Environmental Chemistry - Water

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Hardness of Water:

Hard water is water that will not easily form a lather with soap. Hardness in water is caused by the presence of Ca^{2+} or Mg^{2+} ions.

One of the most common substances in soap is a chemical called sodium stearate ($C_{17}H_{35}COONa$). When soap is added to hard water, the Ca^{2+} ions react with the stearate to form calcium stearate (scum)

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Hardness in water may be classified as :

- Temporary
- Permanent

<u>Temporary hardness</u> is hardness that can be removed by boiling the water. Temporary hardness arises due too dissolved gases in the water (usually CO_2)

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How heating water removes hardness.

Limestone is insoluble in water but reacts with carbonic acid. This reactions forms calcium hydrogencarbonate (soluble).

$$CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2$$

The Ca^{2+} ions cause hardness and the HCO_3^- ions have no effect on hardness. However if water containing the two ions is heated a chemical reaction occurs which removes the Ca^{2+} ions from the water so the water is softened.

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Permanent hardness is hardness that cannot be removed by boiling water.

There are however other methods that can be used:

1) Distillation: this involves boiling the water & cooling the vapour.
2) Using Washing Soda: washing soda contains carbonate ions which react with the calcium ions in the water & removes them.
3) Ion exchange resin

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3. Ion Exchange Resin: this is the easiest way of removing hardness. Essentially the ion exchange resin swaps the ions that cause hardness with ions that do not cause it.

Ion exchange units used to soften water contain cation exchange resin. Thus, the Ca^{2+} & Mg^{2+} ions are swapped for Na^{+} ions.

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In some cases it is necessary to have all of the ions removed from water i.e. deionised water. Such water is produced by passing it through a water deioniser that contains a mixture of cation & anion exchange resin. This mixture is referred to as mixed bed resin.

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Advantages & Disadvantages of Hard Water

Advantages	Disadvantages
Provides calcium for teeth & bones	Blocks pipes, leaves scale on kettles
Nicer taste	Wastes soap
Good for brewing	Produces scum

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Exp: To determine the total water hardness in a water sample using ethylenediaminetetraaccetic acid (edta)

Total hardness of water = calcium hardness + magnesium hardness

Degree of hardness	ppm of $CaCO_3$*
Soft	0-75
Moderately Hard	75-150
Hard	150-300
Very Hard	>300

*it is traditional to use $CaCO_3$ to represent the compound causing hardness even if other compounds might also cause it.

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Ethylenediaminetetraaccetic acid (edta)

You must be able to write the full name!

Ca^{2+} ion forms a complex ion when bonded with edta.

$$H_2X^{2-} + Ca^{2+} \longrightarrow CaX^{2-} + 2H^+ \qquad \text{(Ratio 1:1)}$$

Edta ion — Complex ion

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Eriochrome Black T (Solochrome Black)

Eriochrome Black T is the indicator for the reaction.

The indicator reacts with Ca^{2+} and Mg^{2+} ions to give a wine-red colour. So the initial colour of the solution will be wine-red.

As edta is added complex ions involving the Ca^{2+} and Mg^{2+} ions are formed, reducing the wine-red colour. The endpoint occurs when a colour change of wine-red to blue is observed.

This endpoint is difficult to detect as is it not as obvious as acid-base titrations.

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Complexometric titration

This type of titration is called a complexometric titration.

A complexometric titration is a titration involving the formations of a complex between metal ions and a reagents such as edta. In this type of titration the end point is marked by a sharp decrease in the concentration of the free ions.

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Buffer solution

This experiment requires a pH of 10 to be kept constant, as the edta will not full complex with the Ca^{2+} and Mg^{2+} ions otherwise.

Eriochrome Black T also requires a pH of 8-10 for the colour change to occur

A buffer solution is used to maintain this pH.

A buffer solution is a solution that resists changes in pH i.e. it keeps the pH constant.

