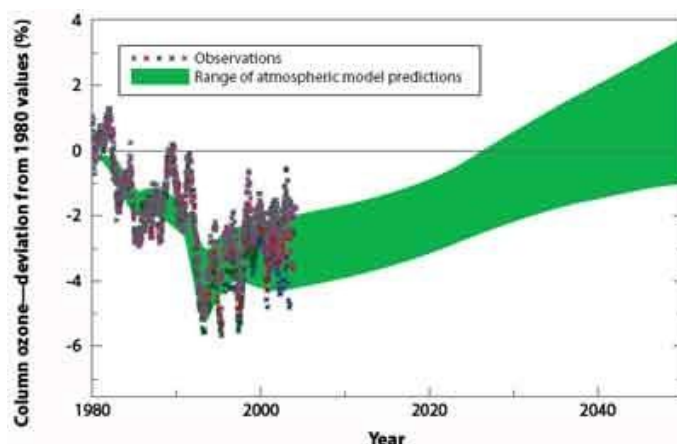
formula> Thus in spring, an extra source of chlorine atoms result in increased production of chlorine radicals due to photodissociation, proceeding to destroy ozone molecules. $\text{Cl}_{2(g)} \xrightarrow{\text{UV}} 2\text{Cl}\cdot$

Note that this also occurs in the Arctic, though less severe as the Arctic stratosphere is generally warmer.

Although there has been a slight uptrend since the start of the century (i.e. 275DU in 2000), low levels of 102DU in 2005 and 85DU in 2006 indicate ozone levels may still fall and fluctuate. However, future projections of stratospheric ozone are expected to recover to pre-1980s levels by mid 21st century. (Eyring et al., 2007)



*Dobson units over Halley Bay, Antarctica in October



present information from secondary sources to identify alternative chemicals used to replace CFCs and evaluate the effectiveness of their use as a replacement for CFCs

To phase out ozone destroying chemicals, hydrochlorofluorocarbons (HCFCs) were used as short term replacement compounds for CFCs and halons.

They differ as only some hydrogen in the parent hydrocarbon is replaced by Chlorine and Fluorine. Presence of a CH bond that is susceptible to attack by reactive radicals in the troposphere means most HCFCs get broken down and only a small proportion reach the stratosphere.

Although their ozone depleting potential (ODP) of 0.01 to 0.1 are 1-10% that of CFCs, this is still damaging and are only used as temporary substitutes:

- I.e. HCFC-123 (CF_3CHCl_2) to produce plastic foam.

Hence, HCFCs are expected to be phased out by 2030 in favour of HFCs (hydrofluorocarbons) which decompose completely in the troposphere and contain no chlorine. As such their ODP is near zero.

HFC's are now widely used replacements for CFCs and HCFCs:

- I.e. HFC-134a (CF_3CFH_2) used in refrigeration and air conditioning.

However, HFC's are more expensive and less efficient than CFCs. In mid-2010, it was decided that HFCs would also be phased out by 2050 due to climate change issues as they are highly damaging greenhouse gases (up to 12500 times more than CO_2).

Hence, neither HCFCs and HFCs have been totally successful, and research on an alternative class of chemicals for a permanent CFC replacement is still needed.

identify and name examples of isomers (excluding geometrical and optical) of haloalkanes up to eight carbon atoms

gather, process and present information from secondary sources including simulations, molecular model kits or pictorial representations to model isomers of haloalkanes

We are required to know the names of various isomers.

Isomers are

Straight chain halo-alkanes are named using the following rules:

Naming straight-chain haloalkanes

Straight-chain haloalkanes are named using the following rules (with examples in Figure 7.4):

- 1 Bromo-, chloro-, fluoro- and iodo- are used as prefixes to the alkane name; for example chloromethane.

gather, process and present information from secondary sources including simulations, molecular model kits or pictorial representations to model isomers of haloalkanes

AND

Naming straight-chain haloalkanes

Straight-chain haloalkanes are named using the following rules (with examples in Figure 7.4):

- 1 Bromo-, chloro-, fluoro- and iodo- are used as prefixes to the alkane name; for example chloromethane.
- 2 The position of the halogen (halo) atom is denoted by a number (as was done for double bonds in alkenes (p. 265 CCPC) and for position of the alcohol group in alkanols (Section 5.16). If more than one of a particular type of halo atom is present, di-, tri-, tetra- are used and a location number is given for each such atom, for example 2-bromopropane, 1,1,1-trichloroethane, but just trichloromethane.
- 3 Number from the end of the molecule that leads to the smaller sum of all the substituent numbers; for example 1,1-dibromo-2-chloroethane, not 2,2-dibromo-1-chloroethane ($1 + 1 + 2 = 4$; $2 + 2 + 1 = 5$).
- 4 If more than one type of halo atom is present, they are listed alphabetically with any di-, tri-, tetra- being ignored in deciding this order; for example 1,1-dibromo-2-chloroethane, not 2-chloro-1,1-dibromoethane.
- 5 If Rules 1 to 4 lead to more than one possible name, then the correct name is the one that gives the lowest numbers to the most electronegative halogen, the order of electronegativity being $F > Cl > Br > I$: for example 1,3,3-trichloro-1,1,3-trifluoropropane not 1,1,3-trichloro-1,3,3-trifluoropropane.

