

WATER TREATMENT

1.1 INTRODUCTION

Water is a universal solvent. It is one of the basic necessities of life and the most abundant commodity in nature. Natural water may be classified as: Surface water, Underground water, Rain water and Sea water. Other than drinking and household purposes, it is mainly required for agricultural and industrial purposes.

1.2 HARD AND SOFT WATER

| Sr. No. | Hard Water | Soft Water |
|---------|--|---|
| 1. | It contains dissolved salts of higher valent metal ions mainly Ca^{2+} and Mg^{2+} . | It does not contain dissolved salts of hardness causing metal ions. |
| 2. | It does not give lathering with soap and produces scum (precipitate). | It gives lathering with soap. |

Disadvantages of using Hard Water: The disadvantages of hard water are listed below:

1. Domestic Use:

- **Washing:** No lather formation, wastage of soap.
- **Bathing:** The resulting scum sticks on body.
- **Cooking:** Due to dissolved salts, boiling point of water is elevated, causing unnecessarily wastage of time and fuel.
- **Drinking:** Bad effect on metabolic system. Calcium oxalate stones may develop in urinary tracts, if used regularly. Also, it causes deposition of Ca in the bone joints.

2. Industrial Use:

- **Textiles:** Loss of soaps during washing of yarn and fabrics. Scum sticks on fabric and dyeing is not uniform. Also, Fe, Mn etc. salts leave colored spots on fabrics.
- **Sugar:** Crystallization of sugar is affected.
- **Paper:** React with chemicals to provide smooth and glossy finishing to paper. Iron salts add unwarranted colour in paper.
- **Pharmaceuticals:** Undesirable products may be produced in medicines.
- Problems from Boiler feed water (scales and sludge formation, corrosion, caustic embrittlement etc.).

1.3 SOFTENING OF WATER

Softening of water means removal of hardness causing salts from water. Hardness is the undesired property of water which not only produces scum while washing but also causes nuisance in various industries. Hence, it needs to be softened initially before use. It involves External and Internal treatment.

External: It involves removal of hardness causing salts from the water using methods such as Lime-Soda method, Zeolite method and Ion-exchange method.

Internal: It involves addition of certain chemicals to the water. In the process, an ion is not allowed to show its original property by complexing or converting it into other more soluble salt by adding a suitable reagent. The added chemicals either precipitate the scale forming impurities as a sludge (which can be removed by a blow-down operation) or the added chemical converts the scale forming impurities into compounds that stay in the dissolved form in the boiler thereby causing no harm. It includes methods like colloidal conditioning, phosphate conditioning, carbonate conditioning, calgon conditioning treatment with sodium aluminate, electrical conditioning and complexometric methods.

Few external softening methods are discussed.

1.3.1 Zeolite Process

[Oct 17, May 18, 19, Dec 18]

Principle: Zeolites are porous, hydrated sodium aluminosilicates with formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ (x and $y = 0, 1, 2, 3, \dots$) denoted by Na_2Ze (Ze implies $-\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$) capable of reversibly exchanging sodium ions (Na^{1+}) for hardness producing ions in water (such as $\text{Ca}^{2+}/\text{Mg}^{2+}$). When Na_2Ze is completely converted into corresponding calcium and magnesium zeolites, it ceases to soften water i.e. it gets exhausted. The exhausted zeolite is regenerated by treating with brine (NaCl) solution back to Na_2Ze . [Thus, two Na^{1+} ions are reversibly exchanged with one $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions.]



Total hardness of water = Total NaCl required for regeneration (in terms of mg CaCO_3 equivalent)

$$\text{Volume of water} \times \text{Hardness of water (mg/L)} = \frac{\text{Volume of NaCl (L)}}{58.5} \times \text{Quantity of NaCl per lit (mg/L)}$$

Process: (Fig. 1.1) A known volume of water is passed over a porous zeolite bed at a specific rate, where the hardness causing metal ions are retained on the zeolite. The sodium ions exchanged for the hardness causing ions pass into the out flowing water. The water thus collected contains sodium salts. This exchange of ions continues till the exchange capacity of the zeolite ceases. At this stage, the zeolite gets completely converted to calcium and magnesium zeolite and needs to be regenerated.

Regeneration: The supply of hard water is stopped and the exhausted zeolite is regenerated by treating the zeolite bed with solutions of sodium chloride (brine) or sodium nitrate or sodium sulphate. Brine is most commonly used because it is cheap, has a relatively low molecular weight and also the products formed by the regeneration reaction are CaCl_2 and MgCl_2 , which are highly soluble in water and can be easily washed out of the zeolite bed.

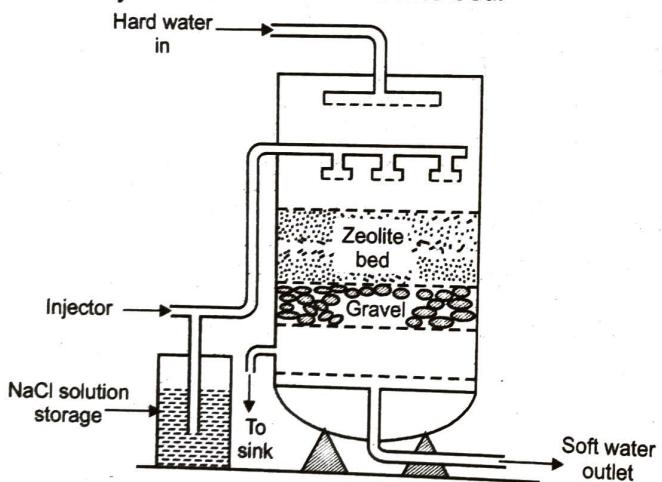


Fig. 1.1: Zeolite process

Advantages:

- The residual hardness after the treatment is very less (10 ppm).
- The equipment used is compact and requires small space.
- No precipitate is obtained, hence no sludge formation.
- The process automatically adjusts itself for different hardness of the incoming water.
- It is a clean process and requires less time.
- No skilled supervision for operation and maintenance is required.

Limitations:

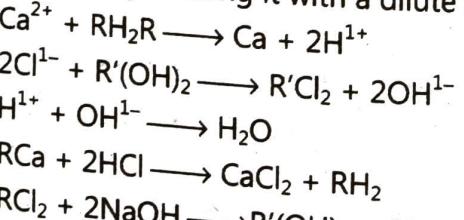
- Turbid water containing suspended matter cannot be directly fed to the zeolite bed, as the turbidity will block the pores of the zeolite making it inactive. The suspended matter should be removed by sedimentation, coagulation, filtration etc. before subjecting the water to zeolite process.
- Water containing large quantities of coloured ions like Mn^{2+} and Fe^{2+} must be removed first before passing through the zeolite as these ions produce their respective zeolites which cannot be easily regenerated.
- Water containing excess of acidity or alkalinity must be neutralized before passing through the zeolite as it destroys the zeolite bed.
- Hot water cannot be used as zeolite may get dissolved in it.
- Since the process does not exchange anions, raw water containing HCO_3^{1-} ions get converted after treatment to NaHCO_3 . If such water is used in boilers, it gets converted to NaOH which causes caustic embrittlement of boiler metal.

