Chemical Monitoring and Management Notes

Section 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
  - Name: Burhan Gemikonakli
  - Place of Work: Qenos, Botany NSW
  - Branch of Chemistry: Analytical Chemistry
  - Type of Manufacture:
    1. Ethene → Ethane (C\textsubscript{2}H\textsubscript{6} → C\textsubscript{2}H\textsubscript{4} + H\textsubscript{2}) (cracking)
    2. Ethane → Polyethylene (nC\textsubscript{2}H\textsubscript{4} → (C\textsubscript{2}H\textsubscript{4})\textsubscript{n})
  - Job Description
    1. To determine the nature (qualitative) and amount (quantitative) of any impurities in the ethene and polyethylene
    2. To monitor and analyse production waste before discharging
    3. To adjust reaction conditions to maximise yield in the cracking furnace
  - Chemical Principle
    - Many industries use GLC (Gas Liquid Chromatography) or GSC (Gas Solid Chromatography) for analytical purposes. The separation is based on the solubility of the compound in the stationary phase.
      - If the stationary phase is polar then the polar substances in the sample injection will come out last, as they are most soluble.
      - The position of the peaks on the graph identifies which compounds are present in the sample, while the height of the peaks indicates the amount.
      - For example, if a mixture containing a small amount of ethanol, a moderate amount of ethane, and a large amount of ethene was used as the sample injection, the resultant graph would identify ethane as the first compound to exit (high peak), followed by ethane (moderate peak) and finally ethanol (low peak).
      - A single peak on the graph indicates a pure sample
      - In gas solid chromatography, adsorption (molecules of a substance collect on the surface of another substance) is used. The gas that needs to be analysed is passed into the sample injector, and the different components of the gas have different adsorbing strength to the solid. Some components adsorb strongly onto the solid, and so move as the solid moves through the column. The components that do not adsorb well are carried through by an inert gas and exit the column much faster.
  - Identify the need for collaboration between chemists as they collect and analyse data
    - Collaboration between chemists:
      - Increases reliability
      - Decreases the occurrence of errors, thus increases accuracy
      - Conditions can be adjusted to maximise the efficiency of an industrial process (e.g. task delegation, etc.)
• Many chemical problems require expertise and in-depth knowledge from a wide range of chemical branches
• EXAMPLE: Polymer chemists work and collaborate with process engineers to adjust reaction conditions so that maximum yields of polymer can be obtained

• Describe an example of a chemical reaction such as combustion, where reactants form different products under different conditions and thus would need monitoring
  ➢ The combustion of fossil fuels, such as octane, have to be monitored on industrial levels, as inefficient moles of oxygen can lead to incomplete combustion, forming toxic carbon monoxide and carbon soot, both of which can damage and pollute the environment
  ➢ Incomplete combustion also does not release as much energy as complete combustion, making complete combustion desirable from an economic standpoint
  ➢ Carbon monoxide inhibits human blood from effectively carrying oxygen, and can cause death in high concentrations
  ➢ Soot is also a major health risk, as it is toxic and aesthetically displeasing
    • \[2\text{C}_8\text{H}_{18(g)} + 25\text{O}_2(g) \rightarrow 16\text{CO}_2(g) + 18\text{H}_2\text{O}_g(g)\] (Complete Combustion of Octane)
    • \[\text{C}_9\text{H}_{18(g)} + 6\text{O}_2(g) \rightarrow 5\text{CO}_2(g) + 3\text{CO}_2(g) + 9\text{H}_2\text{O}_g(g)\] (Incomplete Combustion of Octane)
  ➢ Thus monitoring is required to provide a sufficient air-to-fuel ratio, so that complete combustion takes place and the output of required products is high and the creation of unwanted substances is low
  ➢ NOTE: If the fuel to oxygen ratio is too low, oxides of nitrogen can be formed instead, which is a respiratory irritant and can contribute to the formation of acid rain
    • \[\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)\]
    • \[2\text{NO}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)\]
  ➢ NOTE: If there were sulfur or nitrogen impurities in the octane, combustion would lead to the production of \(\text{SO}_2\) and \(\text{NO}_x\). When these dissolve in rain water, they will result in the formation of acid rain with a pH < 5. This will result in an increase of the acidity of waterways and the burning of tree leaves.
    • \[\text{SO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_3(\text{aq})\]
    • \[2\text{H}_2\text{SO}_3(\text{aq}) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{SO}_4(\text{aq}) \leftarrow \text{Acid Rain}\]

• Gather, process and present information from secondary sources about the work of practising scientists identifying: the variety of chemical occupations and a specific chemical occupation for a more detailed study
  ➢ Chemists will monitor and manage industrial processes. This has to be done to ensure:
    1. Reactions proceed efficiently (high yield and fast production) \(\rightarrow\) Development chemist, Plant chemist
    2. The raw materials and products are pure \(\rightarrow\) Analytical chemist, Quality & control chemist
    3. The workplace is safe and healthy \(\rightarrow\) Work Health & Safety chemist
    4. Wastes do not pollute the environment \(\rightarrow\) Environmental chemist

Different Types of chemical occupations

<table>
<thead>
<tr>
<th>Chemical Occupation</th>
<th>Work Done</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pharmaceutical Chemist</td>
<td>Researches and dispenses drugs for medicinal use</td>
</tr>
<tr>
<td>Analytical Chemist</td>
<td>Analyses concentrations of chemicals in water, food, ores, and manufactured products and develops purification techniques</td>
</tr>
<tr>
<td>Biochemist</td>
<td>Researches chemical reactions in living things and organisms</td>
</tr>
<tr>
<td>Industrial Chemist</td>
<td>Monitors the manufacturing process of chemicals</td>
</tr>
<tr>
<td>Organic Chemist</td>
<td>Studies the chemistry of carbon compounds (Plastics, fibres, synthetic fibres, medicinal drugs)</td>
</tr>
<tr>
<td>Polymer Chemist</td>
<td>Develops new long chain molecules (polymers) such as plastics, synthetic fibres and adhesives</td>
</tr>
<tr>
<td>Inorganic Chemist</td>
<td>Study of synthesis, structure and properties formed by metallic and non-metallic elements such as nitrogen, sulfur, phosphorus and chlorine</td>
</tr>
<tr>
<td>Physical Chemist</td>
<td>Use of physical and mathematical methods to study the laws that govern nature – rates of reactions, structure of compounds and the nature of chemical bonding</td>
</tr>
<tr>
<td>Metallochemical Chemist</td>
<td></td>
</tr>
<tr>
<td>Pharmaceutical Chemist</td>
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<tr>
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<tr>
<td>Inorganic Chemist</td>
<td></td>
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<tr>
<td>Physical Chemist</td>
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</table>
Environmental Chemist | Monitor water/air samples for pollutants using instrumental analysis and other procedures. Analyse and assess environmental data. Advise external bodies such as the Environmental Protection Agency (EPA)

Industrial Chemist | Ensure that chemical reactions have high yield and rate of reaction
Design monitoring procedures and quality control testing
Check that raw materials meet specifications
Monitor weather products are sufficiently pure
Ensure that effluents and solid wastes from the factory do not exceed allowable limits of pollutants

### Section 2

*Chemical processes in industry require monitoring and management to maximise production*

- Identify and describe the industrial uses of ammonia
  - Ammonia is a very strong, pungent and choking gas that is soluble in water. It is produced by the Haber process and is an industrially important chemical
    - **Fertilisers**
      - Compounds which promote the growth of plants, and thus provide significant commercial benefits to the agricultural and horticultural industries
      - 80% of the ammonia produced by industry is used in the production of fertilisers
      - \(2\text{NH}_3(g) + \text{H}_2\text{SO}_4(aq) \rightarrow (\text{NH}_4)_2\text{SO}_4(aq)\)
      - \(\text{NH}_3(g) + \text{HNO}_3(aq) \rightarrow \text{NH}_4\text{NO}_3(aq)\)
      - \(\text{NH}_4\text{NO}_3\) is also used as a fertiliser as Nitrogen is a plant nutrient, and it is an acidic salt that will increase the acidity of soil (good for some plants, like tomatoes)
    - **Explosives**
      - Used in both TNT (Trinitrotoluene) and Dynamite (Trinitroglycerin)
      - \(\text{NH}_3\) is oxidised to \(\text{HNO}_3\) and used to make explosives

- **Fibres**
  - Nylon-6 → Used for gears, fittings, and bearings

- **Household Cleaners**
  - Cloudy Ammonia
    - \(\text{NH}_3(g) + \text{H}_2\text{O}(l) \rightarrow \text{NH}_4\text{OH}(aq)\) ← Alkali that will dissolve in oil and proteins
  - **Cationic Detergents**
    - Cationic detergents are used in fabric softeners and hair conditioners
    - Long hydrocarbon chain, followed by N bonded to 3 CH\(_3\) groups, capped with a Cl\(^-\) ion

- Identify that ammonia can be synthesised from its component gases, nitrogen and hydrogen
  - Ammonia is produced industrially from its component gases in an **exothermic, catalytic and reversible reaction** (Haber Process)
    \[
    \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \quad \Delta H^\circ = -92 \text{ kJ mol}^{-1}
    \]
N₂ from the air is converted to nitrogen compounds (nitrogen fixation) by lightning or by the nitrogen fixing bacteria in the rood nodules of legumes such as beans and snow peas. N₂ is very stable due to its strong covalent triple bond, which must be broken.