In the IUPAC system for naming compounds there must be only one correct name for a compound.

5. Human activities also impacts on waterways. Chemical monitoring and management assists in providing safe water for human use and to protect the habitats of other organisms.

identify that water quality can be determined by considering:

- concentrations of common ions
- total dissolved solids
- hardness
- turbidity
- acidity
- dissolved oxygen and biochemical oxygen demand

Anions

Chloride (Cl^-): Acidified water sample is tested with silver nitrate solution and appearance of white precipitate suggests Cl^- . Gravimetric analysis by precipitation of chloride ions from a known volume of water (AgCl), or **volumetric analysis by titration against AgNO_3 solution**

Sulphate (SO_4^{2-}): Can be determined **gravimetric analysis by BaSO_4 precipitate**. Water sample is first acidified with a few drops of nitric acid to remove carbonate or hydrogen carbonate ions. Drops of $\text{Ba}(\text{NO}_3)_2$ are added and a white precipitate (BaSO_4) suggests presence of sulphate ions.

Hydrogencarbonate (HCO_3^-):

Volumetrically by titration with standard HCl

Fluoride (F^-): Determined via AAS, but a more portable method is an **ion-selective electrode (ISE)** - also for cation testing. Advantages: size, portability. An ISE is a galvanic cell, and voltages measured by these cells are related to concentration using a series of standards.

Cations

Cations are analysed routinely

Aluminium (Al^{3+}): mobilised by the soil by increasing acidity.

AAS is mostly used for cations.

Several qualities such as the ones listed affect the quality of water. Several qualitative and quantitative tests can be carried out by analytical and environmental chemists to determine water quality in rivers and dams. A combination of factors contributes to whether water is potable or not.

Concentration of common ions

Note that the concentration of ions in sea water is high compared to that in fresh river water. However, concentration of ions in fresh water is variable, i.e. some rivers and lakes having high Ca^{2+} ion concentration due to limestone rocks.

Potable water **must have low ion concentration**. Ion concentration is derived traditionally using **gravimetric** or **volumetric** analysis prone to errors and were very time consuming especially if the ions were in low concentrations. However, today, instrumental methods such as the use of **ion-selective electrodes** and **AAS** is more accurate.

A table to ion concentration levels are as follows:

Ion	Concentration of Sydney Water Supply (ppm)	Recommended Max Concentration (ppm)	Concentration in Sea Water (ppm)
Chloride (Cl^-)	20	400	18980
Sulphate (SO_4^{2-})	8	400	2650
Nitrate (NO_3^-)	0.4	10	???
Fluoride (F^-)	1	1.7	1
Sodium (Na^+)	10	300	10550
Calcium (Ca^{2+})	9	200	400
Aluminium (Al^{3+})	0.2	0.2	???

High sodium levels in rivers and lakes indicate salinity problems, while high potassium levels in fresh water indicate leaching of burnt or decaying plant remains has occurred.

Gravimetric analysis for chloride ion

5.0L sample of river water was collected and after acidification with nitric acid, sufficient silver nitrate was added to precipitate chloride ions as silver chloride. Silver chloride was collected, washed, dried and weighed. The mass of silver chloride was found to be 0.235g. Calculate the chloride ion concentration in ppm of river water.

Balanced equation: $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}_{(s)}$. So 1 mole (35.45g) of chloride ions produce 1 mole (143.35g) of silver chloride.

Mass: mass of chloride required to produce 0.235g of silver chloride:

$$m(\text{Cl}^-) = (35.45/143.35) \times 0.235 = 0.0581 \text{ g} = 58.1 \text{ mg.}$$

$$\text{Concentration: } c(\text{Cl}^-) = 58.1 \text{ mg}/5.0 \text{ kg} = 11.6 \text{ mg/kg} = 11.6 \text{ ppm.}$$

Total Dissolved solids

TDS is the **measure of the total mass of solids dissolved in a unit volume of water**, generally reported as **mg/L or ppm**. **Potable water should have less than 500ppm**. Dissolved solids in a water sample are generally ionic salts and high concentrations of dissolved salts make water uninhabitable for many species. Unlike salt water, freshwater contains less dissolved solids and its total amount fluctuates over time due to influx of rainwater and floodwater. TDS can increase due to wastewater plant effluent or industrial discharge.