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Titration

The titration is carried out in the usual manner, key points to note are:

- The pipette is rinsed with hard water, the burette with edta.
- Conical flask contains; 25cm^3 of hard water, 1 cm^3 of pH 10 buffer, and a small amount of Eriochrome Black T (solid).
- Edta is stored in a plastic container as it reacts with the ions in glass if left in glass container for a long period.
- Initial wine-red colour tells us that Ca^{2+} and Mg^{2+} ions are present.
- Usual titration calculation is performed, the ratio is always 1:1.

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Water Treatment:

1. Screening: this passes the water through a wire mesh to remove any floating debris like twigs etc.

2. Flocculation: means the coming together (coagulation) of suspended particles. This is done by adding certain chemicals to the water, called flocculating agents e.g. $Al_2(SO_4)_3$

(A flocculent is a chemical added to water to coagulate suspended particles.)

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<u>3. Settlement: </u>water is passed into settlement tanks. The water flows in at the bottom & rises up slowly to the surface where the clear water is collected. Over 90% of the particles are removed during this stage.

<u>4. Filtration: </u>water from top of settlement tank is passed though beds of sand. These filter beds remove any remaining suspended solids. The sand acts as a sieve of filter paper. The water from this stage comes out clean.

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5. Chlorination: chlorine is added to water to sterilise it & therefore get rid of harmful micro – organisms. Only a small amount of Cl is added so it doesn't affect the taste of water.

6. Fluoridation: small amounts of Fluorine are added to help reduce dental decay – it strengthens the enamel of the teeth.

7. pH Adjustment: the pH needs to be raised above pH 7.

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Chemical	Purpose	Problems when used in excess
Aluminium sulfate	Coagulation of small suspended particles	Taste of water affected. Corrosion of pipes
Chlorine	Sterilise water	Taste and smell of water affected
Fluorine compound (e.g. sodium fluoride)	Reduce tooth decay	Staining of teeth
Sodium Carbonate	Soften water	Taste of water is affected
Calcium hydroxide	Raise pH	Hardness of water
Sulfuric acid	Lower pH	Corrosion of pipes

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Exp: To determine a) the total suspended solids (ppm) in a sample of water by filtration

Procedure	Observation	Explanation
Fill volumetric flask with to mark with sample of water		Volume of water precisely known
Mass of filter paper found using mass balance.		Used in calculation
Filter water through the filter paper	Solids will remain on the filter paper	
Allow filter paper to air dry		Evaporate water for precise result
Find new mass of filter paper.		Used in calculation
Find mass of suspended solids using subtraction		

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Exp: To determine b) to measure the total dissolved solids (ppm) in a sample of water by evaporation

Procedure	Observation	Explanation
Find the mass of a clean dry beaker		Used in calculation
Using graduated cylinder place a known volume of filtered water in the beaker		Known volume of water, with no suspended solids.
Heat beaker until all water is evaporated.	Solids observed on the bottom and side of the beaker.	Dissolved solids are left in the beaker.
Find new mass of the beaker.		Used in calculation
Find mass of dissolved solids using subtraction		

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Exp: To determine c) to measure the pH of a sample of tap water

Procedure	Observation	Explanation
Place pH probe (sensor) in a sample of tap water. Record the result.		

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Water Pollution:

- The release of substances into the environment that damage the environment is called pollution.
- Dissolved oxygen in rivers, lakes etc is essential for the survival of fish & other forms of life.
- When organic waste (like animal slurry, sewage & effluent)_enters a waterway it leads to an increase in bacteria & other organisms.

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- These bacteria / organisms use up the oxygen in the water. The oxygen level may be reduced so much that fish may be reduced or even die.

- If dissolved oxygen drops to zero, anaerobic bacteria will take over & the river will become foul smelling (polluted)

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In the 1900's the Royal Commission on Sewage Disposal introduced a test to measure the demand that water has for dissolved oxygen.

This test is called the Biochemical Oxygen Demand (B.O.D test).

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Biochemical oxygen demand is defined as :

The amount of dissolved oxygen consumed by biological action when a sample of water is kept at 20 ^{0}C in the dark for five days

BOD: is difference in the two dissolved O_2 levels as this is the amount of O_2 that has been used up during the test.

