Module 3: Chemical Monitoring and Management

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

Students learn to:

- This <u>analytical chemist</u> works for the <u>NSW Environmental Protection Agency</u> (EPA) in <u>chemical environmental monitoring</u>. This chemist would have completed a Bachelor of Science (BSc) as well as postgraduate qualifications in scientific communication and management due to their status as a public servant. The chemist would be working in a team using <u>analytical techniques</u> like AAS or AES, colourimetry, infra-red spectroscopy, gas chromatography, mass spectroscopy to examine <u>water way pollutants</u> in areas like public water, storm water and recycled water. This data would provide precise contaminant levels on hundreds of <u>contaminants</u> like carbon compounds, heavy metals, viruses and microorganisms, excessive nutrients, and other hazardous chemicals. They would also study the <u>effects</u> of these chemicals of humans and surrounding environments. If excessive levels were measured, government agencies could be notified to address the problem.
- Like all scientists, <u>chemists must collaborate</u> and <u>work in teams</u>. Some may be specialists in certain areas or equipment can assist in problem solving or to make the collection of data more efficient. This increases the <u>accuracy, reliability and validity</u> of their results. Particularly in industrial chemistry, many of the various chemical industries are interdependent on each other thus collaboration is important. They must also <u>communicate</u> to keep up to date with such new development to maintain expertise in their field.
- It is important to monitor the proportion of reactants as well as correct conditions to maximise desired products. This is seen in <u>combustion</u>; if a high temperature flame and no pollutants (like carbon monoxide or soot) is desired, than complete combustion must occur. To achieve this, the reaction must occur in excess oxygen and ordinary temperature/pressure; CH₂CH_{2(g)} + 3O_{2(g)} → 2CO_{2(g)} + 2H₂O_(l) + heat. However if a low temperature flame is desired, then incomplete combustion is used instead by restricting the oxygen. If the above reaction between ethylene and oxygen is conducted at lower temperatures and with a silver catalyst, <u>ethylene oxide</u> is formed; CH₂CH_{2(g)} + ¹/₂O_{2(g)} → (CH₂CH₂)O_(g). Thus it is important to monitor reactions else bad stuff happens.

Students:

• There are a variety of <u>chemical occupations</u>, of which the following are a broad list. Do I need to come up with another chemist's occupation or will the above be fine? That this is thriller night thriller night, let me hold you tight and let me share a

Analytical	Environment	Pharmaceutical
Bimolecular	Industrial	Colloid /surface science
Organic	Inorganic	Food Processing
Mineral	Physical	Electrochemistry
Polymer	Solid state	Petrochemical

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

Students learn to:

<u>Ammonia</u> ranks second only to sulfuric acid in quantity produced each year. Ammonia is <u>used industrially</u> to <u>synthesise fertilisers</u> (sulfate of ammonia, ammonium nitrate, urea). To achieve the fertilisers, the ammonia (a weak base) is reacted with sulfuric acid to make a sulfate fertiliser, or nitric acid to make a nitrate fertiliser. It is also used to create <u>fibres and plastics</u> (rayon, acrylics, nylon). It's needed in the

High T

Kinetic Energy

Activation

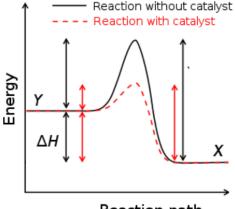
Energy

production of nitric acid, which in turn is used to make fertiliser (ammonium nitrate), dyes, fibres and plastics, and explosives such as ammonium nitrate, TNT (trinitrotoluene) and nitroglycerine (in dynamite). It is further used in household cleaners and detergents (non-ionic ones).

- <u>Ammonia</u> can be <u>synthesised</u> form gaseous nitrogen and hydrogen: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$. This • reaction is called the Haber process, after the scientist Fritz Haber who invented it.
- The synthesis of ammonia is a reversible reaction where the combination of the gases occurs whilst ammonia decomposes. Thus it's a Le Chatelier equilibrium reaction and will reach equilibrium once the forward reaction equals the reverse reaction. Critically conditions can be changed to shift the equilibrium.
- The synthesis of ammonia is an exothermic reaction in its forward progression with a heat of combustion of $\Delta H = -92 \ k J mol^{-1}$. Low T

Number of molecules

- According to the Kinetic Theory, for most reactions, increasing the temperature will result in increased molecular energy and hence increased chance of collisions. By increasing the temperature, you are increasing the chance that one nitrogen and three hydrogen molecules will impact with enough force to create two ammonia molecules. However you also increase the chance of ammonia colliding and **reverted** back to nitrogen and hydrogen too, thus by increasing temperature, you are only increasing the rate of reaction of making it reach equilibrium faster.
- The increase in temperature does actually favour the reverse reaction in the Haber process because of <u>Le Chatelier</u>. As the reaction is <u>exothermic</u>, it can be thought of like this $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} +$ heat. According to Le Chatelier, the equilibrium will shift to oppose a change in conditions. Therefore by adding heat, you are adding excess pressure to the ammonia side and as a result the equilibrium will shift to favour nitrogen and hydrogen more. Thus increasing the temperature will reduce the yield of ammonia.
- Thus there is an **optimal set of conditions** that **compromises** the above **conflicting factors** whilst crucially maintaining economic viability at the same time. This balances the reaction energy and hence reaction rate (> at high temperature) with the equilibrium position (> at low temperature). Industrially the Haber process is hence conducted at about 500°C and 25-35000 kPa Reaction without catalyst (25–35 MPa or 250–350 atm) which produces a yield of about Reaction with catalyst 30%
- According to the kinetic theory, any reaction requires a collision between the reactants of enough energy and the correct angle to break the reactant bonds and then form new ones. This activation energy is seen right in black; as the reaction is exothermic, the ΔH is negative as the product bonds occupy a lower energy state. By adding a catalyst, this lowers the activation energy, seen in red, which enables the same rate of reaction at a much lower temperature. Thus for the Haber process, a catalyst increases rate of reaction and progress to equilibrium whilst allowing the equilibrium to favour ammonia