In the Haber process, N₂ is obtained from the atmosphere while H₂ is obtained from methane gas (CH₄) with a Nickel catalyst

$$2	ext{CH}_4(g) + 	ext{O}_2(g) \rightarrow 2	ext{CO}_2(g) + 4	ext{H}_2(g)$$

The N₂ and H₂ gasses can then be sent to the Haber Process

- **Describe that synthesis of ammonia occurs as a reversible reaction that will reach equilibrium**
  
  - The synthesis of ammonia is a reversible reaction that will reach equilibrium
  - The forward reaction is exothermic, and releases 92kJ of energy per mole
  - The rate of the forward reaction and reverse reaction are equal when the system reaches equilibrium
  - The concentrations will remain constant after equilibrium is reached
  - This reaction is subject to Le Chatelier’s Principle*, and can be influenced through changes in concentration, pressure, volume and temperature.

  *When any system at equilibrium is subjected to change in the concentration of reactants and products, temperature, volume, or pressure, then the system readjusts itself to partially counteract the effect of the applied change and a new equilibrium is established.

- **Identify the reaction of hydrogen with nitrogen as exothermic**
  
  - The reaction between nitrogen and hydrogen gas is exothermic
  - \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \quad \Delta H^\circ = -92 \text{ kJ mol}^{-1} \)
  - The energy absorbed to break the triple covalent bond between nitrogen and the single covalent bond between hydrogen IS LESS THAN the energy released in forming the bonds in ammonia. Therefore, the forward reaction is exothermic as heat is released.

- **Explain why the rate of reaction is increased by higher temperatures**
  
  - Temperature = Rate of Reaction
  - Particles have higher kinetic energies and more molecules have sufficient energy to overcome the activation energy barrier to break the covalent bonds within diatomic N₂ and H₂
  - Increased number of particle collisions between reactant molecules per unit volume per unit of time, hence greater reaction rate
  - NOTE: The reaction rate is increased for both the forward and reverse reaction

- **Explain why the yield of product in the Haber process is reduced at higher temperatures using Le Chatelier’s principle**
  
  - By LCP, increases in temperature favour the reverse (backward) endothermic reaction and so the equilibrium shifts left to reduce this stress and consume the excess heat and hence reduces yield of ammonia

- **Explain why the Haber process is based on a delicate balancing act involving reaction energy, reaction rate and equilibrium**
  
  - Balancing act between yield of NH₃ and the rate and yield at which NH₃ can be formed that is both reasonable and economically feasible
Compromise between cost, safety, reaction energy, reaction rate and the position of equilibrium (yield)

The conditions required to maximise these factors are often conflicting

**Catalyst:** The magnetite ($\text{Fe}_3\text{O}_4$) catalyst is used as it provides an alternate reaction pathway with a lower activation energy, allowing the reaction rate to remain high despite moderate temperatures (provides a surface for the reaction)

**Temperature:** LCP predicts that lower temperatures will produce a higher yield of ammonia at equilibrium, as it is an exothermic reaction. If temperature is too low, the rate of reaction becomes uneconomically slow (collisions reduce thus lower rate of reaction), thus a compromise temperature of 450 – 500 degrees is used.

**Pressure:** LCP predicts that lower temperatures will produce a higher yield of ammonia at equilibrium, as there are fewer moles of gas on the products side than the reactants side. Increasing pressure will also increase reaction rate. However, having the pressure very high is expensive to maintain (due to the required thickness of the reaction vessel). Safety factors with the use of high pressure vessels must also be considered. A compromise pressure of 200 to 300 atmospheres is used.

**Removing Ammonia:** Ammonia is produced is separated from unreacted nitrogen and hydrogen by liquefying it under pressure/cooling. The unreacted nitrogen and hydrogen are then recirculated into the reaction chamber to be used again. This is done despite the costs of this process, because removing ammonia prevents the reaction reaching equilibrium (Yield = 98%)

Each plant decides on profitability: slow (high yield) or fast (lower yield)

- **COMPROMISE:** Carried out at 450 degrees Celsius and at 250 atmospheres of pressure with Fe$_3$O$_4$ catalyst

- Explain that the use of a catalyst will lower the reaction temperature required and identify the catalyst(s) used in the Haber process
  - Magnetite ($\text{Fe}_3\text{O}_4$) is used as a catalyst. The iron in magnetite provides a surface for the gas phase reaction. (It does this by adsorbing the reacting molecules to its surface, which distorts and weakens their bonds so they can be more easily broken)
  - The heterogeneous catalyst takes part in the reaction but does not get 'used up'. Therefore, only a small amount of magnetite is required to increase the rate of reaction by lowering the activation energy (and thus allowing for lower temperatures).
  - It is important to note that the catalyst does NOT reduce the concentration or amount of NH$_3$ produced – it simply increases the rate of the forward and reverse reaction. This means that equilibrium is established faster.
  - The catalyst has a life of 5 – 10 years

- Analyse the impact of increased pressure on the system involved in the Haber process
  - (LCP) When pressure is increased by lowering the volume, the equilibrium will shift to the side with less gas molecules. Therefore, the yield of NH$_3$ will increase.
  - Haber process is carried out at 250 atmospheres (25,000 kPa)
  - NOTE: If pressure is increased by adding an inert gas there is no change in concentrations or to the reaction
  - NOTE: When the pressure is increased, the rate of reaction of both the forward and backward reaction increase. This is because the greater concentration of gas particles increases the frequency of successful collisions.

- Explain why monitoring of the reaction vessel used in the Haber process is crucial and discuss the monitoring required
  - Why the reaction vessel has to be monitored/maintained:
    - The Nitrogen to Hydrogen ratio must be 1:3 to avoid the build-up of one reactant
    - Temperature is 450 degrees and pressure is 250 atmospheres to get an economical yield of ammonia
    - No oxygen is present as hydrogen is a flammable gas which will explode under such conditions
- Carbon monoxide and sulfur compounds will ‘poison’ the catalyst
- No build-up of argon (from atmosphere) which will increase the pressure unnecessarily and decrease the efficiency of the process
- High pressure reactions are dangerous and can cause damage and harm, thus the reaction pressure must constantly be monitored
  - Constant removal of NH3 by liquefying ammonia product as it forms (equilibrium shifts to side with less concentration – right)

• 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
  - Haber was a German scientist who invented the process in 1908
  - This process allowed for the synthesis of ammonia from its gaseous components of hydrogen and nitrogen gas (450 – 500 degrees, 250 atmospheres, magnetite catalyst)
  - With the help of Carl Bosch (chemical engineer), Haber was able to implement the process on an industrial scale by 1913
  - This was a turbulent time in world history (1914 was WWI). The allies blocked German ports, thus preventing access to nitrates from Chile (they relied on imports to make explosives and fertilisers).
  - The commercial application of the Haber process was able to produce 200 tonnes of ammonia by 1914 each day, which was used to help Germany’s war efforts and for the production of fertiliser
  - Advantages
    ▪ Germany could now produce fertilisers to increase crop output and increase its capacity to feed its population. It could also produce significant amounts of explosives for the war.
    ▪ It was also a very significant scientific development which showed the impact of science on greater society
  - Disadvantages
    ▪ It raised severe ethical and moral issues relating to the use of science, as it resulted in the production of explosives which killed people and destroyed the natural environment
    ▪ Fertilisers from ammonia have also been overused. As a result, they wash out of soils and go into waterways, endangering marine life.
  - Assessment: Overall very significant at the time it was developed, and still is significant today. Has impacted the global nitrogen cycle, pollutes groundwater and increases the level of atmospheric nitrogen dioxide. Immense value in fostering increase in global food and chemical production, despite its negative impacts on increasing the feasibility of producing explosive weaponry.