1.3.2 Ion Exchange Process

[Dec. 17, May 19]

Principle: A reversible exchange of ions occurs between the porous, stationary ion-exchange phase and the external liquid phase. The cation exchange resins are capable of exchanging rapidly cations like Ca^{2+} and Mg^{2+} from water by H^+ ions from cation exchange resin. The anion exchange resins are capable of exchanging rapidly anions like Cl^{-} , SO_4^{2-} from water by OH^{1-} ions from anion exchange resin.

When ion exchange capacities are lost (resins are exhausted), the water will no longer be softened. The exhausted cation exchanger is regenerated by passing dilute HCl or H_2SO_4 . The exhausted anion exchanger is regenerated by treating it with a dilute NaOH solution.



Total hardness of water \equiv Total volume of HCl (the acid required for regeneration of cation exchanger in terms of mg CaCO_3 equivalent).

Or

Total hardness of water \equiv Total volume of NaOH (the alkali required for regeneration of anion exchanger in terms of mg CaCO_3 equivalent).

For the purpose of hardness removal, cations like Ca^{2+} and Mg^{2+} are exchanged for H^{1+} ions from the hydrogen cation exchanger along with other cations (non-hardness causing). Thus, the hardness factor of water is removed. Further to improve, the quality of water, it is then passed through an anion exchanger where anions like Cl^- , SO_4^{2-} are exchanged for OH^{1-} ions from the anion exchanger. The water thus obtained is free from all the dissolved salts and only $\text{H}^{1+} + \text{OH}^{1-}$ (H_2O) is obtained. Thus, the demineralized water is obtained.

Ion exchange resins are soluble, cross-linked, long chain organic polymers with porous structure and the functional group attached to the chains undergo the ion-exchange property. Resins containing acidic functional groups ($-\text{COOH}$, $-\text{SO}_3\text{H}$) are capable of exchanging their H^{1+} ions with other cations. Resins containing basic functional groups [Quaternary ammonium salt ($\text{R}_1\text{R}_2\text{R}_3\text{N}^{+}\text{OH}^{-}$)] are capable of exchanging their OH^{1-} ions with other anions.

Process: (Fig. 1.2) A known volume of water is first passed over a cation exchange column at a specific rate, which removes cations from the water and equivalent amount of H^{1+} ions are released from column to water. After the cation exchange, the same batch of water is passed through anion exchange column at a specific rate, which removes anions from the water and equivalent amount of OH^{1-} ions are released from column to water. H^{1+} and OH^{1-} ions released from the cation and anion exchange respectively get combined to form water molecule. Thus, the treated water is free from cations as well as anions. Hence, it is called as deionized or demineralised water. This exchange of ions continues till the exchange capacity of the ion exchangers ceases.

Regeneration: The supply of hard water is stopped and the exhausted ion exchangers are regenerated. The cation exchanger is regenerated by passing a solution of dilute HCl or H_2SO_4 . The anion exchanger is regenerated by passing a solution of dilute NaOH . The columns are then washed with deionized water.

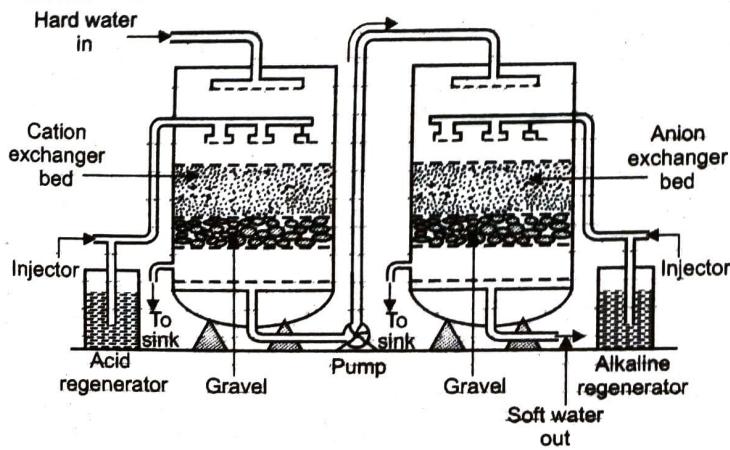


Fig. 1.2: Ion exchange process

Advantages:

- The residual hardness after the treatment is 0 ppm.
- The water can be used in high pressure boilers as it is free from alkalinity.
- The process is suitable to soften highly acidic or alkaline water.

Limitations:

- The equipment is costly and the ion exchangers are expensive.
- Turbid water reduces the process output. Hence, the turbidity must be removed initially by sedimentation, coagulation or filtration.

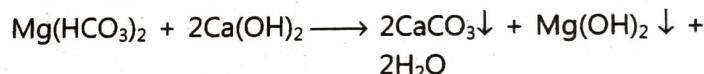
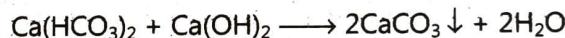
1.3.3 Hot Lime and Soda Process

[May 17]

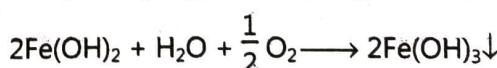
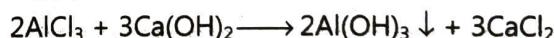
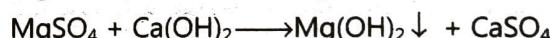
Principle: Hard water is treated with calculated amounts of slaked lime [$\text{Ca}(\text{OH})_2$] and soda ash [Na_2CO_3] in reaction tanks, so as to convert hardness producing chemicals into insoluble compounds [CaCO_3 and $\text{Mg}(\text{OH})_2$] which are then removed by settling and filtration. Usually 10% extra chemical is added for better results.

The reactions are as follows:

Lime removes temporary hardness.



Lime removes permanent hardness imparted by Mg, Fe and Al salts.



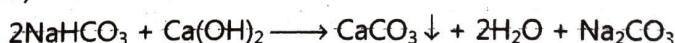
Lime removes dissolved carbon dioxide.



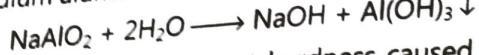
Lime consumes free mineral acids.



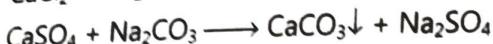
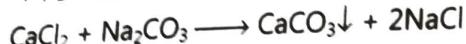
Sodium bicarbonate (NaHCO_3) or Potassium bicarbonate (KHCO_3) consumes lime to generate Na_2CO_3 or K_2CO_3 . (Hence, 1 equivalent of $\text{NaHCO}_3/\text{KHCO}_3$ is added in lime and 1 equivalent of $\text{NaHCO}_3/\text{KHCO}_3$ is subtracted from soda.)



Sodium aluminate (NaAlO_2) is subtracted from lime.