Irrigation is a main source for salinity, as excess water percolates through the soil, it dissolves

significant amounts of salt from the soil, then returns to the river, and the salinity (hence the TDS) of the river increases.

Land clearing and deforestation also increases both run-off and the amount of solids dissolved in the run-off water.

Source	Sydney water reservoirs	Artesian Bore water
TDS (ppm)	40-100	500-1200

Bore water can be used to irrigate some crops, (apples, pears, cabbages, etc.) though some crops are less tolerant and require TDS lower than 500ppm (citrus, carrots, corn, etc.) TDS values greater than 1000ppm indicate a degraded waterway and can **affect aquatic organisms by impairing cell function**.

The amount can be found using gravimetric analysis by **evaporation after filtration**, and **weighing the remaining dried solids**. Though this method is liable to inaccuracies due to experimental techniques.

I.e. evaporating basin of 135.68g, 100mL of filtered creek water poured into an evaporating basin and gently heated. The basin is placed in an oven before being reweighed as 135.70g. Mass difference is 0.02g, therefore 0.02g/100mL is 0.2g/L which is 200mg L⁻¹ i.e. 200ppm. Note concentration = mass/volume.

Modern instrumental methods, especially used in the field due to **portability** is measuring the **electrical conductivity** of water using a **conductivity probe and meter**. Conductivity measurements **assume** that the great bulk of dissolved solids are ionic and contribute to total conductivity of water and this is a reasonable approximation in most cases. Conductivity directly varies with TDS. However, the probe and meter must be **calibrated using known standards**. Although accurate at low ion concentrations, their accuracy drops off as salinity increases.

Electrodes are normally stainless steel rods, and power is supplied from a battery. Modern meters have automatic temperature adjustment. Conductivity is measured in microsiemens/cm (μS/cm).

Hardness

Hard water doesn't lather and forms a grey scum precipitate with soap, and also causes scales to build up on the inside of a kettle, decreasing efficiency. **Hard water describes water containing high concentrations of Ca²⁺, Mg²⁺, and Al³⁺ (together with HCO₃⁻, SO₄²⁻, Cl⁻)** which will not lather with soap. Hence, limestone rocks are conducive to hard water as these ions leach out from their carbonate compounds. Industrial influences such as cement dust can also exasperate hardness of water.

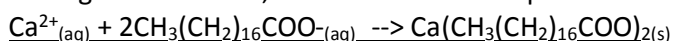
Hardness Class	Soft	Moderate	Hard	Very	Saline
Hardness (ppm)	<60	61-120	121-180	181-500	>500

Hard water can be classified as

- Temporary hard water is due to Ca²⁺ and HCO₃⁻ ions. It can be softened by boiling, removing calcium ions from the water and a precipitate of CaCO₃ forms:

$$\text{Ca}^{2+}_{(\text{aq})} + 2\text{HCO}_3^{-}_{(\text{aq})} \rightarrow \text{CaCO}_{3(\text{s})} + \text{CO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$$
- Permanently hard water cannot be softened by boiling maybe due to presence of Mg²⁺ ions rather than Ca²⁺ ions.

Hardness can be **tested qualitatively** by being shaken in a **stoppered test tube** with flakes of soap. After strong agitation for a minute, and after the tubes are allowed to stand, soft water produces significant lather, whereas hard water produces scum floating on the surface.



Hardness can also be **tested quantitatively** by **analysing [Ca²⁺] and [Mg²⁺] by EDTA** (ethylenediaminetetraacetic acid) **titration** or AAS.

- EDTA reacts with metal ions (M²⁺) such as Mg²⁺ and Ca²⁺ to form a **metal-EDTA compound**. The reaction stoichiometry is 1:1 i.e. **M²⁺ + EDTA⁴⁻ → M-EDTA²⁻**
 - *A pipette delivers a 25.00mL aliquot of hard water to a conical flask, and the water is buffered to a pH of 10 using an ammonia-ammonium chloride buffer. 3 drops of Eriochrome Black-T indicator were added and a standard solution of 0.010 mol/L EDTA was added from a burette. The end point was reached when the solution turned from red to blue. Average titre was 7.4mL. Calculate the total hardness of*

water by expressing the answer in units of $\text{mg}(\text{CaCO}_3)/\text{L}$

- Calculate moles of EDTA at endpoint:
 $n(\text{EDTA}) = cV = (0.010)(0.0074) = 7.4 \times 10^{-5} \text{ mol}$
- Moles of calcium carbonate, reaction stoichiometry is 1:1
 $n(\text{Ca}^{2+}) = n(\text{EDTA}) = 7.4 \times 10^{-5} \text{ mol}$, $n(\text{CaCO}_3) = n(\text{Ca}^{2+}) = 7.4 \times 10^{-5} \text{ mol}$
- Calculate hardness: $M(\text{CaCO}_3) = 100.09 \text{ g/mol}$
 $m(\text{CaCO}_3) = nxM(\text{CaCO}_3) = (7.4 \times 10^{-5})(100.09) = 7.41 \times 10^{-3} \text{ g} = 7.41 \text{ mg}$
 $\text{Total hardness} = 7.41 \text{ mg} / 0.025 \text{ L} = 296 \text{ mg}(\text{CaCO}_3)/\text{L}$
From table, this is classified as very hard.