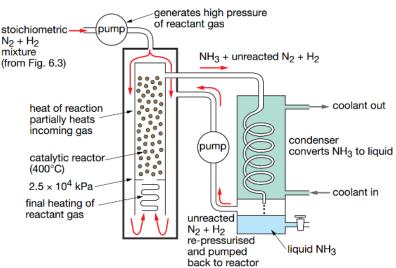


Reaction path

as an exothermic reaction, increasing yield. Industrially, this is achieved by using a finely ground iron oxide catalyst, usually magnetite Fe₃O₄, with small portions potassium oxide and aluminium oxide. The hydrogen and nitrogen are absorbed onto the solid crystal catalyst and then are more easily rearranged into ammonia.

Le Chatelier also points out that increasing the pressure will favour the side with less moles of gas to oppose the change in pressure. As the **Haber process** is $4 \mod a \ge 2 \mod b$, increasing the pressure will produce a greater yield. It will also push greater numbers of molecules together and thus increase chances of collision and hence reaction rate. Thus pressure is desirable and hence pressures of 25–35000 kPa are used. However high pressures are both expensive and dangerous. Industrially, super reinforced metal cylinders must be used and human interference with the cylinders must be reduced. The above pressures are also the **most economical**, anything higher and it becomes counter-productive.

 To the right is the <u>industrial Haber</u> <u>process</u>. The gases are pumped in a <u>stoichiometric mixture</u> (correct molar ratio so there is no excess or wastage) generating high pressure within the <u>catalytic reactor vessel</u>. These gases are then heated as the come in contact with the catalyst and the reaction occurs. A semiequilibrium is reached by the time the gases make it to the top where they are thence cooled so only the <u>ammonia condenses</u> out and hence taken away (nitrogen and hydrogen have very low boiling



points). Any **spare reactants** are then <u>recycled back through</u> and the **excess heat energy** is recycled to **reheat incoming gases**. Thus the entire process is **very delicate balancing act** and if any of the conditions (heat, pressure, activity of catalyst, stoichiometric gases, pump, condensing, quality of reactants and products, etc.) is moved from optimal, it will cause **massive economic inefficiencies** and **possibly damage** the equipment or cause **health hazards** due to dangerous nature of gases under high pressure. Thus it is crucial to <u>maintain and monitor the reaction</u> and all equipment as outline above to **maximise economic efficiency** and **maintain safety**.

Stoichiometry of the Reactants: Nitrogen is sourced easily from the air but reactive hydrogen has to be manufactured. This is achieved as follows; $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$. However the carbon dioxide is **undesirable** and has to be removed; $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$. By **injecting the appropriate ratio** of **steam, air** and **methane** into the reaction chamber, all oxygen will combust with methane as will methane as above then carbon dioxide and the resulting mixture is **carbon dioxide, nitrogen and hydrogen.** By reacting this with a **base** to remove the carbon dioxide, the correct 1: 3 ratio can be reached; just another example for the **need of monitoring** in the Haber process.

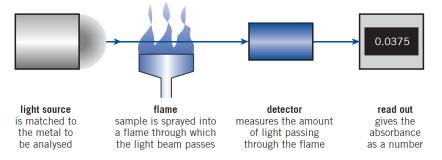
Students:

Nitrogen is essential for plants to grow and comes in fairly scarce quantities naturally, being only produced at a slow rate by microbes. In fact, the natural amount of fixed nitrogen should have limited the population of the globe to just over 2 billion through a global food crisis, the amount of nitrogen available for agriculture just wouldn't have been able to feed us all. However, a process of artificially fixing nitrogen (transforming nitrogen from its diatomic gas molecule to ammonia form) was invented by Fritz Haber, born Jewish in 1868 (ironic yes), and is the German chemist accredited with discovering the Haber-Bosch process. At the time, western countries were relying on their sources of ammonia from mined animal (bat) manure from South America (Chile) for their production of fertilisers and explosives. However with the outbreak of World War I, Germany's supply of nitrogen was blockaded by allied navies. Haber, as a staunch patriot, hence invented his process in 1908 to assist the German war effort by feeding the troops and making explosives. After being promoted as the head of Kaiser Wilhelm Institute for Physical Chemistry and with the help of Carl Bosch by 1913, they managed to industrialise the process which was being implemented on large scales. Whilst he was at it, he also managed to invent the chemical weapons chlorine and mustard gas used to horrible effects by both sides. His wife (also a chemist) committed suicide in protest against his actions, but that had little impact on his patriotism. He was awarded the Nobel Prize for chemistry in 1918 for "improving the standards of agriculture and the wellbeing of mankind." Thus, Haber invented nitrogen fixation in attempt to help Germany win the war, undoubtedly he did prolong the war, but whilst he was at it managed to feed billions of people with what has been called one of the most significant achievements of the 20th century. (Fast fact; it is estimated over 50% of the protein in your body was built on nitrogen fixed by the Haber Bosch process.)