Section 3

Manufactured products, including food, drugs and household chemicals, are analysed to determine or ensure their chemical composition

• Deduce the ions present in a sample from the results of tests and
• 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
  - Most industrial process have impurities in ionic form.
    ▪ Qualitative tests are carried out to identify the ions present (Flame tests, precipitation, colour change of solution)
    ▪ Quantitative tests determine how much of each ion is present (Atomic absorption spectroscopy)
  - Flame Test
    1. Clean the nichrome wire by holding it to the blue Bunsen flame until there is no other colour.
    2. Dip the wire in the sample in concentrated hydrochloric acid. (Chloride salts are the most volatile, and will produce the most visible results)
    3. Hold the nichrome wire to the blue Bunsen flame 1/3 from the base, which is the hottest part of the flame
    4. Observe and record the colour of the metal ion in an appropriately titled enclosed table
      ▪ The electrons will absorb the heat energy from the flame, and jump to a higher energy level. The electron, however, cannot remain in this state indefinitely. When the electron falls back down to
ground state (most stable state), the extra energy is re-released as light. If the wavelength of light is within the visible spectrum, it can be observed in the form of a coloured flame.

- Only cations can be identified by the flame test

<table>
<thead>
<tr>
<th>Cation</th>
<th>Precipitate test(s)</th>
<th>Flame test(s)</th>
<th>Other Test(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium (Ba$^{2+}$)</td>
<td>SO$_4^{2-}$: White</td>
<td>Yellow-green</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>OH$^-$ or F$: None</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium (Ca$^{2+}$)</td>
<td>SO$_4^{2-}$: White</td>
<td>Orange-red</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>F$: White</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead (Pb$^{2+}$)</td>
<td>Cl$: White</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>I$: Yellow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper (Cu$^{2+}$)</td>
<td>OH$: Blue, dissolves in NH$_3$ to form deep blue solution</td>
<td>Blue-green</td>
<td>-</td>
</tr>
<tr>
<td>Iron II (Fe$^{2+}$)</td>
<td>OH$: White, turns brown</td>
<td>-</td>
<td>Decolourises dilute potassium permanganate solution</td>
</tr>
<tr>
<td>Iron III (Fe$^{3+}$)</td>
<td>OH$: Brown</td>
<td>-</td>
<td>SCN$: Deep red solution</td>
</tr>
</tbody>
</table>

**Reactions**

- $\text{Pb}^{2+}_{(aq)} + 2\text{Cl}^-_{(aq)} \rightleftharpoons \text{PbCl}_2(s)$  $\leftrightarrow$ Primary test with HCl
- $\text{Pb}^{2+}_{(aq)} + 2\text{I}^-_{(aq)} \rightleftharpoons \text{PbI}_2(s)$  $\leftrightarrow$ Confirmation test with NaI
- $\text{Ca}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} \rightleftharpoons \text{CaSO}_4(s)$  $\leftrightarrow$ Primary test with H$_2$SO$_4$
- $\text{Ba}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} \rightleftharpoons \text{BaSO}_4(s)$  $\leftrightarrow$ Primary test with H$_2$SO$_4$
- $\text{Fe}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightleftharpoons \text{Fe(OH)}_2(s)$  $\leftrightarrow$ Primary test with NaOH
- $\text{Fe}^{3+}_{(aq)} + 3\text{OH}^-_{(aq)} \rightleftharpoons \text{Fe(OH)}_3(s)$  $\leftrightarrow$ Primary test with NaOH
- $\text{Cu}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightleftharpoons \text{Cu(OH)}_2(s)$  $\leftrightarrow$ Primary test with NaOH

Adding NaF will produce white ppt with Ca but no ppt with Ba

Adding Cu to NH$_3$ solution $\rightarrow$ precipitate dissolves to give a deep blue solution

All precipitation reactions are equilibrium
Tests for Anions

<table>
<thead>
<tr>
<th>Cation</th>
<th>Precipitate test(s)</th>
<th>Other test(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonate (CO₃²⁻)</td>
<td>-</td>
<td>• pH between 8 and 11.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Acid (H⁺): Bubbles of colourless odourless gas (CO₂)</td>
</tr>
<tr>
<td>Sulfate (SO₄²⁻)</td>
<td>• Ba(NO₃)₂ (to acidified sample): Thick white</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>• Pb(NO₃)₂ (to acidified sample): White</td>
<td></td>
</tr>
<tr>
<td>Chloride (Cl⁻)</td>
<td>AgNO₃ (to acidified sample): Thick white, dissolves in ammonia and darkens in sunlight</td>
<td>-</td>
</tr>
<tr>
<td>Phosphate (PO₄³⁻)</td>
<td>• NH₄ followed by Ba(NO₃)₂: White</td>
<td>• Mg²⁺ in an ammonia, ammonium nitrate buffer: White</td>
</tr>
</tbody>
</table>

- 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.
AAS was invented in the 1950s by Sir Alan Walsh (an Australian scientist) at CSIRO.

This method is used to determine concentrations of CATIONS (NO ANIONS) at concentrations lower than 1ppm.

**Principle**
- The light absorbed by atoms or ions in solution is directly proportional to the concentration of the ions (as absorption increases, concentration increases).
- When heat is absorbed, electrons are excited and move up to a higher energy state. When the electron moves back into its original ground state, it releases the energy as light. This emitted light is different for each cation, due to the cation’s unique electron configuration.
- Each element has its own ‘spectrum’, which can be used to identify it (similar to a fingerprint).

**Components**
- **Light Source**: Hollow Cathode lamp of the element that is being tested e.g. If testing for copper, a copper hollow cathode lamp is used.
- **Flame/Nebuliser**: Vaporises the cations in the sample.
- **Monochromator/Prism**: One wavelength/colour is selected to prevent interference by other atoms.
- **Photomultiplier Tube**: Detects transmitted light in terms of intensity.
- **Digital Reading**: Converts the transmitted light into the absorbance as a decimal.

**Initial Light – Transmitted Light = Absorption**

**Method**
1. Prepare a 200ppm standard solution containing the cation to be tested for. (similar to how standard solutions for titrations are prepared)
   - Dissolve mass into small quantity of distilled water, use volumetric flask, top with distilled water.
2. Prepare a series of diluted samples of the ion to be tested (e.g. 100ppm, 50ppm, 25ppm)
3. Measure the absorbance of each of the standard solitons using AAS in order to draw a calibration curve (always linear, passes through origin).
4. Measure the absorbance of the unknown solution.
5. Determine the concentration of the ion in the solution using the calibration curve (ALWAYS LINEAR, ALWAYS PASSES THROUGH/MEETS THE ORIGIN (0,0)).

**Advantages**
- Extremely sensitive (measures concentrations as low as 1ppb)
- Specific due to the hollow cathode lamp which emits light of a specific wavelength
- No prior preparation of the sample required

**Disadvantages**
- Only cations can be tested
- Very expensive (e.g. a different cathode lamp is needed for each cation)
- Only one ion can be tested for at a time (time consuming, impractical in some situations)
- Trained technician required to operate AAS

**Trace Element Analysis**
- Trace elements are those that are required by living organisms in very low concentrations (1-100ppm) for the proper functioning of enzymes in cells (High concentrations are harmful).
- E.g. Zn (essential for amino acid metabolism and energy production), Co, Ni, Cu, Mo, Se
- Before AAS, the presence and amount of these trace elements could not be determined. Now, blood, urine and tissue samples are tested for the amount of trace elements present. If there are deficiencies, these can be identified and treated.

**Summary**
- Introduce chemical principles
- Discuss method, including components
- Discuss Advantages and disadvantages
- Discuss trace elements
- Provide assessment of the technology
• 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
  ➢ Pb\(^{2+}\) (Lead)
  ➢ Toxic, heavy metal – released as inorganic ions or organic lead
  ➢ Enter organisms via ingestion, inhalation, absorption through skin enters food chain and accumulates in body (difficult to excrete)
  ➢ Effects
    ▪ Organ damage by disrupting enzyme systems
    ▪ Intellectual retardation, neurological damage – in children – learning disabilities, impaired hearing – hyperactivity, ADD
    ▪ Inhibits formation of haemoglobin (oxygen carrying molecule in blood)
  ➢ Past Uses
    ▪ White, yellow, red paint, leaded fuels, manufactured toys
  ➢ Monitoring
    ▪ Monitoring in highway areas, soil, atmosphere, urban areas, water
    ▪ Stringent standards (concentrations in paints (0.25%) and unleaded petrol)
    ▪ Problems e.g. when used in mining, the refining of lead (slag wastes, fumes, dust) and lead, acid batteries

• Identify data, plan, select equipment and perform firsthand investigations to measure the sulfate content of lawn fertiliser and explain the chemistry involved
  and