- AAS can determine Ca^{2+} and Mg^{2+} ion concentration of water samples. Calcium ion concentration is determined first with a **calcium lamp and calcium standards for the calibration graph**. This is **repeated** for a magnesium lamp and magnesium standards. Total hardness can be calculated by combining separate data, assuming that one Mg^{2+} ion is equivalent in hardness to one Ca^{2+} ion.

Although, hardness of water is generally reported as mg L^{-1} or ppm CaCO_3 , assuming that calcium ions are from calcium carbonate and there are no magnesium ions present.

Hence, if given the mass of calcium or magnesium, convert into mols, and this is equivalent to mols of CaCO_3 , then convert to mass again.

Turbidity

Turbidity is the measure of the suspended solids in the water contributing to the water's cloudiness or lack of transparency. High turbidity makes water undesirable in appearance and taste.

Heavy rains and floods can increase turbidity by washing soil into rivers or lakes, also causes agitation of water, increasing suspension. These processes are accelerated by human intervention which loosen soil, such as land-clearing and ploughing. Sources of suspended solids in water include clay, silt, plankton, industrial wastes and sewage.

High turbidity is a **problem for photosynthesising plants** as it reduces the penetration of sunlight. Suspended sediments can **smother gills**, and also **carry nutrients and pesticides** into the waterways. Small particles in **upper layers of the water body can absorb infra-red radiation** from sunlight, raising water temperature. Finally, irrigation equipment can be damaged through attrition and blockage.

Turbidity can be assessed in many ways:

- Total suspended solids (TSS) can be determined **gravimetrically** by means of **filtering the water sample**, providing the filter paper has **sufficiently small pores**, and the **dry mass** of the filtered solids can be found. *Freshwater streams should not have TSS of more than 20mg/L.*
- A **secchi disk** which is painted with black and white panels can be lowered into the water until the pattern just disappears. The same principle applies to the **turbidity tube** which is a long cylinder with a black cross on the bottom. In both methods, water depth measured is **inversely proportional** to turbidity and a **calibration graph** is used to determine turbidity.
- A more accurate method uses a **nephelometer** which measures the **intensity of light scattered** at 90° to its original path by suspended solids in the water sample. **More scattering occurs with more turbid water.** Nephelometers are **calibrated using a standard colloidal polymer suspension** along with distilled water. If the sample is too turbid, systematic dilutions are required before measurement.

Acidity

Acidity is determined by the **pH of the sample**, either measured by adding indicator solutions to a sample compared with charts, litmus papers or a **pH meter** (which must be properly **calibrated with buffers**). pH outside the range of 6.5-8.5 indicates a source of pollution i.e. fertiliser run-off, industrial waste, acid drainage from a mine site, or sulphide contamination (forming sulphuric acid).

Freshwater bodies in contact with **limestone** are slightly alkaline ($\text{pH} > 7$), while **peat areas** with high rates of organic decomposition have acidic pH ($\text{pH} < 7$). When $\text{pH} > 9$, **aquatic organisms suffer from toxic ammonia poisoning** as ammonium ions in the water convert to

ammonia. Furthermore, **cell function can be impaired** whilst **egg hatching and spawning can be disrupted**.

Specific pollution sources can result in local changes in a water body's pH, i.e. acid rain, exposure of sulphide ores in mining, discharge from industries, etc. Note that **animal manure is also acidic** and **discharge from pig farms, etc.** will increase river acidity.

Dissolved Oxygen

Dissolved oxygen is an excellent indicator of water quality as it is sensitive to temperature, the presence of organic wastes and the overall health of the system. The extent of DO is summarised as follows:

Quality	Healthy	Moderately Polluted	Severely Polluted	Dead
DO (ppm), 25°C	6-8	4-6	2-4	<1

Photosynthesis of aquatic plants, algae, phytoplankton produces oxygen, some of which dissolve in the water, increasing DO. This can be assisted by **increasing the surface area** of the water or **agitation** of it by wind, water flow, etc. which accelerates the process.

Salinity also affects dissolved oxygen as ion dipole interaction between ions and water molecules are more favourable than dispersion forces between oxygen and water molecules.

However, dissolved oxygen is reduced due to **respiration of aquatic plants and animals** and **decomposition of organic matter** which increases BOD.