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

Students learn to:

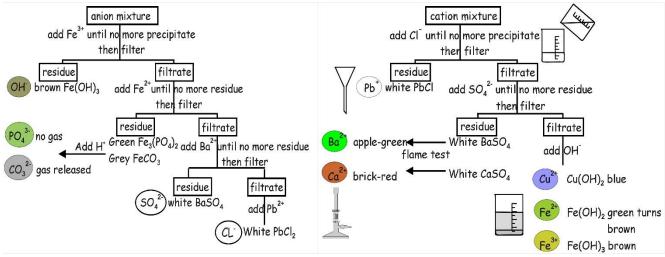
- Various ions can be detected using unique tests that are detailed below in the practical. <u>Precipitation tests</u> rely on the <u>solubility rules</u>, so for a brief recap: all group 1 metals and ammonium are <u>soluble</u>; all nitrates and acetates are soluble; all ionic halogens (except F) are soluble except with Ag, Hg, and Pb; and all sulfates except Ba, Sr, Ca, Ag, Hg, and Pb are soluble. Excepting group 1, all carbonates, hydroxides, oxides and phosphates are <u>insoluble</u>. The other option to test ions is the flame test, which relies on atomic emission of excited atoms. When the ions are burnt in a flame, a very distinct colour is produced. Pretty!
 <u>Atomic Absorption Spectroscopy</u> (AAS) is an analytical technique that can determine the concentration
- of elements up to parts per billion in the most advanced cases. Due to the definite shell structure of an atom, when light is shone, only certain frequency photons have the appropriate energy to excite an electron an hence absorb the energy of the light.



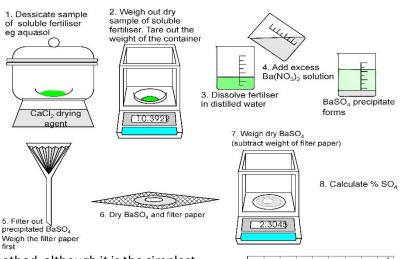
Thus, when **polychromatic light** is shone onto a sample, the differing elements in the sample will absorb specific frequencies of light creating **distinct signatures**. In **AAS**, the light source is coded to the **monochromatic frequency** of the spectra of the element being analysed. This light is then passed through a **flame** which is **consistently vaporising** the sample and into a **detector** which detects the amount of light being received. Several **standard solutions** are also tested to construct a *calibration curve*. Hence, the intensity of the sample can be plotted on the **relative absorption** graph and its **concentration** determined. This invention has led to **quick**, **accurate determinations** of **trace elements** that was not before possible. This has been applied to many areas for instance **plant growth in agriculture** was found to be majorly affected by **trace elements** like zinc, copper, iron, manganese, molybdenum and boron as a direct result of AAS. This has **increased productivity** and dealt with **food security issues** in regard to Earth's growing population. It has also assisted in **environmental monitoring** of pollutants, **detecting metal content** in mineral samples for economic viability, **testing blood or urine** samples for deficiencies of trace elements, and for testing for **toxic materials in food** and to maintain quality. Thus AAs has been crucial for the **chemical understanding** of trace elements.

Students:

• <u>Practical Investigation – Detecting Ions</u>. Aim: to identify unknown ions in solution. Variables – not applicable. Method: using solution, carry out the above flow chart tests to separate and identify the ions.



- Lead is a particularly dangerous ion as it has known harmful effects on humans. Lead has retarding mental effects on developing brains and can cause serious <u>neurological disorders</u>. Lead was commonly used in <u>leaded petroleum</u> and <u>leaded paints</u>, all paint from the 1970's contained lead and thus when renovating houses, lead can often be dispersed. Around old factories or smelter plants, lead poisoning may become an issue. Thus AAS and other analytic techniques need to be used to <u>monitor lead levels in society</u>.
- Practical Investigation Sulfate Content of Lawn Fertiliser. Aim: to measure the sulfate content of a soluble fertiliser. Variables – Weigh that sample then dissolve weighed sample in water. Add excess barium nitrate, the sulfate will displace the nitrate and create a precipitate of barium sulfate. Filter out the BaSO₄, then dry both BaSO₄ and filter paper. Weigh the sample and hence calculate the percentage sulfate.



- There are problems with the above method, although it is the simplest. Few fertilisers are fully soluble, rather forming colloids, thus try and find the most soluble one, we used Aquasol. As most fertilisers are deliquescent, it is difficult to gain their true starting mass so we desiccate (dry out) before weighing. *BaSO*₄ is a very fine precipitate which will pass through most school grade filter paper, thus extra fine filter paper and patience needs to be implemented. The *BaCl*₂ added to precipitate out the sulfate may also precipitate out other salts, affecting measurements. Thus due to the number of uncontrollable values, the experiment is not particularly reliable but could be increased with multiple repetitions.
- This dotpoint requires the interpretation of data for AAS, ie the ability to construct and analyse calibration curves. This is useful in determining pollutants and their strengths as AAS is quantitative.