• Analyse information to evaluate the reliability of the results of the above investigation and to propose solutions to problems encountered in the procedure
  ➢ Gravimetric Analysis of SO\(_4^{2-}\) by precipitating as BaSO\(_4\)
  ➢ Method:
    1. Weigh 0.2g of fertiliser and dissolve in distilled water. Filter to remove any insoluble substances such as sand.
    2. Acidify the solution with 0.5mL of concentrated HCl and gently boil. (Will remove carbonate, which would otherwise precipitate as BaCO\(_3\))
    3. 5% w/v BaCl\(_2\) is added dropwise with a burette until no more precipitate forms. Avoid excess, as extra barium ions will stick to the precipitate, increasing weight.
    4. Check the supernatant for further precipitation by allowing the solid to settle and adding a drop of BaCl\(_2\) to the clear solution. If there is no cloudiness as a result, precipitation is complete.
    5. The beaker with the precipitate is left on a hot plate for an hour to settle. The powdery BaSO\(_4\) will clump together making it easy to filter. Heat encourages recombination of ions. (opposite of dissociation)
    6. Filter the BaSO\(_4\) solid using a weighed sintered glass funnel (superior to filter paper). This is a very slow process, so a vacuum pump can be used to speed up this process.
    7. Wash the precipitate with small amounts of water 3 times (to remove any barium ions sticking to the precipitate). Then rise with small amounts of alcohol 3 times (to remove water).
    8. Dry the precipitate in an oven at 105 degrees Celsius until completely dry. Cool in a desiccator and weigh. Continue this process until the weight is constant.
  ➢ Safety
    1. Barium chloride is toxic if ingested, hence it is important to wash hands thoroughly after the experiment
    2. Concentrated Hydrochloric acid is very corrosive and causes severe damage to the eyes, skin and clothes. Wear safety goggles and gloves (if possible)
    3. Experiment involves the use of a hot plate, which can burn skin. Be careful when handling equipment
  ➢ Results
    ▪ Determine mass of BaSO\(_4\)
    ▪ Divide this mass by the molar mass of BaSO\(_4\) to determine the number of moles
    ▪ In 233.37 grams of BaSO\(_4\) (1 mole), there are 96g of SO\(_4^{2-}\)
    ▪ Multiply (96/233.37) with the mass of BaSO\(_4\) to determine the mass of SO\(_4^{2-}\)
    ▪ To find the percentage SO\(_4^{2-}\), divide the mass of SO\(_4\) by the mass of the original sample of fertiliser
Reliability

- The reliability of results in the above procedure depend upon:
  - Only sulfate ions in the fertiliser being precipitated by barium ions.
  - All of the barium sulfate precipitate being collected by the filter paper.
- The reliability of results in the procedure can be improved by:
  - Using a fine analytical grade quantitative filter paper rather than a qualitative filter paper.
  - Repeating the experiment several times and comparing the results obtained each time.
- Problems, other than reliability problems, that could possibly be encountered during the procedure, and possible solutions, include the following:

<table>
<thead>
<tr>
<th>Problem</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weighing: Some mass may be unaccounted for due to errors in collection and weighing</td>
<td>Wash down the beaker when transferring to the filter to ensure all BaSO₄ is transferred. Filter paper should be dried in an oven instead of air, as moisture could still be present and contaminants added. Use a very precise electronic scale.</td>
</tr>
<tr>
<td>Incomplete Precipitation: BaSO₄ forms in an equilibrium, and thus production of precipitate may not reach equilibrium</td>
<td>Add excess BaCl₂ to shift the equilibrium to the right until no more additional white precipitate forms. Cool the mixture after adding BaCl₂ in ice-water to greatly reduce the solubility of BaSO₄. Do not use great volumes of water and solutions, as BaSO₄ is more soluble in dilute solutions.</td>
</tr>
<tr>
<td>Presence of contaminant ions: Phosphate and carbonates present may react with barium to form excess precipitate</td>
<td>Addition of HCl dissolves these precipitates</td>
</tr>
<tr>
<td>Small size of precipitate crystals: BaSO₄ forms very fine crystals, which easily go through normal filter paper, and even sintered glass crucibles.</td>
<td>Heating the solution before adding BaSO₄ and constantly stirring increases the energy of the solution, which increases the number of collisions, thus larger particles are formed. Adding BaCl₂ slowly allows the BaSO₄ crystals to grow, and thus become larger. Adding a coagulating agent such as agar solution causes the crystals to coagulate.</td>
</tr>
<tr>
<td>Filter paper takes a long period of time to dry</td>
<td>Dry the filter paper in an oven</td>
</tr>
<tr>
<td>Filtration takes a long period of time</td>
<td>Use a weighed sintered glass crucible</td>
</tr>
</tbody>
</table>

- Gather, process and present information to interpret secondary data from AAS measurements and evaluate the effectiveness of this in pollution control

   ADVANTAGES
   - AAS is extremely effective in pollution control of metals → accurately calculate concentrations of pollutants even in low concentrations. This has given us a broader understanding of the environment and helps us improve the health and safety of ecosystems and the public
     - AAS was used in Bangladesh to determine arsenic concentrations of groundwater. This allows the public to avoid drinking ground water with high concentrations of Arsenic, which can cause hard patches on the skin, skin cancer, lung cancer, kidney and bladder cancer and gangrene.
     - Lead is another toxic heavy metals which can damage the brain, kidneys and reproductive system by disrupting enzyme system mediated by other metals such as calcium, iron and zinc.
       \[2\text{PbS} + \text{O}_2 \rightarrow 2\text{PbO} + 2\text{SO}_2\]
       \[2\text{PbO} + \text{C} \rightarrow 2\text{Pb} + \text{CO}_2\]
   - These equations show how lead may accumulate in workers
   - AAS is a relatively cheap method (following the initial start-up costs) of regularly analysing waterways and air quality to ensure that the level of pollution is at an acceptable level, allowing the maintenance of the health of the population
   - AAS is highly specific and fast for each sample analysed, as the sample can be analysed without having to be physically separated
   - Thus, AAS provides a quick and easy way of routinely monitoring/detecting such harmful heavy metals in such workplaces, to ensure that they are in concentrations below what is recommended by the appropriate health authorities
DISADVANTAGES

- AAS is only useful for testing the concentration of metal pollutants, as it cannot be used to determine the concentration of non-metal pollutants.
- Although inexpensive to operate, the initial cost of setting up the AAS device is high, and thus makes them unaffordable for some pollution monitoring agencies.
- It can only be used to test for one metal at a time. Also for each new metal tested, a new hollow cathode lamp with the specific metal has to be set up → time consuming and expensive.
- Destructive analysis → Sample tested cannot be reused or reanalysed.
- Water: Heavy metals such as lead, magnesium and calcium form industrial waste.
- Soil: Lead, Mercury, Cadmium, Nickel from leaching of batteries and rubbish dump.
- Air: Lead from leaded petrol and demolition of old buildings with leaded paint.
- Food: Lead in fruits grown in orchards near highways. Mercury bioaccumulation in fish.
- Mining: Test for metals in ores to determine whether it is economical or not to mine a certain region.
  - Assessment: AAS has had a very positive impact on our ability to control pollution. With AAS, we have the ability to accurately and reliably analyse substances for dangerous cations that would otherwise go undetected. This has allowed us to take better care of society and the environment.

Section 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 layer of gasses about 200 to 300km thick surrounding the Earth.

- Troposphere (0-15km)
  - As the altitude increases, temperature decreases
  - The hot air on the surface of the Earth will rise due to convection, and the cold air will come down
  - Due to this disturbance, gasses are well mixed and weather events are frequent
  - Pollutants are diluted in this layer due to the constant movement of gasses

- Stratosphere (15-50km)
  - As altitude increases, temperature increases
  - Hot air remains on top and cold air remains at the bottom (no mixing of gasses)
  - Ozone layer is present at an altitude of about 20km

- Atmospheric Composition
  - 90% of gasses are concentrate within the troposphere.
Identify the main pollutants found in the lower atmosphere and their sources