Soda removes permanent hardness caused due to calcium salts (CaCl_2 and CaSO_4) which are already present in water plus those generated in the reactions of permanent Mg^{2+} + Al^{3+} + Fe^{2+} salts and H^+ (free mineral acids) with lime.



$$\text{Amount of Lime required (in mg/L)} = \frac{74}{100} [\text{Temporary Ca}^{2+}]$$

$$+ 2 \times \text{Temporary Mg}^{2+} + \text{Permanent} (\text{Mg}^{2+} + \text{Al}^{3+} + \text{Fe}^{2+}) + \text{CO}_2 + \text{H}^{1+} (\text{HCl or H}_2\text{SO}_4) + \text{NaHCO}_3 / \text{KHCO}_3 - \text{NaAlO}_2]$$

All constituents in terms of CaCO_3 equivalent

$$\text{Amount of Soda required (in mg/L)} = 106/100 [\text{Permanent} (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Al}^{3+} + \text{Fe}^{2+}) + \text{H}^{1+} (\text{HCl or H}_2\text{SO}_4) - \text{NaHCO}_3 / \text{KHCO}_3]$$

All constituents in terms of CaCO_3 equivalent

When volume of water (in Litre) is given and percentage purity of lime is specified,

$$\text{Amount of Lime required (in mg)} = 74/100 [\text{Temporary Ca}^{2+} + 2 \times \text{Temporary Mg}^{2+} + \text{Permanent} (\text{Mg}^{2+} + \text{Al}^{3+} + \text{Fe}^{2+}) + \text{CO}_2 + \text{H}^{1+} (\text{HCl or H}_2\text{SO}_4) + \text{NaHCO}_3 / \text{KHCO}_3 - \text{NaAlO}_2] \times \text{Volume of water} \times 100/\text{Purity}$$

When volume of water (in Litre) is given and percentage purity of soda is specified,

$$\text{Amount of Soda required (in mg)} = 106/100 [\text{Permanent Ca}^{2+} + \text{Mg}^{2+} + \text{Al}^{3+} + \text{Fe}^{2+}) + \text{H}^{1+} (\text{HCl or H}_2\text{SO}_4) \text{NaHCO}_3 / \text{KHCO}_3] \times \text{Volume of water} \times 100/\text{Purity}$$

When purity of lime and/or soda is not specified, it is to be taken as 100% pure.

Process: (Fig. 1.3) The equipment for the process consists of three parts :

Reaction tank where raw water, chemicals and steam are uniformly mixed.

A conical sedimentation chamber where the sludge or precipitate settle down.

A sand filter, which ensures complete removal of sludge from the softened water.

Known volume of water is mixed with calculated amounts of lime and soda in the reaction tank. The temperature of the reaction mix is raised between 80° to 150°C through super-heated steam coming in through an inlet. Due to high operating temperature, the precipitate and sludge settle down quickly and hence no coagulants are needed. The sludge is removed from outlet of the sedimentation chamber periodically and the treated water is passed over sand filter where suspended matter gets adsorbed. The

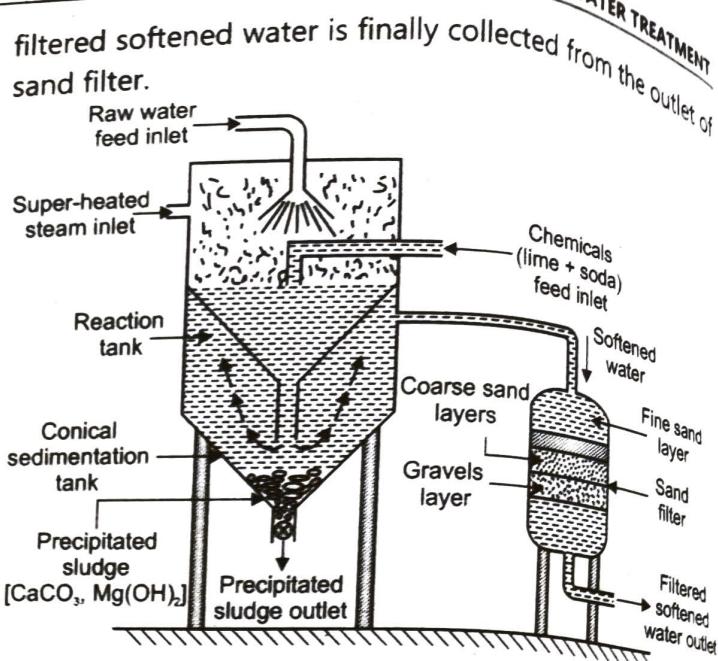


Fig. 1.3: Hot lime and soda process

Advantages:

- The residual hardness after the treatment is 15-30 ppm.
- The process is economical.
- Due to high temperature, the rate of reaction is rapid.
- Degassification takes place for dissolved gases like CO_2 .
- Viscosity of softened water is less, so water gets quickly filtered.
- Pathogenic micro-organisms are reduced due to higher pH of treated water.
- Besides hardness removal, other dissolved impurities are also removed.
- The treated water becomes alkaline, hence corrosion of distribution pipes is reduced.

Limitations:

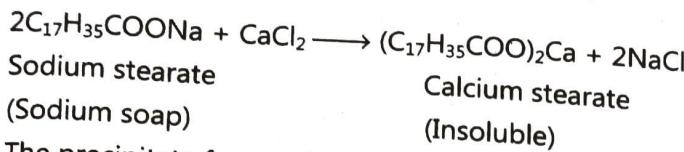
- Hardness upto 15 ppm is achieved, which is not good for boilers.
- Since treated water becomes alkaline, it leads to caustic embrittlement of boilers.
- Careful operation and skilled supervision is required.
- Disposal of large amount of sludge causes a problem.

1.4 WATER CHARACTERISTIC

The impurities present in water influence its characteristics such as colour, turbidity, taste, odour, acidity. Other important characteristics are discussed.

1.4.1 Hardness

Hardness of water is that characteristic which prevents the lathering of soap. The hardness is imparted due to the presence of certain salts of multivalent cations like Ca^{2+} , Mg^{2+} , Fe^{2+} , Mn^{2+} , etc.

Reaction:

The precipitate formed is called scum.

Hardness is classified as:

- 1. Temporary Hardness :** (Carbonate/Alkaline Hardness) is caused by the soluble bicarbonates of Ca and Mg. These soluble bicarbonates decompose to form insoluble precipitates when the water is heated. Hence, temporary hardness is removed by mere boiling and filtering off the precipitates formed.



- 2. Permanent Hardness :** (Non-carbonate/Non-alkaline Hardness) is due to the more soluble chlorides, sulphates, nitrates of Ca, Mg, Fe and other heavy metals. The permanent hardness removal needs softening techniques.

Unit: mg/L or ppm (parts per million) of CaCO_3 equivalent
Hardness is the number of milligrams of CaCO_3 equivalent hardness of a constituent present in 1L of water.