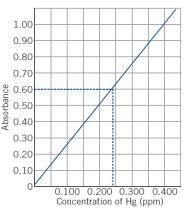


Figure 11.10 Absorbance of various standard solutions of mercury at 254 nm

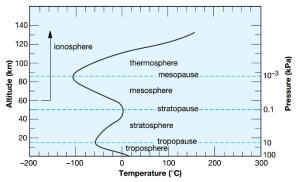
4. Human activity has caused changes in the composition and structure of the atmosphere. Chemists monitor these changes so further damage can be limited.

Students learn to:

The <u>atmosphere</u> is not consistent, rather separated into <u>four regions</u> marked by abrupt changes in temperature. The <u>troposphere</u> is lowest to earth extending 15 km up and contains the majority of the atmosphere (>70%). The <u>stratosphere</u> is next extending from 15–50 km up and the <u>ozone layer</u> is

Percentage Breakdown			
Nitrogen	78.09%		
Oxygen	20.94%		
Argon	0.93%		
Carbon Dioxide	0.036%		
Trace Molecules	<0.01%		

here. The <u>mesosphere</u> extends from **50–80 km** and is



the **coldest region**. Finally the **<u>thermosphere</u>** including the <u>ionosphere</u> is anything great than**80 km**, important in the bounce back effect of **radio communications**. Pressure in these layers **decreases exponentially**.

Lower atmosphere pollutants occur in such • small quantities that they are measured in parts per million. However the can disastrous impacts on ecosystems and the environment. To the right are **some common pollutants**.

Photochemical Smog: is a product of several pollutants, mainly nitrous oxides but also sulfur oxides and ozone. The NO_{χ} is produced in internal combustion engines where high energies allow nitrogen and oxygen gas to fuse. These then progressively combine with oxygen to generate the brown smog. These NO_{χ} then decay; $NO_{2(g)} + UV \ light \rightarrow NO_{(g)} + \cdot O_{(g)},$ oxygen free radical will combine with O₂ to form ozone. Photochemical smogs are becoming

Pollutant	Source	
Lead	Vehicles using leaded petrol.	
Sulfur Oxides	Fossil fuels, mineral smelter.	
Nitrogen Oxides	High temperature	
	combustion.	
Methane	Organic decay, natural gas	
	leakage, ruminants (cows).	
Particulates	Combustion, industry, dust	
	storms, bush fires, asbestos.	
Hydrocarbons	Vehicle w hydrocarbon fuels	
Carbon Monoxide	Fossil fuels (vehicles).	
Carbon Dioxide	Fossil fuels, deforestation.	
Chlorofluorocarbons	Spray cans, refrigerant/ air	
(CFCs)	con coolant, foaming agent.	

increasing problems in major cities as more and more vehicles appear and can only be solved with the reduction of vehicles; although the use of catalytic converters can reduce the quantities of NO_{x} being ejected.

Ozone is the triatomic allotrope of oxygen. It's structure, as below, is bent because of the unbonded pair. This also makes it unusually **polar**. It is found in the **troposphere as a pollutant**, being an indicator and component of **photochemical smog**. It is also irritating, unpleasant odour in concentrations >1 ppm and is poisonous >20 ppm due to its ability to react with biological hydrocarbons. It can cause respiratory problems (especially those already suffering them like asthma), fatigue, and lowers resistance to disease. It is powerful enough to be used to sterilise swimming pool water. However it is crucial in the stratosphere where it forms the ozone layer, found in concentrations up to 8 ppm. Here, it absorbs the energy of UV light by decomposition; $O_{2(g)} \rightleftharpoons 2 \cdot O_{(g)}$ and then $O_{2(g)} \leftrightarrow O_{3(g)}$. The reactions are reversible because ozone easily decays down to diatomic oxygen, often induced by UV light too. Thus the ozone layer regenerates and blocks UV rays. This radiation shield is crucial as UV light has high enough

 $c \equiv o$ $c \equiv o$

energy to break the bonds in important biological structures like proteins and DNA. Excessive exposure to UV leads to skin cancer, sunburn, and increased mutations. It would also disastrously impact on other life forms and effectively destroy the known food system.

Hydronium

$$H \underbrace{\stackrel{O}{\underset{H}{\longrightarrow}}}_{H} H \xrightarrow{\stackrel{O}{\underset{H}{\longrightarrow}}}_{H} H + H^{+} \rightarrow \left[H : \overset{O}{\underset{H}{\otimes}} : H \right]^{+}$$
Ammonium

$$\stackrel{H}{\underset{H}{\longrightarrow}}_{H} H : \overset{O}{\underset{H}{\otimes}} : H + H^{+} \rightarrow \left[H : \overset{O}{\underset{H}{\otimes}} : H \right]^{+}$$

Η

А coordinate covalent bond is formed where two non-metallic atoms bond to form a covalent bond however only one atom contributes the electrons to the bond. However once this bond is formed. it is indistinguishable from an ordinary covalent bond, they function exactly the same.

Lewis electron dot structures of coordinate covalent bonds as left.