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Source</th>
<th>Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>• Leaded petrol in cars</td>
<td>Direct poison that affects the central nervous system (causes mental retardation)</td>
</tr>
<tr>
<td></td>
<td>• Demolishing old buildings with leaded paint</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Mining Fumes</td>
<td></td>
</tr>
<tr>
<td>Nitrogen Oxides</td>
<td>• Internal combustion engines</td>
<td>Contributes to acid rain and photochemical smog</td>
</tr>
<tr>
<td></td>
<td>• Burning fossil fuels containing nitrogen impurities</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Burning vegetation</td>
<td></td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>• Burning fossil fuels containing sulfur</td>
<td>Contributes to the formation of acid rain</td>
</tr>
<tr>
<td></td>
<td>• Smelting metal sulfides in metal extraction</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Production of H₂SO₄</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>• Bacterial decomposition of organic matter</td>
<td>Contributes to photochemical smog and the greenhouse effect (climate change)</td>
</tr>
<tr>
<td></td>
<td>• Natural gas seepage</td>
<td></td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>• Vehicles using petrol</td>
<td>Contributes to photochemical smog and peroxyacetylinitrates (PANs)</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>• Incomplete combustion of hydrocarbons</td>
<td>Combines with haemoglobin faster than oxygen gas, thereby reducing the oxygen carrying ability of blood</td>
</tr>
<tr>
<td></td>
<td>• Forest fires</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Slow combustion stores</td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>• Forest Fires</td>
<td>Contributes to global warming and climate change</td>
</tr>
<tr>
<td></td>
<td>• Vehicles</td>
<td></td>
</tr>
<tr>
<td>Chlorofluorocarbons (CFCs)</td>
<td>• Refrigerators</td>
<td>Destroys the ozone layer, allowing short wavelength UV radiation to come down to the Earth’s surface and cause skin cancer, sunburn and eye cataracts</td>
</tr>
<tr>
<td></td>
<td>• Air Conditioners</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Aerosol Cans</td>
<td></td>
</tr>
<tr>
<td>Ozone</td>
<td>• Internal combustion engines</td>
<td>Photochemical smog</td>
</tr>
<tr>
<td></td>
<td>N₂ + O₂ → 2NO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2NO + O₂ → 2NO₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO₂ → (sunlight) NO + O (both radicals)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O (radical) + O₂ → O₃</td>
<td></td>
</tr>
<tr>
<td>Particulates</td>
<td>• Soot from incomplete combustion</td>
<td>Causes repository difficulties, carcinogenic and dirts the environment</td>
</tr>
<tr>
<td></td>
<td>• Dust</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Asbestos</td>
<td></td>
</tr>
</tbody>
</table>

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

- In the Troposphere
  - Ozone is a serious pollutant in the troposphere, existing at concentrations around 0.02ppm in clean air
  - As shown in the table, ozone is formed in the troposphere by internal combustion engines
- Ozone (photochemical smog) is a very strong oxidant and will oxidise soft tissue in eyes and throat, disrupts normal biochemical reactions
- Ozone, in higher concentrations, can cause breathing problems, aggravation of respiratory problems, headaches, fatigue and death (in high concentrations)
- Thus, Ozone is a serious and toxic pollutant in the ‘lower atmosphere’ (troposphere)

- In the Stratosphere
  - Ozone exists at much higher concentrations in the stratosphere naturally, at around 2 to 8ppm
  - Ozone has a very important role in the stratosphere, in which it is responsible for absorbing dangerous UVB radiation from the sun that would otherwise cause serious damage to life on Earth (cancers, burns and eye cataracts)

- Formation of Ozone
  - \( O_2(g) \rightarrow (UV\ on\ arrow) 2O^-(g) \)
  - \( O_2(g) + O^-(g) \rightarrow O_3(g) + \text{heat} \)

- Action of Ozone
  - \( O_3(g) \rightarrow (UV\ on\ arrow) O_2(g) + O^-(g) \)
  - \( O_3(g) + O^-(g) \rightarrow 2O_2(g) + \text{heat} \)
  - UV radiation is converted to heat energy + harmless \( O_2 \) - no other atmospheric molecules have the ability to absorb solar radiation in UV range
  - Stratosphere gets warm as light energy is constantly converted to heat energy
  - Hence Ozone has an important role in the Stratosphere, in which it acts as a ‘UV radiation shield’

- Describe the formation of a coordinate covalent bond
  - When the two electrons that are shared to form a covalent bond come from a single atom, the bond is known as a coordinate covalent bond

- Demonstrate the formation of coordinate covalent bonds using Lewis electron dot structures
  - Covalent bond where both of the shared electrons for the bond come from the same atom – more reactive
  - Bonds are indistinguishable from regular covalent bonds when formed
  - E.g. \( \text{NH}_4^+ \), \( \text{H}_3\text{O}^+ \) and \( \text{CO} \)
  - Bond comes from lone pairs of one atom

- In order to draw a compound containing coordinate covalent bonds
  - Number of electrons needed = number of atoms * 8
  - Number of electrons present = number of electrons atoms present currently have
  - Number of shared electrons = needed – present
  - Number of bonds = number of shared electrons/2
  - Position bonds appropriately to satisfy all atoms (octet)
  - Coordinate covalent bonds are denoted with arrows

- Compare the properties of the oxygen allotropes O2 and O3 and account for them on the basis of molecular structure and bonding
  - Allotrope: Different physical form of the same element.
  - Oxygen has 2 allotropes: Ozone and oxygen
➢ Chemical Properties
   ▪ Depend on the strength of the covalent bonds. The strong double bond in oxygen gas is hard to break but the single bond in O₃ (coordinate covalent) is broken easily (998kJ/Mol vs 107kJ/Mol)
   ▪ Ozone is more reactive than oxygen
   ▪ Both are oxidising agents (ozone is stronger)

➢ Physical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Gaseous Colour</th>
<th>Liquid Colour</th>
<th>Solvent Colour</th>
<th>REASON</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaseous Colour</td>
<td>Colourless</td>
<td>Pale blue</td>
<td>Pale blue</td>
<td>-</td>
</tr>
<tr>
<td>Liquid Colour</td>
<td>Pale blue</td>
<td>Deep blue</td>
<td>Black-violet</td>
<td>-</td>
</tr>
<tr>
<td>Solvent Colour</td>
<td>Lower (-183° and -219°C)</td>
<td>Higher (-111° and -193°C)</td>
<td>O₃ is slightly polar due to its asymmetric electron density and its bent shape - greater intermolecular forces</td>
<td></td>
</tr>
<tr>
<td>BP/MP</td>
<td>O₂</td>
<td>O₃</td>
<td></td>
<td>Presence of additional O atom in ozone</td>
</tr>
<tr>
<td>Density as Gas</td>
<td>Lower</td>
<td>Higher</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Sparingly soluble (9ppm)</td>
<td>More soluble than O₂</td>
<td>O₂ is non-polar, but O₃ is bent and thus polar</td>
<td></td>
</tr>
<tr>
<td>Reactivity</td>
<td>Highly reactive with many metals and non-metals</td>
<td>Very highly reactive, attacks double bonds on alkenes</td>
<td>Coordinate covalent bond in O₃ is extremely reactive Intermediate single and double bonds creating O⁻ (an oxidant)</td>
<td></td>
</tr>
<tr>
<td>Odour</td>
<td>Odourless</td>
<td>Pungent</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

➢ Ozone has a slight polarity due to the bent structure. Therefore, there are dipole-dipole forces between ozone molecules which are stronger than the weak dispersion forces in oxygen gas. This results in higher melting and boiling points, as well as solubility in water as compared to oxygen gas.

➢ Compare the properties of the gaseous forms of oxygen and the oxygen free radical
   ➢ Free Radical: A neutral species atom with an unpaired electron. Oxygen free radicals are present in the upper atmosphere due to the effects of radiation such as UV light

<table>
<thead>
<tr>
<th>Property</th>
<th>Gases Forms (O₂, O₃)</th>
<th>Free Radical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactivity</td>
<td>Less reactive (full outer valence shell)</td>
<td>Very reactive (unpaired)</td>
</tr>
<tr>
<td>Oxidation Ability</td>
<td>Lower</td>
<td>Higher (unpaired electron, high tendency to take electrons to complete valence shell)</td>
</tr>
</tbody>
</table>

➢ Identify the origins of chlorofluorocarbons (CFCs) and halons in the atmosphere
   ➢ Chlorofluorocarbons (CFCs) are compounds containing Carbon, Chlorine and Fluorine ONLY (No H)
   ➢ Halons are compounds containing Carbon, Bromine, Fluorine (may or may not contain Cl) (No H)
   ➢ During the 1930s, CFCs (and, to a lesser extent, halons) replaced ammonia (NH₃) as the gas in refrigerators and air conditioners
   ➢ CFCs were cheaper, non-toxic, non-flammable easily compressible
   ➢ Such uses of CFCs released millions of tonnes of CFC gasses into the atmosphere over a period of over half a century, introducing CFCs and Halons into the atmosphere
   ➢ Naming CFCs
      ▪ List C, H and F (in that order) and subtract 90
      ▪ E.g. Cl-CFCl-CF₂-Cl = 203-90 = CFC 113 (as there are 2 carbons, 0 hydrogens and 3 fluorines)
Naming Halons

- List C, F, Cl, Br e.g. 1211
- CFC-11 was used in refrigerators and air conditioners (CCl$_3$F)

- Identify and name examples (excluding geometrical and optical) of haloalkanes up to eight carbon atoms
  - Isomer: Same molecular formula but different structures
    - Isotope → Atoms, Allotrope → Element, Isomer → Compounds
  - Haloalkanes: Alkanes with halogens F, Cl, Br and I functional groups
  - Naming
    1. Longest carbon chains as you would for alkanes
    2. Position of double bond (if present) takes precedence over halogen but named after
    3. Add functional group prefixes F: fluoro- Cl: chloro- Br: bromo I: iodo-
    4. Number according lowest numbered locant (if more than 1 type is on side to start on counting from the side
       that you begin to count from first alphabetically)
    5. Use di, tri etc. for writing number of halogen atoms
    6. Order (if more than 1 different type of halogen atom) alphabetically – i.e. chloro, fluoro