Low levels of DO may indicate pollution in the form of:

- **Heat pollution**, reducing oxygen solubility
- Addition of **organic wastes** that use up dissolved oxygen in the decomposition process.
- **Eutrophication** resulting from excessive growth of aquatic plants and subsequent oxygen demands associated with increased respiration and decomposition processes.
 - This can be caused by **fertilisers** which increase phosphate and nitrate in water, encouraging algae growth.

DO is measured in various ways:

- The simplest and most reliable method is the use of **oxygen probes**:
 - A potentiometric oxygen probe which uses a thallium oxygen sensitive electrode connected to a reference electrode as part of a galvanic cell. This needs to be calibrated with solutions of known oxygen concentration to produce a calibration graph.
 - Or polarographic oxygen probe which has a porous membrane permeable to dissolved oxygen which diffuses across the membrane from the water sample into the potassium chloride electrolyte. A platinum disk cathode and silver ring anode is separated by this and a constant polarising voltage (e.g. 800mV) is applied across the electrodes. As the oxygen diffuses, the size of the current depends on the rate of oxygen diffusion and external dissolved oxygen levels.
- Winkler titration is a **volumetric technique** based on a **series of chemical reactions** to determine DO:
 - Firstly, it involves the quantitative **reaction** between dissolved oxygen and Mn^{2+} ions in alkaline solution, where Mn^{2+} is oxidised to Mn(IV) .

$$2\text{Mn(OH)}_{2(s)} + \text{O}_{2(aq)} \rightarrow 2\text{MnO(OH)}_{2(s)}$$
 - Secondly, **acidified KI solution** is added and **Mn^{4+} oxidises I^-** to form molecular iodine (I_2).

$$\text{MnO(OH)}_{2(s)} + 2\text{I}^-_{(aq)} + 4\text{H}^+_{(aq)} \rightarrow \text{I}_{2(aq)} + \text{Mn}^{2+}_{(aq)} + 3\text{H}_2\text{O}_{(l)}$$
 - The amount of iodine generated is determined by titrating the solution with **standard sodium thiosulfate** ($\text{Na}_2\text{S}_2\text{O}_3$) with **starch indicator**.

$$\text{I}_{2(aq)} + 2\text{S}_2\text{O}_3^{2-}_{(aq)} \rightarrow 2\text{I}^-_{(aq)} + \text{S}_4\text{O}_6^{2-}_{(aq)}$$
 - DO can be determined as the moles of iodine molecules relate to the dissolved oxygen which reacted in the first step. Oxygen molecules in mol L^{-1} is converted to mg L^{-1} or ppm.
 - The overall reaction is: $\text{O}_{2(aq)} + 4\text{S}_2\text{O}_3^{2-}_{(aq)} + 4\text{H}^+_{(aq)} \rightarrow 2\text{H}_2\text{O}_{(l)} + 2\text{S}_4\text{O}_6^{2-}_{(aq)}$

Analysis requires water free of sediments and air bubbles, i.e. sample taken underwater. The **temperature** should also be noted during collection as this affects gases solubility. (increase in temperature, decrease in gas (i.e. O_2) solubility).

A 100mL water sample (20°C) was collected. Several millilitres of fresh starch solution were added to 100mL treated water sample in a conical flask. Mixture was titrated with 0.010mol/L sodium thiosulfate solution. End point was reached at 9.60mL. Calculate dissolved oxygen concentration in water.

- Calculate number of moles of thiosulphate ions added to flask
 $n(S_2O_3^{2-}) = cV = (0.010)(9.60 \times 10^{-3}) = 9.60 \times 10^{-5} \text{ mol.}$
- Calculate number of moles of dissolved oxygen in 100mL sample
 $O_{2(aq)}:S_2O_3^{2-}=1:4$, hence, $n(O_2) = 1/4 \times n(S_2O_3^{2-}) = 2.4 \times 10^{-5} \text{ mol.}$
- Calculate mass of dissolved oxygen:
 $m(O_2) = n(O_2) \times M(O_2) = (2.4 \times 10^{-5})(32.0) = 7.7 \times 10^{-4} \text{ g} = 0.77 \text{ mg}$
- Calculate dissolved oxygen concentration
 $DO = 0.77 \text{ mg } O_2 / 0.100 \text{ L water} = 7.7 \text{ mg/L} = 7.7 \text{ ppm}$

Biochemical Oxygen Demand

BOD is a measure of the capacity of organic matter in a water sample to consume oxygen.

Hence, it is a measure of **organic pollution**, particularly due to **aerobic respiration of microscopic decomposers of dead waste**. Water bodies with **high BOD** (i.e. sewage or abattoir effluent) become **quickly deficient in DO** due to action of aerobic bacteria, affecting aquatic life. Ponds and slow moving streams can quickly become stagnant and toxic if fresh water doesn't flush out organic waste.