Ozone

Η

 H^{\prime}

Property	Oxygen	Ozone	Explanation
Symbol	02	03	Yeah
Melting/ Boiling	M: -219° <i>C</i> B: -193° <i>C</i>	M: −183°C B: −111°C	As ozone has greater mass, it generates more dispersion forces thus increasing
Point			melting and boiling point.
Odour	Odourless.	Sharp, irritating odour.	Umm?
Colour	Colourless	Pale blue	I knew we should've done Chemistry of Art
Density	A bit denser than air.	About 1.5 denser than air.	Good question
Stability	Stable.	Unstable.	The coordinate bond and the bent structure do not have the strength so ozone readily dissociates.
Reactivity	Good oxidant, will react with most metals.	Even better oxidant, will react with everything. Also attack alkene bonds.	The oxidation reaction can be used to return to a diatomic state without producing a free radical.
Solubility	Sparingly soluble.	More soluble.	The bent and polar structure of ozone allows it to be more soluble than oxygen in water due to dipole-dipole bonding.
Uses	Respiration and combustion, amongst others.	Sterilising pool water or stagnant air.	Biology stuff. The toxicity of ozone allows it to kill harmful bacteria then decay into oxygen.
Preparation	Distillation of liquid air or decomposition of hydrogen peroxide. Electrical discharge or UV light through oxygen.		
Test	Combustion test.	Characteristic odour.	

The oxygen molecule is a stable gaseous diatomic allotrope of oxygen. It has four pairs of electrons in each valence shell of both atoms due to the **double bond**. The **oxygen radical** just has 2 electron pairs and 2 radicals or unpaired electrons. This makes it highly reactive and very unstable thus it doesn't remain unbonded for long, often bonding with diatomic oxygen to form ozone.

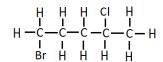


Haloalkanes are a class of alkanes that contain one or more halogens in the chain. Chlorofluorocarbons (CFCs) are haloalkanes that contain only chlorine and fluorine attached to carbon. Halons are CFCs with the addition of **bromine**. They are both **inert** with a low **boiling point** (assuming they are short chained). are non-toxic and non-flammable (halons are excellent fire retardants) and thus replaced ammonia as a refrigerant because they were considered 'safer'. They were also used for aerosol propellant and foaming agents. Halons were also used extensively in fire extinguishers. When these were inevitably released into the atmosphere their inertness

meant they built up in the troposphere and then diffused into the stratosphere where they cause problems.

- Haloalkanes are named just like hydrocarbons, any non-hydrogen atom is given a prefix (chloro, fluoro, bromo, iodo) that are ordered in alphabetical order. Numbers are attached to indicate the placing of each atom. Right are several isomers of $C_5 H_{10} Br Cl$.
- When CFCs and Halons are used, they are discarded into the atmosphere where they are inert, non-toxic and with low solubility allow them to build up the troposphere and then diffuse into the stratosphere. Once there, they are decomposed by UV light and Chlorine free radicals are released. These are highly effective at decomposing ozone as shown on the next page and take a very long time to stop as they continue to cycle through. This destruction of the ozone layer is dangerous as it means more UV radiation reaches earth.

1-bromo-2-chloropentane



1-bromo-4-chloropentane

3-bromo-2-chloropentane

UV photons have high enough energy to break chemical bonds in proteins like DNA and can thus cause <u>vast biological harm</u> such as cancer, cataracts, and decreased crop productivity. UV also degrades plastics. CFCs are also known greenhouse gases thus contribute to climate change which is also undesirable. When scientists realised the damage CFCs were causing, extensive lobbying brought about the <u>Montreal Protocol</u> in 1987 which aimed to phase CFCs out of developed countries by 1995. Two amendments, in London (1990) and Copenhagen (1992) decreased CFC use further to virtually zero today. As a result, <u>replacements</u> had to be sourced. Pure

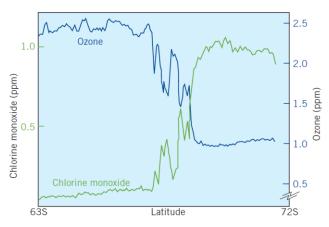


Figure 13.15 Levels of $\cdot \rm CIO$ and $\rm O_3$ in stagnant air above the Antarctic, spring 1987

hydrocarbons or manual pressure packs have replaced CFCs as aerosol propellant whilst hydrochlorofluorocarbons (HCFCs) and hydroflurocarbons (HFCs) are used as refrigerants. These are much more reactive so rarely make it to the stratosphere to react with ozone. Halons were also phased out to be replaced with other fire retardants like CO_2 . The effectiveness of these steps are reliant on global governments adhering to the treaty, with much success so far, however we lack technology to remove CFC's directly from the atmosphere. These measures have been effective in <u>stabilising Chlorine</u> radicals however it is predicted that these levels will only reach pre-1970 concentrations until after 2050 and until then we must live with the consequences like encouraging humans to apply increased sun protection and building UV stabilisers into polymers.

In 1987 the NASA experiment entitled the <u>Airborne Antarctic Ozone Experiment</u>, measured the concentrations of Chlorine Monoxide and Ozone at different latitudes resulting in the graph on the left. Other instruments include the <u>Total Ozone Measuring Spectrometer</u> (TOMS) which is satellite spectroscopy of ozone levels and ground spectrophotometers, both of these instruments rely of the

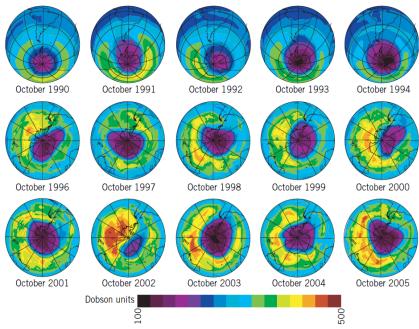


Figure 13.16 TOMS total column ozone measured over the period 1990-2005

absorption spectra of ozone. **Balloons** with physical measuring devices are also used and together have extensively mapped ozone concentrations globally since 1957. These ozone levels are measured from the ground to the limit of the atmosphere and recorded in Dobson Units. The trend has been noted that ozone levels deplete by up to 50% in the spring over lower latitudes, shown left, and this ozone hole has been increasing. It is estimated we have lost 3% of global ozone levels. Thus many statistical measurements of global ozone levels have shown they are decreasing. However some more recent records are showing a stabilisation of ozone levels.