The CaCO_3 equivalent for a given quantity of constituent (mg/L) is expressed as,

$$\frac{\text{Weight of the constituent (mg/L)}}{\text{Chemical equivalent of the constituent (Eq.wt of constituent)}} \times \frac{\text{Chemical equivalent of } \text{CaCO}_3}{\text{(Eq.wt of } \text{CaCO}_3)}$$

Equivalent weight = Molecular weight/n,

where, n is either the positive or negative charge on the ions(present in the constituent)

1.4.2 Dissolve Oxygen (DO)

[May 18, 19, Dec. 18]

The dissolved oxygen (DO) is the oxygen dissolved in the water. DO is expressed as the number of oxygen (O_2) molecules in milligrams dissolved in 1000 mL of water.

Unit: mg/L or ppm

DO is freely available to aquatic life. It is vital to aquatic flora and fauna. It is also useful to prevent the odours. One of the best indicators that tell the health of a water body is DO parameter. DO can range from 0-18 mg O_2/L . Most natural water systems require 5-6 mg O_2/L to support a diverse population.

Factors Affecting DO Levels are,

- Water temperature
- Aquatic plant population
- Stream flow

- Atmospheric pressure
- Human activities
- Water discharge
- Organic waste

DO can be determined by Winkler's method (iodometric titration), by titrating a known volume of water sample against standard sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$). Dissolved oxygen (DO) can be calculated as follows:

$$N_a V_a = N_b V_b$$

N_a = Normality of sample (DO) solution

V_a = Volume of sample (DO) solution

N_b = Normality of $\text{Na}_2\text{S}_2\text{O}_3$

V_b = Volume of $\text{Na}_2\text{S}_2\text{O}_3$

Weight of dissolved oxygen per litre (DO) is,

$$\frac{V_b \times N_b \times 8 \times 1000}{V_a} \text{ mg of O}_2$$

1.4.3 Chemical Oxygen Demand (COD)

[May, Oct., Dec. 17, May 18]

Chemical Oxygen Demand (COD) is defined as the amount in milligrams of oxygen required to oxidise the oxidisable material present in 1000 mL of water using a strong oxidising agent such as acidified potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$).

Unit: mg/L or ppm

COD is calculated by refluxing a known volume of the water sample (V mL) with a known excess of $\text{K}_2\text{Cr}_2\text{O}_7$ (Y mL) and dilute H_2SO_4 in presence of Ag_2SO_4 catalyst for about two hours. The oxidisable material gets completely oxidized to produce CO_2 and H_2O .

Initially, known excess of $\text{K}_2\text{Cr}_2\text{O}_7$ (Y mL) is titrated against standard Mohr's salt solution (x N FAS i.e., ferrous ammonium sulphate,) using ferroin indicator (Blank titration reading). The unreacted $\text{K}_2\text{Cr}_2\text{O}_7$ leftover after the oxidation is titrated against the same x N FAS using ferroin indicator (Back titration reading). The $\text{K}_2\text{Cr}_2\text{O}_7$ consumed for oxidation is equivalent to the Blank minus Back FAS titration readings (V1 mL).

The $\text{K}_2\text{Cr}_2\text{O}_7$ consumed for the oxidation is equivalent to the oxygen required for the oxidation of oxidisable material.

$$\text{COD} = \frac{\frac{\text{Volume of oxidising agent consumed (V1)}}{\text{Volume of water taken (V)}} \times \frac{\text{Normality of FAS}}{\text{Normality of FAS}} \times 8 \times 1000}{(\text{Blank} - \text{Back}) \times \text{Normality of FAS} \times 8 \times 1000}$$

where,

Blank = Volume of burette solution (FAS) required to consume the total (i.e. known excess) $K_2Cr_2O_7$ added.

Back = Volume of burette solution (FAS) required to consume the excess $K_2Cr_2O_7$ left over after oxidizing the oxidisable matter in the water.

1.4.4 Biological Oxygen Demand (BOD) [May 18]

- Biological Oxygen Demand (BOD) is defined as the amount in milligrams of oxygen required by micro-organisms to oxidize the organic matter present in 1000 mL of water over a period of 5 days under aerobic conditions.
Unit: mg/L or ppm
- BOD can be determined by diluting a known volume (V mL) of water sample to a known volume (V_1 mL) with distilled water. Equal quantities (V_2 mL) of the diluted water are taken in two BOD bottles.
- In the first bottle $(DO)_1$ is determined immediately by iodometric titration against standard sodium thiosulphate (x N $Na_2S_2O_3$). The titre value obtained (a mL) is the blank value and it is used to calculate the dissolved oxygen available at the start of the experiment.
- The water in the second bottle is incubated under aerobic conditions for 5 days and then $(DO)_2$ is determined by iodometric titration against standard sodium thiosulphate (x N $Na_2S_2O_3$). The titre value obtained (b mL) is the back value and it is used to calculate the dissolved oxygen remaining or leftover after 5 days of aerobic oxidation.
- $(DO)_1$ implies the dissolved oxygen present in water at the beginning of the experiment. This DO will be consumed by microbes under aerobic conditions. Therefore, the DO on the fifth day of the experiment will be decreased over day one. Hence, the difference in $(DO)_1$ and $(DO)_2$ implies the dissolved oxygen consumed by the microbes present in V_2 mL sample.
- $(DO)_1$ = Dissolved oxygen of diluted water sample (V2) immediately after its preparation
- $(DO)_2$ = Dissolved oxygen of diluted water sample (V2) after incubation for 5 days at $20^\circ C$

$$\therefore BOD = \frac{(a - b) \times x \times N \times 8 \times V_1}{V_2} \times \frac{1000}{V}$$

$$BOD = \frac{(Blank - Back) \times \left\{ \text{Normality of } Na_2S_2O_3 \right\} \times 8 \times \left\{ \text{Volume of sample water after dilution} \right\}}{\left\{ \text{Volume of diluted sample water taken for titration} \right\}} \times \left\{ \frac{1000}{\text{Volume of initial sample water taken}} \right\}$$

COD is the total amount of oxygen required to oxidise all oxidisable impurities in a sample of sewage waste. COD is always greater than BOD since COD measurement involves both biodegradable and non-biodegradable oxidisable impurities. The difference in COD and BOD is equivalent to the quantity of biologically resistant oxidisable impurities.

Significance : COD and BOD serve as a yardstick to measure the effect an effluent (effect of oxidisable matter in water) will have on the receiving water body. However COD is less specific, since it measures everything that can be chemically oxidized, rather than just levels of biodegradable organic matter.

Many governments impose strict regulations regarding the maximum COD allowed in waste water before they can be returned to the environment.

BOD can be used as a gauge to check the effectiveness of wastewater treatment plants.

SOLVED EXAMPLES

Example 1.1: The hardness of 80000 L of a water sample was completely removed by a permutit. The exhausted permutit then required 2000 L of NaCl containing 117 mg NaCl per litre for regeneration. Calculate the hardness of water sample.