Chemists measure the BOD using the **5-day BOD test**, taking a sample's DO at the beginning and end of a 5-day test period: $BOD_5 = DO_0 - DO_5$.

5 days is usually sufficient for natural organic waste to be decomposed in non-polluted waterways.

Water System	Unpolluted water	Polluted water	Domestic, untreated sewerage	Abattoir effluent	Effluent from Paper pulp factory
BOD (ppm)	1-3	>5	350	2600	25000

Samples from more polluted waterways need to be **systematically diluted** before measuring or re-aerated every few days as appropriate to obtain an accurate reading as they quickly run out of required DO. The diluted sample's BOD_5 is measured and the BOD_5 of the original undiluted water sample can be calculated.

The newest method of measuring BOD involves use of a **respirometer**. Water sample fills a special bottle with a **pressure sensor in the lid**, and as oxygen is depleted, it is replaced by diffusion into the water from air in the bottle. Hence, net reduction in pressure is a direct measure of BOD, and readouts of up to 400000ppm BOD can be calculated.

What would be a test to indicate the degree of organic matter? BOD as this indicates the oxygen removed by organic matter in the sample.

Water with 45ppm, diluted by 20 times, once waste is completely decomposed, it reduces DO by 45/20ppm.

Consequence of high BOD - water becomes stagnant. Smell, discolouration, destruction of most aquatic life. Low BOD - negligible effects, small increases in TDS and nutrients.

Nitrogen and Phosphorus

Regular monitoring of nitrogen and phosphorous levels are important because of the impacts of excessive nutrient input into aquatic ecosystems.

- Nitrates and other ionic forms of nitrogen (NO_2^- , NH_4^+) are often analysed by visible spectrometry following addition of particular reagents. In school labs, presence of nitrate ions in aqueous solutions can be determined by adding a few drops of **sulphuric acid** and a small piece of **copper foil** to a millilitre of sample. This mixture is heated gently in a fume hood, and **brown fumes of noxious NO_2 gas** will form if nitrate ions are present.
- Phosphates (usually present as $H_2PO_4^-$) is commonly determined by visual spectrometry. Analysis depends on addition of particular reagent forming a coloured complex in the absence of phosphate ion. The intensity of coloured solution can be measured by a **spectrophotometer** and the concentration can be determined using a calibration curve to **compare absorbance of light** by the coloured solution to a series of **standard phosphate**

solutions similarly treated.

Both nitrogen and phosphates are necessary for plant growth, but excess levels can lead to algal blooms and eutrophication.

Overview of typical vs. polluted values

Property	Typical Clean Water	Polluted Water
TDS (mg/L)	<100	>1000 (for fresh water, more for salt water)
Turbidity (NTU)	<3	>20
pH	6.5 to 8.5	<6, >9
DO (mg/L)	7-9	<4
BOD (mg/L)	<5	>10
Phosphate (mg/L)	<0.03	>0.05 (lakes), >0.1 (streams and rivers)
Nitrate (mg/L)	<0.1	>0.50

Appropriateness of qualitative and quantitative:

1. State what each would determine.
2. Limitation of qualitative, can't determine exact amount.
3. Limitation of quantitative, some tests cannot be used in the field, i.e. titration.
4. Advantage of both, and say that it really depends on the situation required.

Precautions to collecting water sample (risk assessment):

Must prevent entering water if possible. When collecting wear safety goggles and gloves. Dispose of gloves safely after use.

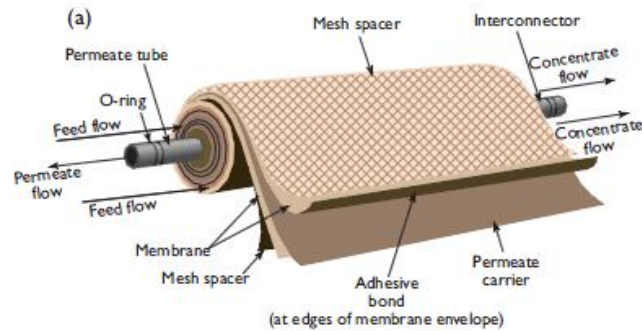
identify factors that affect the concentrations of a range of ions in solution in natural bodies of water such as rivers and oceans

Natural ion concentrations in water bodies are easily disturbed by a number of natural and artificial factors.