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Eutrophication: another way to reduce the amount of dissolved in water is to overload the water with plant nutrients, especially nitrate ions & phosphate ions. This 'over – enrichment' is called eutrophication.

As nitrate / phosphate levels rise, many plants undergo population explosions. When they die off a heavy oxygen demand is placed on water.

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This causes the dissolved oxygen to drop & many forms of animal life are killed.

Eutrophication is the enrichment of water with nutrients, which leads to excessive growth of algae.

Eutrophication: can occur naturally or artificially, can occur naturally in lakes or as a result of artificial fertiliser being washed into rivers.

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Exp: To measure the amount of dissolved oxygen in a sample of water by redox reaction (Winkler method)

This experiment involved three key reactions;

$4Mn(OH)_2 + O_2 + 2H_2O \longrightarrow 4Mn(OH)_3\downarrow$ …addition of manganese dioxide to water produces a brown ppt.

$2Mn(OH)_3 + 2I^- + 6H^+ \longrightarrow I_2 + 6H_2O + 2Mn^{2+}$ …addition of sulphuric acid and potassium iodide liberates iodine

$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$ …titration of sodium thiosulphate and iodine can measure the concentration of iodine.

$1\ O_2 : 4Mn(OH)_3 : 2I_2 : 4\ S_2O_3^{2-}$

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Procedure	Observation	Explanation
Bottle is rinsed out with water with water being analysed, bottle is submerged in the water and filled to the brim.		Rinsing: remove impurities, avoid traped air bubbles. Submerging: make sure no air bubbles are trapped
Dropper is inserted below the water level and concentrated manangese(II) sulphate is added.	Manganese(II) sulphate sinks to the bottom, some water is displaced. White precipitate formed	Sinks: solution is more dense than water Concentrated: to minimize the amount of water sample displaced. White ppt: $Mn(OH)_2$ is formed
Method above repeated for alkaline potassium iodide.	Potassium iodide sinks to the bottom, some water is displaced. Brown precipitate formed	Sinks: solution is more dense than water Concentrated: to minimize the amount of water sample displaced. Brown ppt: $Mn(OH)_3$ is formed
Bottle is shaken and then allowed to settle out again. Small volume of concentrated sulphuric acid is added. Bottle is stoppered taking care not to trap any oxygen, and is inverted.	Brown ppt dissolves Red-brown solution forms.	Brown ppt dissolves: $2Mn(OH)_3 + 2I^- + 6H^+ \longrightarrow I_2 + 6H_2O + 2Mn^{2+}$ Red-brown colour is caused by iodine being liberated.
Titration of the solution containing iodine and sodium thiosulphate is carried out.	Red-brown to straw yellow Starch added Blue-black to colourless	Concentration of iodine is found which can be used to calculate the concentration of oxygen in the sample of water.

Sewage Treatment: The process for the treatment of sewage can be divided into 3 stages:

- Primary
- Secondary
- Tertiary

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Primary Treatment:

- Solids that are floating in the sewage are removed by passing the sewage through steel bars, this process is called screening.

- The sewage then flows into large settling tanks. The solids settle at the bottom of these tanks to form sludge. Process is called settlement or sedimentation.

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Secondary Treatment: is a biological process in which the levels of suspended & dissolved organic material are reduced.

One of the most common methods of bringing about this bacterial breakdown involves the Activated Sludge Process. This consists of an aeration tank followed by a settling tank.

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- Sewage is pumped into large aeration tanks where it provides nutrients for a large number of growing micro – organisms – Activated Sludge.
- These micro-organisms digest the sewage & it is broken down.
- The liquid in the aeration is kept aerated by a mechanical rotor that continually churn the liquid & sludge with the air.

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- From the aeration tanks, the sewage flows into a settling tank.
- Some of the sludge is removed & some is recycled back to the aeration tanks to come in contact with fresh sewage.

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Tertiary Treatment: involves the removal of phosphorus & nitrogen compounds from effluents.

- Phosphates come from household detergents. They are removed by precipitation. eg adding aluminium sulfate.
- Nitrates come from organic materials in sewage. Its removal is difficult & expensive.