Students:

- The following reactions are the **catalytic reaction** between chlorine and ozone:
 - $0 \cdot + 0_2 \rightarrow 0_3$ (ozone formation).

- \circ $CCl_3F \rightarrow Cl \cdot + CCl_2F \cdot$ (free radical formation as a result of UV radiation)
- \circ $Cl \cdot + O_3 \rightarrow ClO \cdot + O_2$ (chlorine monoxide as intermediary free radical)
- $ClO \cdot + O \rightarrow Cl \cdot + O_2$ (regeneration of chlorine free radical)

The cycle terminates in these equations:

- $Cl + CH_4 \rightarrow HCl + CH_3$ · (the reaction with methane result in unreactive HCl)
- \circ ClO + NO₂ \rightarrow ClONO₂ (the reaction with nitrogen dioxide is also unreactive)

However the winter particulates can **catalyse** this reaction and <u>reintroduce chlorine radicals</u>: \cap HCl + ClONO₂ \rightarrow Cl₂ + HNO₃

Thus **Chlorofluorocarbons** in the Antarctic atmosphere can last for up to **150 years** before dissipating and are thus extremely destructive to ozone.

<u>HCFCs</u> are more reactive and thus have less chance of making it to the stratosphere however they still contain <u>Ozone Depletion Potential (ODP)</u>. They are more expensive, harder to handle but still get the job done however are only considered a temporary solution. <u>HFCs</u> have zero ODP and are thus the ultimate goal for replacement however they are much more expensive and more inefficient than even HCFCs. These substitutes have been enforced by the <u>Montreal Protocol</u> and are thus highly effective however they only prevent further damage, as described above.

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.

Students learn to:

- Water quality is essential to monitor due to its wide variety of uses and impacts it can have, for instance on drinking water. A healthy environment is one in which the water quality supports a rich and varied community of organisms and protects public health. Water quality is determined by considering the following factors:
 - <u>Concentrations of lons</u>: including salinity, if there are too many salts or ions present, the excess may be harmful to biological processes. The opposite is also true for marine ecosystems where salts including Na^+ , Cl^- , and SO_4^{2-} are necessary. Excess carbonates (CO_3^{2-}) can increase pH (bases) and increased Ca^{2+} and Mg^{2+} can increase hardness. Phosphates (PO_4^{3-}) and Nitrates (NO_3^{-}) as excess nutrients can cause eutrophication. These ions are identified qualitatively through precipitation and quantitatively through <u>AAS</u>.
 - <u>Total Dissolved Solids (TDS)</u>: water is generally considered cleaner if it has less solids dissolved. TDS and salinity are often synonyms but TDS refers to every impurity dissolved. They can be easily quantitatively described gravimetrically after evaporation. Can also be tested quantitatively by <u>electrical conductivity</u> (although this only test ions).
 - <u>Hardness</u>: hardness of water is the amount of Ca^{2+} and Mg^{2+} . Hard water is not a health hazard but is undesirable because it <u>doesn't allow soap to lather</u>, instead forming scum in its place thus limiting its uses. It also forms scale under high temperatures which can coagulate and reduce efficiency. It is best determined quantitatively via volumetric titration with <u>ethylenediaminetetraacetic acid (EDTA)</u> but can also be determined gravimetrically through precipitation.
 - <u>Turbidity</u>: is the cloudiness or murkiness cause by the number of <u>particles suspended</u> in the water, often clay, silt, plankton or human waste. It can affect aquatic ecosystems by altering the sunlight penetration. It is generally determined using a <u>secchi disk</u> or <u>turbidity tube</u> where the disk is lowered until it can no longer be seen then compared against a calibration scale. It can be determined more accurately with spectroscopy. With an appropriate filter, turbidity can also be measured gravimetrically. It is measured in nephelometric turbidity units (NTU).
 - <u>Acidity:</u> water should have a pH of between **6.5 and 8.5**. Anything else indicates a polluted environment, probably from **acid rain** or **detergent pollution**. If the water is out of this range,

it can have large **detrimental effects on aquatic ecosystems**. The pH can be measured qualitatively using a **<u>universal indicator</u>** or a quantitatively with **<u>pH meter</u>**.