Factor	Effect
Agriculture	Farmers usually fertilise soils to grow crops, some of which is carried by rainwater from the soil into water bodies. This increases concentration of NO_3^- , NH_4^+ , PO_4^{3-} . Leeching of animal faeces from grazing properties also lead to increased nitrogen and phosphorus concentration in the waterway.
Industrial effluent	Industrial discharge of diluted waste into rivers may lead to increase in certain ions and possible heavy metal contamination
pH of rain water	The greater the acidity of rain or ground water, the more minerals that will be dissolved.
Heavy rain, flooding	Ion concentration in water will temporarily decrease due to large input of fresh water from sustained heavy rain. Greater turbidity may result as sediment is stirred up, however, great agitation may increase dissolved oxygen levels.
Leaching of rocks and soils	Ground water remaining in contact with minerals in the ground for a long time cause minerals to dissolve. This ground water may find their way to water bodies.
Differing solubilities of rocks and soil minerals	Some minerals dissolve in water more easily, i.e. SO_4^{2-} and Cl^- compounds, unlike silicates. Limestone is readily leached, increasing Ca^{2+} and HCO_3^- ions.
Water Temperature	Minerals dissolve faster at higher temperatures
Rate of evaporation	Hot climates with greater evaporation rate increases ion concentration
Aquatic organisms	Marine organism activity changes ion balance in water, especially Ca^{2+} and CO_3^{2-} due to shelled invertebrate exoskeletons.

describe the design and composition of microscopic membrane filters and explain how they purify contaminated water

Microscopic membrane filters are relatively thin films of synthetic polymer through which pores filter out unwanted particles. More particles and impurities are filtered by smaller pores, but this is more expensive. As an alternative for large scale chemical treatment of water to remove harmful microorganisms, these also have the added advantage of removing molecules of carbon compounds.



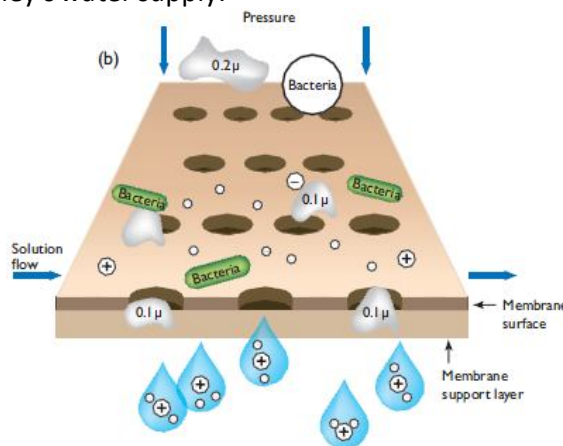
Porous polymer sheets (usually polypropylene and polytetrafluoroethene) are folded or wound across a central rigid core to form a cartridge, held in place by surrounding mesh. The use of gravity, vacuum/pressure pumps, or centrifugal force, forces the water through the membrane resulting in clean water being collected inside the tube, leaving impurities behind.

Water is made to flow across the membrane, not through it, reducing the blockage factor. The membrane filters have microscopic pores, and application of appropriately sized filters can remove the need to chemically treat water.

Filters can be classified according to pore size, in categories: microfiltration, ultrafiltration, nanofiltration, or reverse osmosis membranes.

- Microfiltration can remove protozoans, bacteria, colloids, some colouration and some viruses.
- The finest filtration cannot remove particles less than 10^{-9}m (nanometre), and so dissolved substances such as nitrates, phosphates, and heavy metal ions cannot be removed.
- To remove dissolved substances, reverse osmosis is used

No purification technology removes all contaminants, however, each technology has its own advantages and limitations, removing a specific type of contaminant. While microscopic filters can be employed for domestic and industrial use, economic considerations limit their use for large applications and they are not used to filter Sydney's water supply.



Examples of some filters

Screen filters	Acts like sieve with pores of uniform size. Produced by firing ions into a polymer sheet of precise depth to produce pores. Usually made from polyesters and polycarbonate.
Surface filters	Composed of a lot of layers to remove 99.9% of suspended solids. This removes large particles which accumulate mainly on the filter's surface. Used as pre-filters.
Depth membranes	Consists of sheet of compressed fibrous materials forming a maze of flow channels. This traps larger particles, economically removing most suspended particles. Used as

	pre-filter.
Composite or layered filters.	A combination of different technologies, allowing combined benefits of different filtering methods.
Capillary membrane filter	Porous material made into hollow capillaries. Dirty water enters, and water flows through outside wall of capillary into inside with internal diameter of 100 µm. Large number of capillaries are bundled together to increase surface area of filtering unit, speeding up filtration process. Filters can be cleaned by blowing air to dislodge trapped particles.
Microfiltration	Filter pore size of 100-1000nm, removing fine silt, colloids and a range of microbes such as bacteria and protozoa. However, viruses generally get through. Composed of bundles of hollow polymer threads. Filters used in small rural treatment plants as it's easiest to operate with less operational control.
Ultrafiltration	Filter pore size of 5-50nm. Improves water colour and removes all microbes including viruses. A vacuum pump usually draws water through filtering surface. Usually used to remove synthetic chemicals, but these are generally not present in Australian water supply, therefore, not used widely in Australia.
Nanofiltration	Filter pore size of 0.5-5nm. Removes all organic molecules down to 300amu. Can remove hard ions or heavy metal ions if appropriate surface coating is used. Uses higher operating pressures and even more expensive.
Reverse Osmosis	0.1 to 1nm. Removes all solutes, including ions. Used for desalination, much more expensive than nanofiltration.

describe and assess the effectiveness of methods used to purify and sanitise mass water supplies

Water in the catchment is 'raw' and isn't potable due to suspended solids, dissolved materials and organic material (i.e. biological spores and microbes). So it must be purified and sanitised.