    E.g. 1,1 dibromo 2-chlorohexane

- Discuss the problems associated with the use of CFCs and assess the effectiveness of steps taken to alleviate these problems
  - CFCs are extremely stable and insoluble in water. Therefore, they do not come down from the atmosphere with
    rain water or other weather events, and remain in the troposphere for decades.
  - Slowly, over many years, CFCs migrate towards the Stratosphere until they finally reach the Ozone layer
  - The UV radiation present in the ozone layer breaks the Carbon-Chlorine bond in the CFC and a chlorine free radical is formed

  \[
  \text{CCl}_3\text{F}_2(g) \rightarrow (\text{UV on Arrow}) \text{CCl}_2\text{F}^* + \text{Cl}^*
  \]

  - This chlorine free radical then attacks ozone, forming a hypochlorite free radical and oxygen gas. The hypochlorite free radical then reacts with an oxygen free radical, forming oxygen gas and reforming the original chlorine free radical.

  \[
  \text{Cl}^* + \text{O}_3(g) \rightarrow \text{ClO}^* + \text{O}_2(g)
  
  \text{ClO}^* + \text{O}^* \rightarrow \text{O}_2(g) + \text{Cl}^*
  \]

  - This process can be described as a ‘chain reaction’ as chlorine is not destroyed in the process (can be thought of
    as a homogenous catalyst). The only way this can be stopped is if chlorine reacts with methane. Typically, a single
    CFC compound can destroy around 1000 ozone molecules.
  - The mass destruction of ozone in the stratosphere leads to the thinning of the ozone layer. These are known as
    ozone ‘holes’ (not actual holes, just areas of lower concentration of ozone)
  - Just a 1% reduction in the ozone layer increases the chance of skin cancer by 8%
  - If the UVB radiation is increased by 2% it has the ability to kill surface plankton and disrupt the food chain
  - Halons are more destructive than CFCs as the C-Br bond breaks more readily. The bromine free radical destroys
    ozone in a similar process to chlorine.
  - In 1987, the Montreal Protocol banned the use of CFCs and other compounds in developed countries
    - Stop using Halons by 1994
    - Stop manufacturing CFCs by 1996
    - Phase out HCFCs by the 21st century (2020)
    - Allow less developed countries some grace period and provide financial support

- Replacements
  - HCFCs
    - Have C-H bonds with are decomposable by radicals – but significant amount still reaches
      upper atmosphere
    - Less harmful than CFCs despite still having Cl atoms
    - Temporary substitute with plants to phase out by 2020 (not ideal)
  - HFCs
    - Contain no Cl/Br atoms and C-F bond is strong – no F free radicals produced
    - Do not contribute to ozone depletion
    - More expensive; R-124a is used refrigerant in Aus.
It is predicted that by 2050 the ozone layer will be repaired naturally

Equations
- \( \text{CCl}_2\text{F}_2(g) \rightarrow (\text{UVB Radiation on top of arrow}) \text{CClF}_2(g) \) (radical) + \( \text{Cl}(g) \) (radical)
- \( \text{Cl}(g) \) (radical) + \( \text{O}_3(g) \rightarrow \text{OCl}(g) \) (radical) + \( \text{O}_2(g) \)
- \( \text{OCl}(g) \) (radical) + \( \text{O}(g) \) (radical) \( \rightarrow \text{Cl}(g) \) (radical) + \( \text{O}_2(g) \)

Reactions that will stop the chain reaction
- \( \text{CH}_4(g) + \text{Cl}(g) \rightarrow \text{CH}_3(g) \) (radical) + \( \text{HCl}(g) \)
- \( \text{NO}_2(g) + \text{OCl}(g) \rightarrow \text{ClONO}_2 \)
- \( \text{Cl}^* + \text{Cl}^* \rightarrow \text{Cl}_2(2g) \)

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

High ozone depletion over Antarctica could be due to
- The ice crystals in the air catalysing the reaction between HCl and ClONO\(_2\) in the air
- HCl + ClONO\(_2\) \( \rightarrow \) (ice crystals on top of arrow) Cl\(_2\) + HNO\(_3\)
- \( \text{Cl}_2 \rightarrow \) (sunlight on top of arrow) 2Cl (radical)
- By October, the ozone layer over Antarctica is extremely thin, but is partially repaired by late December

Ozone concentration is measured in Dobson Units

Instruments to Collect Data
- Dobson Spectrophotometer (1960s)
  - Ground based instruments for long term data \( \rightarrow \) specific area only
    - Measures the intensity of four standard wavelengths of UV radiation reflected back to ground (2 absorbed by ozone, 2 not)
    - Ratio between two intensities determined to calculate total ozone
    - Comparing the values. The greater the difference, the greater the ozone (good - to absorb UV)
- LIDAR
  - Rely on scattering of laser light by ozone
  - Fire 2 beams (one absorbed by ozone – 308nm and one not – 351 nm)
  - Compare values – profile of ozone concentration (conc. vs. altitude) measured
  - Difference in laser light intensity/wavelengths similarly shows presence of O\(_3\) (which is good if it is higher)
- TOMS (Total Ozone Mapping Spectrometers) (1980s)
  - Satellite, balloon or ground based – unit is Dobson Unit \( \rightarrow \) daily global coverage
  - Measures intensity of a wavelength of UV radiation absorbed by ozone – compares to intensity of wavelength not absorbed
  - Satellite (at alt. above ozone layer) observes incoming UV light at 6 diff. wavelengths + observes UV light backscattered by ozone and compares intensity of incoming radiation with backscattered radiation to form a profile
  - Compares the different values having passed through
- OMI (Ozone Measuring Instrument) (current)
  - Improvement of TOMS with smaller pixel size but larger viewing angle \( \rightarrow \) allow to maintain daily global coverage but with more detail
  - Look between clouds at troposphere

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 (Covered Earlier)

Gather, process and present information from secondary sources including simulations, molecular model kits or pictorial representations to model isomers of haloalkanes (Self-Explanatory)
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

1. Hydrochlorofluorocarbons (HCFCs)
   - These have carbon hydrogen bonds which break in the troposphere before the compound can diffuse to the stratosphere. Ozone depletion, however, is still possible as it also contains chlorine.

2. Hydrofluorocarbons (HFCs)
   - These have no chlorine atoms. The carbon-fluorine bond is extremely strong and does not break in the presence of UV light. Therefore, no fluorine-free radicals are generated that can harm the ozone later.
   - 1,1,1,2-Tetrafluoroethane is the gas used in air conditioners and refrigerators

<table>
<thead>
<tr>
<th>Compound Type</th>
<th>Ozone Depletion Potential (ODP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halon</td>
<td>10</td>
</tr>
<tr>
<td>CFC</td>
<td>1</td>
</tr>
<tr>
<td>HCFC</td>
<td>0.1</td>
</tr>
<tr>
<td>HFC</td>
<td>0</td>
</tr>
</tbody>
</table>

Section 5

*Human activity 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
  - Concentrations of Common Ions (generally measured in ppm).
  - Total dissolved solids (TDS): A measure the mass of solids dissolved in a unit volume of water (generally measured in ppm).
  - Hardness: A measure of the concentration of calcium and magnesium ions.
  - Turbidity: A measure of the amount of colloidal suspended matter, which translates into a degree of cloudiness or transparency (measured in relative units called nephelometric turbidity units, or NTUs).
  - Acidity: A measure of the concentration of hydrogen ions (measured in pH).
  - Dissolved oxygen (DO): A measure of the concentration of oxygen (generally measured in ppm).
  - Biochemical oxygen demand (BOD): A measure of the concentration of dissolved oxygen that is needed for the complete breakdown of the organic matter in a sample by aerobic bacteria (generally measured in ppm).