Solution:

(i) To calculate amount of NaCl used for regeneration, 1 L of NaCl solution contains 117 mg NaCl.

∴ 2000 L of NaCl solution contains $(117 \times 2000) = 23400$ mg NaCl

Amount of NaCl used for regeneration = $\frac{23400}{50/58.5}$ mg $CaCO_3$ equivalent

∴ Amount of NaCl used for regeneration = 20000 mg $CaCO_3$ equivalent

(ii) To calculate hardness of water sample, Let x mg/L be the hardness of water sample.

∴ Total hardness of 80000 L of water = $80000 \times x$

∴ $80000 \times x \equiv NaCl$ required for regeneration
 $= 200000$ mg $CaCO_3$ equivalent

$$\therefore x = 2.5$$

∴ The hardness of water sample = 2.5 mg/L

Example 1.2: After treating 50000 L of water by exchanger, the cationic resin required 350 L of 0.5 N HCl and anionic resin required 350 L of 0.5 N NaOH solutions for regeneration. Find the hardness of the above sample water.

Solution:

Total hardness of water \equiv Total volume of HCl or NaOH required for regeneration of ion exchange resin in terms of mg CaCO₃ equivalent

$$\begin{aligned}\text{Total hardness of } 50000 \text{ L water} &\equiv 350 \text{ L of } 0.5 \text{ N HCl} \\ &= 350 \text{ L of } 0.5 \text{ N CaCO}_3 \text{ equivalent} \\ &= (350 \times 0.5) \text{ L of } 1 \text{ N CaCO}_3 \text{ equivalent} \\ &= 175 \text{ L of } 1 \text{ N CaCO}_3 \text{ equivalent} \\ &= (175 \times 50) \text{ g of CaCO}_3 \text{ equivalent} \\ &= 8750 \text{ g of CaCO}_3 \text{ equivalent}\end{aligned}$$

$$\therefore \text{Hardness in } 1 \text{ L water} = \frac{8750}{50000} = 0.175 \text{ g of CaCO}_3 \text{ equivalent}$$

$$\therefore \text{Hardness (mg CaCO}_3 \text{ equivalent) in } 1 \text{ L water} = 175 \text{ mg of CaCO}_3 \text{ equivalent}$$

$$\therefore \text{Hardness of water} = 175 \text{ mg/L}$$

Example 1.3: A water sample has following salts per litre:
Ca(HCO₃)₂ = 16.2 mg, Mg(HCO₃)₂ = 7.3 mg, CaSO₄ = 17 mg,
MgSO₄ = 12 mg, MgCl₂ = 19 mg, NaCl = 4.7 mg. Calculate
the quantity of lime and soda required for softening 50000L
of hard water.

Solution:

| Constituent (Salt / Chemical / Ion) | Quantity (ppm) | Conversion factor = Quantity \times (Eq.wt of CaCO ₃ /Eq.wt of constituent) | CaCO ₃ equivalent (ppm) | Requirement of L and/or S |
|-------------------------------------|----------------|--|------------------------------------|---------------------------|
| Ca(HCO ₃) ₂ | 16.2 | 16.2 \times 50/81 | 10 | L |
| Mg(HCO ₃) ₂ | 7.3 | 7.3 \times 50/73 | 5 | 2L |
| CaSO ₄ | 17 | 17 \times 50/68 | 12.5 | S |
| MgSO ₄ | 12 | 12 \times 50/60 | 10 | L + S |
| MgCl ₂ | 19 | 19 \times 50/47.5 | 20 | L + S |
| NaCl | 4.7 | Does not consume L and/or S | | |

$$\begin{aligned}\text{amount of lime required} &= \frac{74}{100} [\text{CaCO}_3 \text{ equivalents of } \text{Ca}(\text{HCO}_3)_2 + 2 \times \text{Mg}(\text{HCO}_3)_2 + \text{MgSO}_4 + \text{MgCl}_2] \times 50000 \\ &= \frac{74}{100} [10 + (2 \times 5) + 10 + 20] \times 50000\end{aligned}$$

$$\begin{aligned}&= \frac{74}{100} [50] \times 50000 \\ &= 1850000 \text{ mg} \\ &= 1.850 \text{ kg}\end{aligned}$$

$$\therefore \text{Amount of lime required} = 1.850 \text{ kg}$$

$$\begin{aligned}\text{amount of soda required} &= \frac{106}{100} [\text{CaCO}_3 \text{ equivalents of } \text{CaSO}_4 + \text{MgSO}_4 + \text{MgCl}_2] \times 50000 \times 100/100 \\ &= 106/100 [12.5 + 10 + 20] \times 50000\end{aligned}$$

$$= 106/100 [42.5] \times 50000$$

$$= 2252500 \text{ mg}$$

$$= 2.253 \text{ kg}$$

$$\therefore \text{Amount of soda required} = 2.253 \text{ kg}$$

Example 1.4: Calculate the temporary, permanent and total hardness for a water sample in ppm containing following salts: Mg(HCO₃)₂ = 18.25 ppm, Al(NO₃)₃ = 12 ppm, CaCO₃ = 15 ppm.

Solution:

| Constituent (Salt / Chemical / Ion) | Quantity (ppm) | Conversion factor = Quantity \times (Eq.wt of CaCO ₃ /Eq.wt of constituent) | CaCO ₃ equivalent (ppm) | Type of Hardness |
|-------------------------------------|----------------|--|------------------------------------|------------------|
| Mg(HCO ₃) ₂ | 18.25 | 18.25 \times 50/73 | 12.5 | Temporary |
| Al(NO ₃) ₃ | 12 | 12 \times 50/71 | 8.45 | Permanent |
| CaCO ₃ | 15 | 15 \times 50/50 | 15 | Temporary |

$$\text{Temporary hardness} = 12.5 + 15 = 27.5 \text{ ppm}$$

$$\text{Permanent hardness} = 8.45 = 8.45 \text{ ppm}$$

$$\text{Total hardness} = 35.95 \text{ ppm}$$

Example 1.5: 30 mL of waste water is mixed with 35 mL of acidified potassium dichromate and refluxed. The unreacted potassium dichromate required 12.5 mL of 0.25 N ferrous ammonium sulphate. The blank titration reading was 26.4 mL. Calculate COD of water sample.

Solution:

$$\text{Volume of water taken} = 30 \text{ mL}$$

$$\text{Blank reading} = 26.4 \text{ mL}$$

$$\text{Back reading} = 12.5 \text{ mL}$$

$$\text{Normality of ferrous ammonium sulphate (FAS)} = 0.1 \text{ N}$$

$$\text{COD} =$$

$$\frac{\text{Volume of oxidising agent consumed (V1)} \times \text{Normality of FAS} \times 8 \times 1000}{\text{Volume of water taken (V)}}$$

$$\text{COD} = \frac{(\text{Blank} - \text{Back}) \times \text{Normality of FAS} \times 8 \times 1000}{\text{Volume of water taken (V)}}$$

$$\text{COD} = \frac{(26.4 - 12.5) \times 0.25 \times 8 \times 1000}{30}$$

$$\text{COD} = 926.67 \text{ mg/L}$$

$$\therefore \text{COD of water sample} = 926.67 \text{ mg/L}$$

Example 1.6: 60 mL of water sample was diluted to 100 mL. Equal volumes of it are taken for DO estimation. The DO on day 1 was 770 ppm and DO after incubation for 5 days was 340 ppm. Calculate the BOD of the sample.