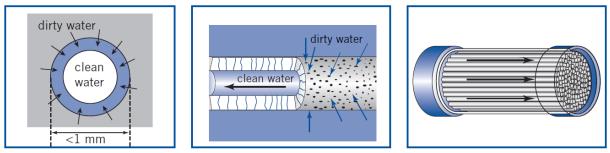
- **Dissolved Oxygen (DO):** refers to the amount of **diatomic oxygen** dissolved in the water. This is an excellent test of water quality as many factors of healthy water rely on oxygen. Normal oxygen concentrations range from **6-9 ppm** but low oxygen of 5 ppm will cause **death** for some aquatic species. The amount of oxygen dissolved is greatly affected by the **temperature** of the water and the **pollutants** in the water. There are two ways of testing quantitatively for DO; the <u>Wrinkler Titration</u> $(4H^+_{(aq)} + O_{2(aq)} + 4S_2O_3^{2-}_{(aq)} \rightarrow 2S_4O_6^{2-}_{(aq)} + 2H_2O_{(l)})$ where **Manganese** and **lodine** ions are added and then titrated against **sodium thiosulfate** to determine the oxygen dissolved or simply using an <u>DO meter</u> based on electrochemical cells.
- <u>Biochemical Oxygen Demand (BOD)</u>: is the amount of time it takes for aerobic bacteria to decompose organic matter in the water. It is essentially a test for the amount of organic pollution in a sample and is achieved by measuring the DO then sealing and incubating at 20°C for 5 days in the dark and measuring the consumed DO after. Generally, absorptions of more than 4 ppm are considered polluted.
- The pathway the water takes is one crucial aspect in determining the ion concentration of natural bodies. If the water passes quickly over land there will be less ions present as there is less opportunity for dissolving. Common ions dissolved here are CO₃²⁻, SO₄²⁻, Cl⁻, Ca²⁺, Na⁺, Mg²⁺, and K⁺. If the water flows deeper into underground aquifers, it may dissolve heavy metals like Fe, Mn, Cu, and Zn. The more frequent the rain, the more likely than ions will collect in natural water bodies. Also higher temperatures will increase the tendency to dissolve ions. The pH of acid rain makes it more soluble for ions like Ca²⁺, Mg²⁺ and Fe³⁺. If human practices are present through the water pathway then this can increase ion concentrations. If land is cleared, then mineral rich dirt is exposed which greatly increases ion availability. Unnatural effluent discharge like sewers or storm water can also have greatly increased and varied ion concentrations. Leaching form rubbish tips and industrial waste can increase heavy metal concentrations like Hg²⁺ and Cd²⁺. Agricultural practices also largely contribute to ion concentrations of PO₄³⁺ and NO₃⁻ due to artificial fertilisers.
- Drinking water is carefully monitored to ensure that is suitable for human consumption. It undergoes eight main purification methods to reach suitable drinking standards, listed below:
 - <u>Screening</u>: water from the catchment area is passed through a sieve like filter to ensure all sticks, leaves, aquatic life, etc. is removed from the incoming water. Effective in its purpose but useless isolated.
 - <u>Aeration</u>: the water is sprayed into the air to increase dissolved oxygen levels (also making it taste better) and to oxidise metallic salts like iron which are later easier removed as insoluble $(2Fe^{2+}_{(aq)} + O_{2(a)} \rightarrow 2FeO_{(s)})$.
 - Flocculation: or coagulation is where alum (Aluminium sulfate) or is added with calcium hydroxide to form a gelatinous precipitate aluminium hydroxide which attracts and gathers colloid particulates, precipitate iron and some bacteria. This method is highly cost effective and very fast, thus extremely useful.
 - <u>Sedimentation</u>: or clarification is where the water is distilled and decanted (in massive tanks with pumps). 90% of the flocs of about 1000 μm form <u>sludge</u> which is in turn dried and composted. This utilises a natural force (gravity) for separation reducing the plants running costs but the time taken to settle may effect efficiency.
 - \circ **Filtration:** is where the water is passed through layers of **sand and gravel** of increasing fineness where the effective pore size is about 100 µm. Charcoal filters may also be used to remove colour. This is effective in **filtering particulates** but not microorganisms. A granular method is effective as it is cheap and good enough for urban consumption. For a finer filter, membrane filters are used.
 - <u>Chlorination</u>: the water is treated with chlorine gas $(Cl_{2(g)} + H_2O_{(l)} \rightarrow H^+ + Cl^- + HOCl)$. This successfully sterilises the water of many pathogenic organisms due to the <u>hypochlorous</u> <u>acid</u> (HOCl) but fails to have a huge effect on viruses. Chlorine can also impart an unfortunate

taste to the water. Thus <u>ozone</u> is also being used as it is both effective against **pathogens and viruses** whilst also oxidising water thus **increasing taste**. These are effective ways and killing microorganisms that are relatively cheap and effective.

- <u>pH Adjustment</u>: various acids or bases (ammonia or hydrated lime) is used to bring the pH of the water to between 7 and 8.5. This is crucial in drinking suitability and corrosion during transport.
- **Fluoridation:** a **health measure**, fluoride compounds like sodium hexaflourosilicate (Na_2SiF_6) to raise the fluoride ion concentration to 1 ppm. This helps with **tooth decay** and is considered one of the most effective public health measures.

This is the **<u>purification cycle</u>**. Each step is **effective** at its job but **useless** if not combined with the rest of the cycle. The effectiveness of the purification method is now **monitored daily** after two bacteria strains made it through chlorination and filtration. Thus the purification of mass water supplies is **highly effective**.