Good quality drinking water is known as potable water. It should have the following properties.
- Completely clear and colourless
- Odourless
- Pleasant Taste
- Low salt content
- No pathogens
- No toxic materials/substances

Tests can be carried out to determine water quality by measuring the:
- Concentration of common ions
  - Qualitative Tests
    - Flame Test (C)
    - Precipitation Test (C & A)
    - Line Spectrum (Emission or absorption) (C)
  - Quantitative Tests
    - Titrations (C & A)
      - The concentration of chlorine can be determined through titration with HNO₃, along with K₂CrO₄ (yellow) indicator. The colour changes from yellow to brick red when the end point has been reached. Red Ag₂CrO₄ precipitates when there is no more chlorine. (Precipitation Titration)
      - Chlorine can also be determined by reaction with excess silver nitrate
        - Gravimetry (C & A)
        - AAS (Atomic Absorption Spectroscopy) (C)
        - Ion Sensitive Electrode (A)
• Similar to pH meters
• Measure voltage difference and convert result to chlorine or fluorine concentration
  o Example: Gravimetric Analysis of Chlorine
    § Weight a known amount of water \(\rightarrow\) Evaporate \(\rightarrow\) Concentrated Sample \(\rightarrow\) Acidify with \(\text{HNO}_3\) and add \(\text{AgNO}_3\) \(\rightarrow\) \(\text{AgCl}\) Precipitate \(\rightarrow\) Filter and Dry \(\rightarrow\) Weigh

• Total Dissolved Solids (TDS)
  o Quantitative Tests
    § Gravimetric Analysis
    • Filter the water sample to remove insoluble substances
    • Weigh
    • Evaporate to dryness in a previously weighed evaporating basin
    • Cool and weigh
    • Provide results in ppm
    § Measurement of conductivity converted to TDS in ppm

• Hardness
  o Hardness is due to \(\text{Ca}^{2+}\) and \(\text{Mg}^{2+}\) ions being present in the water
  o Qualitative \(\rightarrow\) Check if soap lathers in water, or if it forms an insoluble scum
  o Quantitative \(\rightarrow\) EDTA Complexometry Titration, AAS
    § Add 25.0mL of water into a flask
    § Add 2mL of \(\text{NH}_3/\text{NH}_4\text{Cl}\) basic buffer solution \(\rightarrow\) Will maintain pH when EDTA makes solution acidic
    § Add 3 drops of Eriochrome Black T indicator
    § Titrate with 0.020 mol/L EDTA until there is a change in colour (red \(\rightarrow\) blue)
    § Repeat titration until 3 readings within 0.1mL of each other
    § \(\text{Ca}^{2+}\) Indicator Complex (Red) + EDTA \(\rightarrow\) [CaEDTA]\(^{2-}\) + Indicator (Blue)
    • Hardness is reported as \(\text{CaCO}_3\) ppm even if it is due to Magnesium
    • \(\text{nCaCO}_3 = \text{nCa} = \text{nEDTA (as 1:1 ratio)} = \text{C}_\text{EDTA} \times V_\text{EDTA} = 0.01 \times \text{Volume of EDTA used in Litres.}\)
    • Divide this result by 25, multiply by 1000 (1 litre), then 100 (mm \(\text{CaCO}_3\), then 1000). This will give a reading of \(\text{CaCO}_3\) in mg in 1000mL (ppm).
      § If < 75ppm then low
      § If 15-150ppm then moderate
      § If 150-300ppm then hard
      § If 300-500ppm then very hard
      § If >500 then saline
  o There are two types of hardness
    § Temporary: If there is dissolved \(\text{CO}_2\), boiling will remove \(\text{Ca}\) as \(\text{CaCO}_3\)
    § Permanent: Need to add washing soda \(\text{Na}_2\text{CO}_3\) which removes \(\text{Ca}\) as \(\text{CaCO}_3\)

• Turbidity
  o Cloudiness or lack of transparency is known as turbidity
  o Suspended solids, such as clay, result in turbidity
  o Qualitative Tests
    § Secchi Disks: Insert disk into water until the cross at the base cannot be seen. The length of the string is compared.
    § Turbidity Tube: Add water into tube until the cross at the base of the tube cannot be seen.
  o Quantitative
    § Turbidity is measured in NTU (Nephelometric Turbidity Units)
    § Turbidity Meter
      • Light is passed through a sample of the water, and the resultant light transmitted is measured. The light transmitted is inversely proportional to the turbidity in NTU.
      • Nephelometer: Light is passed through a sample of water. The resultant scattering of light is measured. The scattering of light is proportional to the turbidity in NTU.
1-5 NTU is potable
Less than 25 NTU is suitable for water life

Acidity
- The main cause of acidity is acid rain
- Mining can also cause acidity as FeS gets oxidised to $SO_4^{2-} \rightarrow H_2SO_4$. Low pH will dissolve toxic metals ions such as aluminium, which will be taken up by plants and aquatic life.
- Potable water should have a pH of 6.5-8.5
- It is normal for water to appear acidic at higher temperatures, as the forward reaction of the self-ionisation of water equilibrium is exothermic. This causes greater concentrations of hydronium and hydroxide. Since pH meters only measure hydronium, the water appears acidic at higher temperatures.
- Qualitative Indicators
- Quantitative Indicators
  - Calibrated pH meter + thermometer to measure temperature (as temp affects pH)

Dissolved Oxygen
- Oxygen diffuses from the air into the water and water plants produce $O_2$ in photosynthesis
- Moving water (e.g. rapids) have more DO due to the greater surface area
- DO is measured in ppm
  - 6-8ppm Unpolluted
  - 4-6ppm Polluted
  - 2-4 Severely Polluted
  - <2 Dead Water
  - At lower than 5ppm, aquatic life is in severe stress
- DO depends on
  - Temperature ($O_2(g) \rightleftharpoons O_2(aq) + \text{heat}$) (LCP) (Thermal Pollution)
  - Atmospheric Pressure: As pressure increases, equilibrium shifts forward, increasing DO (LCP)
  - Presence of salt: As salt concentration increases, DO decreases as salt is more soluble in water than non-polar oxygen
  - Biological Oxygen Demand (BOD): As BOD increases, DO decreases.
- Qualitative Tests: Methylene blue indicator turns blue if there is oxygen in the water
- Quantitative Tests
  - Calibrated DO meter
  - Winkler Titration
    - $O_{2(aq)} + 2Mn^{2+}_{(aq)} + 4OH^-_{(aq)} \rightarrow 2MnO(OH)_{2(s)}$  
    - $MnO(OH)_{2(s)} + 8H^+_{(aq)} \rightarrow 2Mn^{4+}_{(aq)} + 6H_2O_{(l)}$
    - $2Mn^{4+}_{(aq)} + 4I^-_{(aq)} \rightarrow 2Mn^{2+}_{(aq)} + 2I_{2(aq)}$
    - $2I_{2(aq)} + 4S_2O_3^{2-}_{(aq)} \rightarrow 4I^-_{(aq)} + 2S_4O_6^{2-}_{(aq)}$
    - 1:4 ratio between oxygen gas and thiosulfate
  - Method
    - A 250.0 reagent bottle is filled with water and stoppered underwater to prevent any air bubbles entering
    - Add 5mL of $MnSO_4 / NaOH / KI$ and allow the precipitate to settle
    - Add 1mL of concentrated $H_2SO_4$ and mix to dissolve the precipitate
    - Transfer 100mL into a titration flask and titrate with 0.025M sodium thiosulfate $Na_2S_2O_3$ in a burette using starch as the indicator (Blue → Colourless)
    - Repeat
  - Results
    - $nO_2 = nNa_2S_2O_3 / 4$ (as 1:4 ratio) = 0.025 * volume of $Na_2S_2O_3$ used / 4
    - $nO_2 * 32$ (molar mass) * 1000 (mg) * 1000/100 (1 L) = oxygen in mg/L (ppm)
Biochemical Oxygen Demand (BOD)
- A measure of the organic matter in a sample of water that is broken down by bacteria (lower the bottle)
- The standard is BOD-5: This is the amount of oxygen (ppm) that is 1L of water will react with at 20 degrees Celsius in the dark (prevent photosynthesis) in 5 days
- Method BOD-5
  - Fill two 250.0mL reagent bottles with water and stopper underwater
  - DO of one bottle is measured immediately using the Winkler Titration
  - The other bottle is left in a dark place at 20 degrees Celsius for 5 days, then DO is measured by the Winkler Titration
- Results
  - Subtract second result from first result to obtain BOD in ppm
  - If BOD > 3ppm, then the water is polluted
- BOD in various locations
  - Clean river water = 1-3 ppm
  - Domestic Sewage = 350ppm
  - Abattoir waste = 2600ppm
  - Paper pulp mills = 25000ppm

Identify factors that affect the concentrations of a range of ions in solution in natural bodies of water such as rivers and oceans
- Rain
  - CO$_3^{2-}$ from dissolved CO$_2$
  - Na$^+$, Cl$^-$, SO$_4^{2-}$ from sea spray
  - When rain water runs along the ground, it can pick up NO$_3^-$, PO$_4^{3-}$, Mg$^{2+}$
  - If the rain water is acidic, toxic heavy metals like aluminium can dissolve
- Human Activity
  - Land clearing
  - Growing crops and pasture, fertiliser run off, etc.
- Effluent Discharge
  - Raw or treated sewage
  - Storm water run off
  - Industrial effluent e.g. Pb$^{2+}$, Cd$^{2+}$, Cr$^{2+}$, Cu$^{2+}$, Zn$^{2+}$
- Leaching from rubbish dumps
  - Ni$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Hg$^{2+}$ from discarded batteries can leach into waterways with rain water