Solution:

Volume of sample before dilution = 60 mL

Volume of sample after dilution = 100 mL

$$(DO)_1 = 770 \text{ ppm}$$

$$(DO)_2 = 340 \text{ ppm}$$

Volume of sample after dilution

$$\text{BOD} = [(DO)_1 - (DO)_2] \times \text{Volume of initial sample water taken}$$

$$= (770 - 340) \times (100/60)$$

$$= 716.67 \text{ ppm}$$

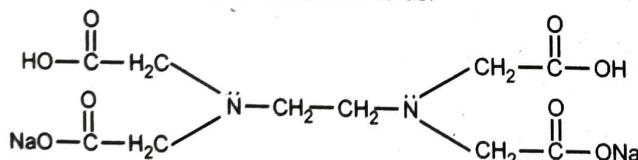
∴ BOD of water sample = 716.67 ppm

Note: For more solved numericals and practice problems refer 'Numericals in Engineering Chemistry, Sameera Rege & Geetanjali Gokhale-Ashtekar (Nirali Prakashan)'.

1.5 DETERMINATION OF HARDNESS BY EDTA METHOD

[Dec. 17, 18, May 18]

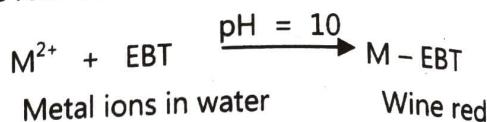
- The most commonly used experimental method to determine the total hardness of water is the complexometry using ethylene diamine tetra acetic acid (EDTA) as a complexing agent.
- This is a volumetric method of analysis using Eriochrome black-T (EBT) dye as an indicator. Sometimes chalcones can also be used as indicators under suitable conditions.
- The commercially available form of EDTA is its disodium salt and its structure is as:



Disodium salt of EDTA

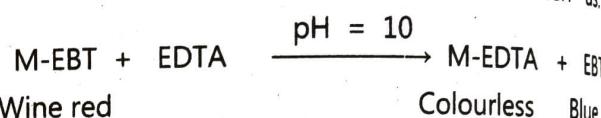
- It is well known that EDTA forms a stoichiometric 1:1 complex with monovalent and divalent cations. Hence, if suitable reaction conditions are maintained, this complexometric reaction can be used to determine the metal ion concentration in water responsible for causing hardness.
- This complexometric reaction takes place at pH = 10, hence suitable basic buffer solution ($\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$) must be used to maintain constant pH throughout the reaction/titration.
- Initially during the titration, the indicator (EBT) is added to water sample whose hardness is to be determined along with the buffer solution. The indicator reacts with metal ions in water to give wine red complex.

- This reaction can be written as:

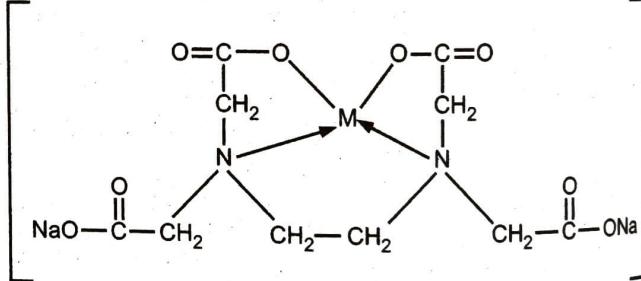


- Then this wine red solution is titrated with standardized EDTA. This leads to formation of M-EDTA (metal-EDTA) complex because M-EDTA complex is more stable than M-EBT complex i.e. EBT in the complex is displaced by EDTA.

- Once M-EDTA complex is formed, then the reaction mixture contains EBT (displaced) which gives blue colour to the solution. This reaction can be written as:



- A sharp colour change from wine red to blue can be taken as the end point of the reaction and using the concentration and volume of EDTA required to achieve the end point, the concentration of metal ions causing hardness to water can be calculated.
- The structure of M-EDTA complex can be written as:

**Experimental Procedure:**

The experiment can be performed in two parts:

Part I: Standardization of EDTA:

- Prepare accurately 0.01 M ZnCl_2 solution and approximate 0.01 M EDTA solution.
- Fill the burette upto the mark with EDTA solution.
- In a conical flask, pipette out 25 ml of ZnCl_2 solution. Add 10 ml of pH = 10 buffer and 2 ml of EBT indicator. The colour of reaction mixture becomes wine red.
- Titrate this reaction mixture with EDTA solution from burette till colour changes to blue.
- Record the burette reading at the end point.
- Calculate concentration of EDTA using following equality.

$$1 \text{ M } 1000 \text{ ml } \text{ZnCl}_2 \equiv 1 \text{ M EDTA}$$

Alternatively, the standardization of EDTA can also be done using standard hard water.

Part II: Total Hardness of Water:

- Fill the burette with standardized EDTA.
- Pipette out 25 ml of the given water sample in a conical flask and repeat the procedure as mentioned above to get the constant burette reading at the end point.
- Calculate the hardness of water using following equality:

$$1 \text{ M } 1000 \text{ ml EDTA} \equiv 1 \text{ M } \text{CaCO}_3 \text{ eq. hardness}$$

$$\text{i.e. } 1 \text{ M } 1000 \text{ ml EDTA} \equiv 100 \text{ g } \text{CaCO}_3 \text{ eq. hardness}$$

(Molecular weight of $\text{CaCO}_3 = 100$)

- Express the obtained hardness in terms of parts per million (ppm).
- If the water sample is taken without boiling and then filtered then the hardness obtained by EDTA method is total hardness.
- Then take the same sample, boil and filter and then if again EDTA method is performed on this sample, then the permanent hardness is obtained.
- Then using total and permanent hardness, the temporary hardness can be calculated.

Example 1.7: It was found that, 50 ml of a water sample requires 12.7 ml of 0.02 M EDTA during titration. Calculate hardness of water.

(Note: Hardness is always calculated as CaCO_3 equivalents, molecular weight of $\text{CaCO}_3 = 100$, equivalent weight = 50).

Solution: Given: Volume of EDTA required = 12.7 ml

Concentration of EDTA = 0.02 M

Volume of water = 50 ml

Water \equiv EDTA

$$M_1 V_1 = M_2 V_2$$

$$M_1 \times 50 = 0.02 \times 12.7$$

$$M_1 = \frac{0.02 \times 12.7}{50}$$

$$M_1 = 0.00508 \text{ M}$$

\therefore Concentration of hardness causing substances is 0.00508 M.