Microscopic membrane filters are made from polymers and filter out molecules from the water. The uniform pore size can effectively filter out very small particulates in the water, with nanofiltration they can filter ions out of water although the <u>average pore size is 0.5 µm</u>. They are very effective at filtering microorganisms and are thus use when <u>high quality filtration</u> is needed. They work on pressure, the water is made to flow across the filter (which reduces blockage) and forced through to the other side due to pressure generated from pumps, gravity, etc. As below, the filters are often implemented in tubes where water is passed along and hence through the filter. They have three main designs, <u>depth membranes</u> which are randomly organised combinations of polymers that ultimately lead to a fairly regular pore size. <u>Screen filters</u> are much more controlled but more expensive as they are designed by firing ions through thin polymer to create the appropriate pore. <u>Composite and layered filters</u> are last and are effectively a strategic combination of two membranes for a specific purpose. Common polymers used are polypropylene and polytetrafluoroethylene (PTFE). They can be blocked by excess particles easily if not used correctly but can be easy to clean and reuse.



Students:

- When <u>comparing water quality</u>, two types of tests are applied. <u>Qualitative tests</u> detect the presence (or absence) of ions or the aspect of water quality. They can be subjective relying on human senses or can use chemical reactions. <u>Quantitative tests</u> are tests that assign a number to the value, whether this be %, ppm, gL⁻¹, molL⁻¹. Above are lists of tests, both qualitative and quantitative, that test the various factors of water quality.
- <u>Heavy metals</u> can be toxic to human health in high quantities. They are found in small percentages in the crust however if leaked they can gather in some organisms and thus proceed up the food chain in high quantities. Heavy metals are the transition metals including lead and arsenic but the ones of most concern to human health are mercury, lead, cadmium, chromium and arsenic. They are easily <u>quantitatively</u> identified using AAS however one of the most common chemical tests is the sulfide test. The sample is first acidified, then sodium sulfide is added; when a precipitate is formed then lead, silver, mercury, copper, cadmium or arsenic is present. If no precipitate is formed then the sample is made alkaline. If a precipitate is formed, then chromium, zinc, iron, nickel, cobalt, manganese or aluminium is present. This is because the

sulfide reacts in **equilibrium**, $(S^{2-}_{(aq)} + 2H_3O^+_{(aq)} \rightleftharpoons H_2S_{(aq)} + 2H_2O_{(l)})$ acid favours the right whilst alkaline favours the left thus dictating the amount of sulfide available and hence ease of precipitation. Other **<u>qualitative tests</u>** for heavy metals include **precipitation tests** and **flame tests**. Eutrophication is where excess nutrients are deposited into a body of water which sparks an excessive algal bloom. The nutrients are all eaten up and so the algae dies, stopping sunlight reaching lower water depths whilst also leaching oxygen due to increased BOD. Thus, levels of nitrates and phosphates need to be measured to prevent the aquatic dead zones that occur with eutrophication. Nitrates are measured by identifying the total nitrogen levels. This is achieved with quantitative Kjeldahl digestion, where the nitrates are treated with sulfuric acid and sodium hydroxide to form ammonia which is in turn back titrated against hydrochloric acid. Both phosphates and nitrates can be measured with the quantitative colorimetric test. For nitrates, the sample is digested as above by sulfuric acid to form ammonium sulfate which is then reacted with **Nessler's reagent** which reacts with nitrogenous compounds to form a yellow compound. For phosphates, measured quantities of ammonium molybdate and ascorbic acid is reacted which forms an intensely blue complex compound called molybdenum blue. The colorimeter then measures the concentration of colour determining the level of nutrients. COFFS

- The **<u>Coffs Harbour Water Supply</u>** supplies all of Coffs Harbour's water needs:
 - Catchment Area: are areas of land where rain water drains into a common 0 body. Coffs Harbour sources its water from the Clarence River catchment which is 23,000 km² in size. Our main source is the Orara River which is periodically pumped into Karangi Dam (holds 5.6 Gigalitres) during high flow seasons and when raw quality is good. As a further security measure, we can source water from the Shannon Creek Dam (holds 30 Gigalitres) which is filled by the Nymboida River similarly but also supplies the Clarence Valley.



- Contamination: Land clearing activities can make soil unstable increasing turbidity and 0 TDS, especially during flood periods. Agricultural activity throughout the catchment increases nutrient levels and also increases pesticides and animal faeces contamination. Mining activities are also a major source of contaminants, especially from the Dorrigo Antimony Mine and Coal Seam Gas emplacements where toxic ions can leach into the catchment. Sewage overflow during flood season can also largely contaminate with bacteria and excess ions. Decaying animals in water systems can release dangerous pathogens into the water. Natural soil also provides high ion concentrations.
- **Chemical Testing:** the testing for Coffs Harbour is controlled by the **NSW Health Drinking** 0 Water Monitoring Program where our NATA accredited Environmental Laboratory collects samples for testing by the Forensic & Analytical Science Service (FASS) in Sydney. Both FASS and the Environmental Laboratory conduct chemical tests as described above on alkalinity, pH, TDS, hardness, colour turbidity, various ions and E.coli.
- Physical/Chemical Treatment: Coffs Harbour Water selectively 0 pumps (controlled abstraction) in water of turbidity levels less than 2 NTU to ensure raw water quality. Aeration at the dam is also employed then the water is processed at the **Dissolved Air Flotation and Filtration (DAFF) Treatment Plant** using the above processes (although UV irradiation is also added for further disinfection). From here, it is distributed.
- Chemical Additives: Coffs Harbour Water currently adds 0 Fluoride as per NSW Health directions, described above. It also treats its water with chlorine as a disinfectant and even uses Chlorine Booster Plants to ensure that chlorine levels remain constant for all water as described above.