- **Screening** of water is done with a mesh that acts as a sieve, removing large objects (i.e. fish and plant debris). **Filters** are also used (305-140 µm)
- **Aeration** - Water is sprayed into the air to increase concentration of dissolved oxygen. This oxidises manganese and iron salts to form insoluble oxides that to be removed in later stages.
- **Flocculation** occurs in coagulant tanks. The water contains fine suspended particles and these clay colloids may be 10^{-4} - 10^{-6} mm. Since they cannot settle due to repulsion between their negative surfaces, they are **made to precipitate** by flocculation.
Chemicals such as alum $\text{Al}_2(\text{SO}_4)_3$ are added to produce a gelatinous precipitate of aluminium hydroxide: $\text{Al}^{3+}_{(\text{aq})} + 3\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Al}(\text{OH})_{3(\text{s})} + 3\text{H}^{+}_{(\text{aq})}$
Hydrogen ions produced in this hydrolysis reaction are attracted to the surface of aluminium hydroxide flocs. The negatively charged surface of clay colloids are then attracted to this. As they coagulate to form larger particles, they settle out under gravity.
 - $\text{Ca}(\text{OH})_2$ is added to raise pH to around 7, and allows flocs to remain stable.
 - Iron oxides and other soluble coloured compounds also adhere to flocs
- **Sedimentation** of flocs to the bottom of settling tanks forms a sludge that can be periodically removed and reused as compost. 95% of suspended impurities (particle size >25 µm) are removed by sedimentation.
- Water from settling tanks is now **filtered** through layers sand and gravel or anthracite filters, removing suspended material. If water is still not clear, it can be passed through layers of activated charcoal which adsorbs the coloured ions and inorganic solutes to its surface. Turbidity at this stage is less than 0.5NTU.
- Filtered water is disinfected with chlorine gas. **Chlorination** produces hypochlorite ions (OCl^-) which kills bacteria and other microbes (i.e. E.Coli):
 $\text{Cl}_{(\text{g})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow 2\text{H}^{+}_{(\text{aq})} + \text{Cl}^{-}_{(\text{aq})} + \text{OCl}^{-}_{(\text{aq})}$
 - Microbiological tests is also done to test for coliforms (indicative of faecal

- contamination). Should be <2CFU/100mL.
 - Monitoring ensures no chlorinated alkanes are produced.
- **Fluoridation** of water by adding small amounts of chlorine can reduce tooth decay by hardening tooth enamel. (compounds such as NaF, CaF₂ and Na₂SiF₆)
- pH of water is adjusted with buffers to ensure the required 7-8.5
 - Use of hydrated lime/Na₂CO₃ (or HCl for very alkaline water).
 - Also prevents corrosion of pipes in water distribution.
- Water is now potable and transferred to storage reservoirs.

Treatment chemicals added to water are very low in concentration or undetectable. Left over chlorine forms ferric chlorine which is effectively inert and has little health impacts.

Note that samples are removed for testing many times, after sedimentation, filtration and before finally being transferred to storage reservoirs.

Assess effectiveness

These methods are effective since they are fast and reliable, removing 99.9% of bacteria and 99% of viruses by flocculation, and 95% of suspended particles by sedimentation.

Chlorination also proves to be a cost-effective way to removing large amounts of contaminated matter, pathogens and other disease inducing agents.

However, chlorination doesn't remove all organisms and these organisms might be too fine to be filtered by sand filtration. This resulted in the death of more than 100 people during the *Giardia* and *Cryptosporidium* scare in Warragamba Dam, Sydney. More than 204300 people were infected in 1998. This prompted improvement to purification and filtration methods. Today, a sample of at least 100L of water must be taken to effectively monitor for those organisms before water can be transferred to homes.

Daily monitoring of water supplies by microbiological testing of water samples is essential. And this occurs throughout all treatment plants and all catchments (especially during storms or other events that may affect water quality or result in contamination). Careful monitoring prior, during and after treatment greatly increases the effectiveness in ensuring that water is properly treated (by removal of coloured substances, odour, suspended solids and organic contaminants i.e. bacteria, viruses).

Overall, the combination of water treatment methods and careful monitoring effectively provides clean and potable water.