Describe and assess the effectiveness of methods used to purify and sanitise mass water supplies
- SCREENING
  Prior to leaving dam site and again on entering the treatment plants, water is screened to remove macro-objects and screenable solids. Freshwater passes through fine screens to remove solid objects like fish, logs and leaves.
- AERATION
  Aeration is the intimate exposure of water and air. When air is mixed with water, some impurities in the water, such as iron and manganese, become oxidized. Once oxidized, these chemicals fall out of solution and become suspended in the water. Aeration will remove tastes and odours from water if the problem is caused by relatively volatile gases and organic compounds.
- COAGULATION/FLOCCULATION
  During coagulation, liquid aluminium sulfate (alum Al$_2$(SO$_4$)$_3$) (or sometimes FeCl$_3$, which forms Fe(OH)$_3$) is added to untreated water. When mixed with the water, this causes the tiny particles of dirt in the water to stick together or coagulate. Next, groups of dirt particles stick together to form larger, heavier particles called flocs which are easier to remove by settling or filtration.

\[
Al^{3+} + 3H_2O(l) \rightarrow Al(OH)_{3(s)}
\]
SEDIMENTATION
As the water and the floc particles progress through the treatment process, they move into sedimentation basins where the water moves slowly, causing the heavy floc particles to settle to the bottom. Floc which collects on the bottom of the basin is called sludge, and is piped to drying lagoons.

FILTRATION
The flocculated stream is then sent under pressure to a filter where it passes through a bed comprised of crushed anthracite, sand and gravel. Remaining suspended solids are removed giving a stream of low turbidity.

CHLORINATION
Water is disinfected before it enters the distribution system to ensure that any disease-causing bacteria, viruses, and parasites are destroyed. Residual concentrations can be maintained to guard against possible biological contamination in the water distribution system.

FLUORIDATION
Fluoride is added to the water under the direction of NSW Health to help prevent tooth decay. Drinking water must contain one milligram of fluoride for each litre of water.

pH ADJUSTMENTS
Lime is added to the filtered water to adjust the pH and stabilise the naturally soft water in order to minimise corrosion in the distribution system, and within customers’ plumbing.

Effectiveness of Water Treatment

o Advantages
  - Flocculation
    - Remove 99.9% of bacteria + 99% of viruses
    - Some organic matter from soil/vegetation removed
  - Sand Filtration
    - Removes a high proportion of particulate matter in large volumes (not efficient for small particulates)
  - Chlorination
    - Removes most micro-organisms from water and relatively low cost

o Disadvantages
  - Cl economically effective (limited against some protozoans that form cysts in water) (some such as Giardia or Cryptosporidium can still survive)
  - Membrane filtration and disinfection with ozone are more effective alternatives (but more expensive)
  - Hard water cannot be softened by the water purification method in NSW. To do this, ion exchange tubes must be used (or microscopic membrane filters).

  Effective if accompanied by proper catchment management (combination of flocculation, sand filtration, chlorination)

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

Composition

- Thin sheets of polypropylene, polysulfone or polytetrafluoroethylene with tiny holes

\[
\text{CH}_3  \\
\text{CH} \quad \text{CH}_2  \\
\text{n}
\]

Polypropylene Structure

Design

- Rolled into thin tubes. Large number of tubes are bundled into a filter.
- Water run across the surface (not at) to prevent clogging
  - Use gravity, vacuum, pressure pumps to force liquid through membrane where particulates are collected
- Sheet
  - Folded by pleating/winding in spiral around a core
  - Housed in an outer plastic container to form a cartridge – inserted/removed easily into filtration line
• Can be back flushed and reused
  ▪ Capillary
    ▪ Composed of hollow fibres
    ▪ Water runs along outside of capillaries and clean water penetrates pores to inside of each capillary
    ▪ Many capillaries bundled together to form a micro-filtration unit with large surface area
    ▪ Filters purify water by remove particulates/microorganisms etc. to improve water quality
  ➢ Water goes through the holes but particles such as bacteria cannot pass through the sheets. The filter can be cleared by passing compressed air in the opposite direction to which the water would normally flow in. The bacteria can then be dislodged.
  ➢ If the sheets are coated with deoxycholic acid, heavy metal ions can also be removed (calcium and magnesium). Used in industry where soft drinks and bottled water are produced.
  ➢ Microfiltration
    ▪ 100 – 1000 nm pore size
    ▪ Bundles of hollow polymer threads
    ▪ Remove fine silt, colloids, range of microbes (but few viruses)
  ➢ Ultrafiltration
    ▪ 5 – 50 nm pore size
    ▪ Polymers (e.g. Polysulfone and cellulose acetate) – ions removed only if membranes have special surfactant coating
    ▪ Removes all microbes incl. viruses + larger organic molecules
  ➢ Nanofiltration
    ▪ 0.5 – 5 nm pore size
    ▪ Polymers (e.g. polyamide or cellulose acetate)
    ▪ Removes all organic molecules > 300 FW + some salts containing divalent and trivalent ions
  ➢ Advantages
    ▪ Filter very small particles
    ▪ Thin, so liquids flow rapidly
    ▪ Reasonable strong; can be cleaned and reused
  ➢ Disadvantages
    ▪ Expensive; sometimes clogged with sewerage

• Perform first-hand investigations to use qualitative and quantitative tests to analyse and compare the quality of water samples (Covered in 3.5.1)

• Gather, process and present information on the range and chemistry of the tests used to: identify heavy metal pollution of water and monitor possible eutrophication of waterways
  ➢ Phosphates (PO₄³⁻)
    ▪ Phosphates are used in detergents and fabric softeners as they are capable of tying up calcium, magnesium, iron and manganese ions, thereby improving overall washing performance. Phosphates also aid in killing germs.
    ▪ Phosphates can contribute to an oversupply of phosphate (eutrophication) in waterways and cause an imbalance of the aquatic ecosystem. Excessive algal growth (sometimes in the form of algal blooms) can occur with the addition of available phosphates to the freshwater system. Blooms of cyanobacteria (blue-green algae) may also be toxic. This toxicity may be acute (short term severe) or chronic (longer-term low-level), and can be carcinogenic. Decomposer organisms that require oxygen may increase, which can deplete the amount of oxygen dissolved in the water. This can cause other aquatic life, such as fish and crustaceans, to die. The algae also cover the surface of the waterway, preventing light from penetrating into the water. This prevents aquatic plants from photosynthesising.
• Total phosphorus is determined using colourimetry. Boil the water sample with concentrated sulfuric acid and concentrated nitric acid to convert all phosphates to PO₄³⁻. Add ammonium molybdate and ascorbic acid to give a blue solution. Make a series of PO₄³⁻ standards, measure the absorbance, and plot the calibration graph. Determine the [PO₄³⁻] in the water sample from the graph.

- Nitrates (NO₃⁻)
  - Nitrates also contribute to the eutrophication of waterways and encourage excessive algal growth
  - Enter the waterway due to Sewerage and Fertiliser
  - Can be measured quantitatively through Kjeldahl method
    - The water sample is boiled with concentrated sulfuric acid to convert all nitrogen to (NH₄)₂SO₄
    - Excess NaOH is added and boiled to remove all ammonium as ammonia gas
    - NH₄⁺(aq) + OH⁻(aq) → NH₃(g) + H₂O(l)
    - The unreacted NaOH is backtitrated with HCl
    - HCl(aq) + NaOH(aq) → NaCl(aq) + H₂O(l)
    - The reacted NaOH is calculated nNaOH = nNH₃ = nN

- Heavy Metals
  - Lead, Mercury, Cadmium, Chromium, Copper, Zinc
  - Pollution of water by transition metals (Hg, Cd, As) – enter waterways from industrial discharges, road run off, landfill, agricultural runoff
  - Heavy metals Interfere with enzyme systems and metabolism in the body, Bio accumulate (build up in tissue), Bio magnify (concentration increases as heavy metal moves up food chain) and persist in environment for long periods of time
  - Can be tested for using precipitation reactions (if > 1ppm) and AAS (Atomic absorption spectroscopy)
  - Other tests: Ion Selective Electrodes (ISE), Flame Atomic Absorption Spectroscopy (FAAS), Graphite Furnace (GFAAS), X-Ray Fluorescence Spectroscopy (XRFS)

- Gather, process and present information on the features of the local town water supply in terms of: catchment area, possible sources of contamination in this catchment, chemical tests available to determine levels and types of contaminants, physical and chemical processes used to purify water, chemical additives in the water and the reasons for the presence of these additives

(Refer to Research Document for this section)