Hardness (CaCO_3 eq) = Concentration \times 100 g/L

$$= 0.508 \text{ g/L}$$

$$= 508 \text{ mg/L}$$

$$\text{Hardness} = 508 \text{ ppm } \text{CaCO}_3 \text{ eq.}$$

OR

$$\text{Total hardness} = \frac{V_1 \times M \times 10^5}{50} \text{ ppm } \text{CaCO}_3 \text{ eq.}$$

where,

V_1 = Volume of EDTA required to achieve end point

V = Volume of water sample taken for analysis

M = Molarity of EDTA

$$\therefore \text{Total hardness} = \frac{12.7 \times 0.02}{50} \times 10^5 \text{ ppm } \text{CaCO}_3 \text{ eq.}$$

$$= 5.08 \times 10^{-3} \times 10^5 \text{ ppm } \text{CaCO}_3 \text{ eq.}$$

$$= 508 \text{ ppm } \text{CaCO}_3 \text{ eq.}$$

Example 1.8: 50 ml of a water sample consumed 15 ml of 0.01 M Na_2EDTA before boiling and 5 ml of same EDTA after boiling. Calculate total, permanent and temporary hardness.

Solution: Given:

Volume of water sample = 50 ml

Volume of EDTA before boiling = 15 ml

Volume of EDTA after boiling = 5 ml

Concentration of EDTA = 0.01 M

Hardness = ?

Part-1: Total Hardness (Before Boiling)

EDTA \equiv Water

$$M_1 V_1 = M_2 V_2$$

$$0.01 \times 15 = M_2 \times 50$$

$$M_2 = \frac{0.01 \times 15}{50}$$

$$= 3 \times 10^{-3} \text{ M}$$

$$\begin{aligned} \text{Total hardness} &= \text{Concentration} \times \text{Molecular weight of } \text{CaCO}_3 \\ &= 3 \times 10^{-3} \times 100 \text{ g/L} \\ &= 0.3 \text{ g/L} \end{aligned}$$

$$\therefore \text{Total hardness} = 300 \text{ ppm } \text{CaCO}_3 \text{ eq.}$$

Part-2: Permanent Hardness (After Boiling and Filtering)

EDTA \equiv Water

$$M_3 V_3 = M_4 V_4$$

$$5 \times 0.01 = M_4 \times 50$$

$$M_4 = \frac{5 \times 0.01}{50} = 1 \times 10^{-3} \text{ M}$$

$$\begin{aligned} \text{Permanent hardness} &= 1 \times 10^{-3} \times 100 \\ &= 100 \text{ ppm } \text{CaCO}_3 \text{ eq.} \end{aligned}$$

Part-3: Temporary Hardness:

$$\begin{aligned} \text{Temporary hardness} &= \text{Total hardness} - \text{Permanent hardness} \\ &= 300 - 100 \text{ CaCO}_3 \text{ eq.} \end{aligned}$$

$$\text{Temporary hardness} = 200 \text{ ppm } \text{CaCO}_3 \text{ eq.}$$

$$= \frac{0.5}{100 \times 0.5} = 0.01 \text{ M CaCO}_3$$

SHE \equiv EDTA

$M_1V_1 = M_2V_2$

$$0.01 \times 50 = M_2 \times 48$$

$$M_2 = \frac{0.01 \times 50}{48} = 0.0104 \text{ M}$$

i.e. Concentration of EDTA = 0.0104 M

Part-2: Hardness Calculations :

(a) Total Hardness (Before Boiling):

Given: Volume of EDTA = 7.5 ml

Volume of water = 25 ml

Concentration of EDTA = 0.0104 M

$$\text{Total hardness} = \frac{V_1}{V} \times M \times 10^5 \text{ ppm CaCO}_3 \text{ eq.}$$

$$= \frac{7.5}{25} \times 0.0104 \times 10^5 \text{ ppm CaCO}_3 \text{ eq.}$$

$$= 312.5 \text{ ppm CaCO}_3 \text{ eq.}$$

(b) Permanent Hardness (Non-Carbonate Hardness after Boiling):

Given: Volume of EDTA = 5 ml

Volume of water = 25 ml

Concentration of EDTA = 0.0104 M

$$\text{Permanent hardness} = \frac{V_1}{V} \times M \times 10^5 \text{ ppm CaCO}_3 \text{ eq.}$$

$$= \frac{5}{25} \times 0.0104 \times 10^5 \text{ ppm CaCO}_3 \text{ eq.}$$

$$= 208 \text{ ppm CaCO}_3 \text{ eq.}$$

(c) Temporary Hardness (Carbonate Hardness):

Temporary hardness = Total hardness - Permanent hardness

$$= 312.5 - 208 \text{ ppm CaCO}_3 \text{ eq.}$$

$$= 104.5 \text{ ppm CaCO}_3 \text{ eq.}$$

Hardness = 11.5 ppm CaCO₃ eq.

(ii) Due to MgCl₂,

$$\text{Hardness} = \frac{19 \times 100}{95} = 20 \text{ ppm CaCO}_3 \text{ eq.}$$

(iii) Due to MgSO₄,

$$\text{Hardness} = \frac{24 \times 100}{120} = 20 \text{ ppm CaCO}_3 \text{ eq.}$$

(iv) Due to CaCl₂,

$$\text{Hardness} = \frac{22.2 \times 100}{111} = 20 \text{ ppm CaCO}_3 \text{ eq.}$$

$$\text{Total hardness} = 11.5 + 20 + 20 + 20 \text{ ppm}$$

$$\text{Total hardness} = 71.5 \text{ ppm CaCO}_3 \text{ eq.}$$

Example 1.11: 0.8 g of ZnSO₄ is dissolved in water diluted to 250 ml. 25 ml of this ZnSO₄ solution is titrated with Na₂-EDTA solution from burette to obtain end point at 14.3 ml. This standardized EDTA solution was titrated with 50 ml of water sample to obtain 8.6 ml burette reading. Calculate hardness of water.

Solution: Part-1: Standardization of EDTA:

Given: Weight of ZnSO₄ = 0.8 g,

Volume of ZnSO₄ = 0.25 L

Molecular weight of ZnSO₄ = 161.4.

$$\text{Molarity of ZnSO}_4 = \frac{\text{Weight}}{\text{Molecular weight} \times \text{Volume}}$$

$$= \frac{0.8}{161.4 \times 0.25} = 0.0198 \text{ M}$$

ZnSO₄ \equiv EDTA

$M_1V_1 = M_2V_2$

$$0.0198 \times 25 = M_2 \times 14.3$$

$$M_2 = \frac{0.0198 \times 25}{14.3} = 0.0347 \text{ M}$$

∴ Concentration of EDTA = 0.0347 M

Part-2: Determination of Hardness:

$$\begin{aligned}\text{Total hardness} &= \frac{V_1}{V} \times M \times 10^5 \text{ ppm CaCO}_3 \\ &= \frac{8.6}{50} \times 0.0347 \times 10^5 \text{ ppm CaCO}_3 \text{ eq.} \\ &= 596 \text{ ppm CaCO}_3 \text{ eq.}\end{aligned}$$

1.6 DETERMINATION OF DISSOLVED OXYGEN BY WINKLER METHOD**Introduction:**

The concentration of dissolved oxygen can be readily, and accurately, measured by the method originally developed by Winkler in 1888. Dissolved oxygen can also be determined with precision using oxygen sensitive electrodes; such electrodes require frequent standardization with waters containing known concentrations of oxygen. They are particularly useful in polluted waters where oxygen concentrations may be quite high. In addition, their sensitivity can be exploited in environments with rapidly-changing oxygen concentrations are very low. For these reasons, the Winkler titration is often employed for accurate determination of oxygen concentrations in aqueous samples.