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Heavy Metal Pollution of Water:

Metals with high atomic masses such as lead (Pb), mercury (Hg) or cadmium (Cd) are known as heavy metals.

Deposit ions of these metals can get into water from industrial effluent and eventually into drinking water.

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These elements are cumulative poisons, in that frequent exposure causes a build up in the body with consequent serious health damage.

Removal of Heavy Metals

Metal ions can be removed by means of precipitation. For example lead (II) hydroxide, $Pb(OH)_2$ is insoluble in water so if waste containing Pb^{2+} ions is treated with hydroxide the lead will precipitate as $Pb(OH)_2$

$$Pb^{2+} + 2OH^- \longrightarrow Pb(OH)_2$$

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Instrumental Methods of Water Analysis

pH Measurement

pH probe used to insure correct pH.

Atomic Absorption Spectrometry

Detect and measure the concentrations of heavy metals in water.

Colorimetry

Principle of colorimetry is that the amount of absorbance of light by a coloured solution is proportional to the concentration of the solution.

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Exp:To estimate the concentration of free chlorine in swimming-pool water or bleach using a) a comparator or b) a colorimeter

$Cl_2 + H_2O \rightleftarrows HOCl + HCl$

Chlorine, Water, Hypochlorous acid, Hydrochloric acid

Hypochlorous acid is a weak acid and dissociates in water

$HOCl \rightleftarrows H^+ + OCl^-$

Hydrogen ion, Hypochlorite ion

Chlorine that is present in water as hypochlorous acid or hypochlorite ion is call free chlorine (this is a good disinfectant).

Chlorine can also exist comibined with ammonia or other organic nitrogen compounds (NH_2Cl, $NHCl_2$). This is called combined chlorine.

Compounds that will produce hypochlorous acid are added to swimming pools to kill bacteria, such as calcium hypochlorite ($Ca(OCl)_2$)

Free chlorine level in a swimming pool is higher than drinking water as swimmers add more bacteria to the water that need to be killed.

Free chlorine is kept in the range 1-5 ppm. If the chlorine is too low bacteria will survive in the water and infect swimmers. If the chlorine is too high NCl_3 may form which irritates swimmer's eyes.

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A) Comparator (Hach test kit)

Procedure	Observation	Explanation
Deionised water is placed in one of the viewing tubes, this is the **reference tube.**		Reference tube indicates how much light is absorbed by this depth of water.
The reference tube is placed in the left of the comparator box.		
Swimming pool water is paced in the other viewing tube		
Chorine DPD sachet contents is added to the swimming pool water	Solution turns pink.	Chlorine in the water reacts with the DPD. Concentration of chlorine will determine the shade of pink.
The swimming pool sample is placed in the comparator box and held up to a white light source.		
Colour disc is rotated until the two samples match in colour. The number related to this shade on the colour disc is read off.		Colour disc is calibrated to different free chlorine ppm based on the shade of colour.

B) Colorimeter

- A narrow beam of light is passed through the sample of swimming pool water. A filter is used to select a particular wavelength of light.
- Wavelength chosen based on which is strongly absorbed by the solution. This increases the accuracy of the results.
- Colorimeter is calibrated by using a range of solutions on known concentration. This calibration establishes the relationship between absorbance and concentration.
- A **calibration graph** is drawn of this data.

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B) Colorimeter

Procedure	Observation	Explanation
Five standard solutions of chlorine ranging from 1 to 5ppm are made up.		
A Free Chlorine DPD tablet is added to each solution	Solutions turn a pink colour.	Free Chlorine in the water reacts with the DPD.
A sample of each solution is placed in a **cuvette** (container that goes in colorimeter)		
A cuvette of deionized water is paced in the colorimeter.	Zero absorbance is displayed	This is part of the calibration process for the colorimeter.
The five samples of known concentration are tested.	Various absorbances will be displayed, increasing with concentration.	This data is used to create a calibration graph
A cuvette of a swimming pool sample of unknown concentration is tested.		The absorbance displayed has a corresponding concentration on the calibration graph. Concentration of unknown sample is read off.