Definition:

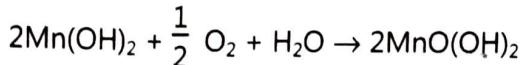
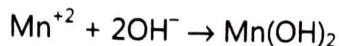
The dissolved oxygen concentration of seawater is expressed as the number of milliliters of dioxygen gas (O_2) per liter of seawater (ml/L).

Principle of Analysis:

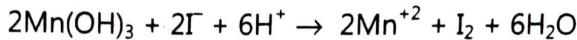
The chemical determination of oxygen concentrations in seawater is based on the method first proposed by Winkler (1888) and modified by Strickland and Parsons (1968). Oxygen in the water sample oxidizes iodide ion (I^-) to iodine (I_2) quantitatively. The amount of iodine generated is then determined by titration with a standard thiosulfate ($S_2O_3^{2-}$) solution. The endpoint is determined by using starch as a visual indicator. The amount of oxygen can then be computed from the titer: one mole of O_2 reacts with four moles of thiosulfate. This is a redox titration called as Iodometry.

At the time of sampling, dissolved oxygen is fixed by the addition of Mn(II) under basic conditions, resulting in a brown precipitate, manganic hydroxide ($MnO(OH)_2$). Prior to analysis, the sample is acidified to pH 1.0-2.5. This causes the precipitated hydroxides to dissolve, liberating Mn(III) ions. Mn(III) ions oxidize previously added iodite ions to iodine. Iodine forms a complex (I_3^-) with surplus iodite ions. Iodine and the complex exist in equilibrium; thus, I_3^- serves as a reservoir of I_2 . The iodine is then titrated with

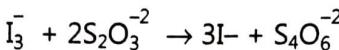
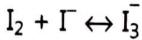
thiosulfate; iodine is reduced to iodide and the thiosulfate is oxidized to tetrathionate. The stoichiometric equations for the reactions described above are :



(oxidation of Mn(II) to Mn(III))

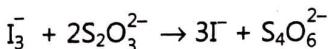
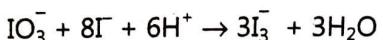


(oxidation of I^- to I_2)



(oxidation of $2S_2O_3^{2-}$ to $S_4O_6^{2-}$; reduction of I_3^- to I^-)

The thiosulfate solution is not stable and therefore must be standardized with a primary standard, typically potassium iodate (KIO_3). Standardization is based on the co-proportionation reaction of iodide with iodate, thereby forming iodine. As described above, the iodine binds with excess iodite, and the complex is titrated with thiosulfate. One mole of iodate produces three moles iodine, which are consumed by six moles of thiosulfate.

**Sampling Apparatus:**

- Sample Flasks: Glass stoppered dissolved oxygen bottles (115 mL nominal capacity – also called "BOD bottles"). 1 clean and dry bottle per sample, blanks and standard.
- Volumetric dispensers (or manual volumetric pipettes (disposable, glass)).
- Four dispensers capable of accurately dispensing 1 mL aliquots. These should be labeled "Reagent 1", "Reagent 2" and "Reagent 3", and "KIO₃ Blank".
 - One dispenser capable of accurately dispensing a 10 mL aliquot. This should be labeled "KIO₃ standard".
 - One dispenser capable of accurately dispensing a 50 mL aliquot. This should be labeled "Sample".
 - Tygon tubing: long enough to reach from spigot to the bottom of the sample bottle.

Titration Apparatus:

- Titration Box : A three-sided box containing the titration apparatus. The inside walls should be covered with white lab paper to aid in end point detection.
- Magnetic stirrer and stir bars.
- Clean, dry 125 mL Erlenmeyer flasks (one per titration – 125 mL beakers can also be used)
- Glass eye dropper bottle for starch indicator.

Reagents:

- Reagent 1:** Manganese (II) chloride (3M : reagent grade): Dissolve 600 g of $MnCl_2 \cdot 4H_2O$ in 600 mL distilled water. After complete dissolution, make the solution up to a final volume of 1 liter with distilled water and then filtered into an amber plastic bottle for storage.
- Reagent 2:** Sodium iodite (4M: reagent grade) and sodium hydroxide (8M: reagent grade): Dissolve 600g NaI in 600 ml of distilled water. If the color of solution becomes yellowish brown, discard and repeat preparation with fresh reagent. While cooling the mixture, add 320g NaOH to the solution, and make up the volume to 1 liter with distilled water. The solution is then filtered and stored in an amber glass bottle.
- Reagent 3:** Sulfuric Acid (50% v/v): Slowly add 500 mL of reagent grade concentrated H_2SO_4 to 500 mL distilled water. Cool the mixture during addition of acid.
- Starch Indicator Solution (Manual Titration Only):** Place 1.0g of soluble starch in a 100 mL beaker, and add a little distilled water to make a thick paste. Pour this paste into 1000 mL of boiling distilled water and stir for 1 minute. The indicator should be stored in a refrigerator.
- Sodium Thiosulfate Stock Solution (0.18 M: Reagent Grade):** Dissolve 45g $Na_2S_2O_3 \cdot 5H_2O$ and 2.5g sodium borate, $Na_2B_4O_7$ (reagent grade) for a preservative, in 1 liter of distilled water. This solution is stored in a refrigerator and used to make the working thiosulfate solution. Some variation on the method call for a 0.1N (Normal) solution, which can be purchased ready-made.
- Sodium Thiosulfate Working Solution (0.018 M: Reagent Grade):** Bring 100 mL of the sodium thiosulfate stock solution to 100 mL with distilled water in a 1 liter volumetric flask. This solution is stored in a refrigerator and used for titrations. If a ready-made 0.1 N solution was used for the stock, a working solution of 0.01 N will be fine.
- Potassium Iodate Standard (0.00167 M = 0.01 N: Analytical Grade):** Dry the reagent in a desiccator under vacuum. Weight out exactly 0.3567g KIO_3 and make up to 1.0 liter with distilled water. It is important to note the temperature of the solution so that a precise molarity can be calculated.

Procedures:

- First, the precise concentration of thiosulfate in the titrating solution must be determined. Next, a "black" analyzed. Impurities in the reagents may participate in the oxidation-reduction reactions involved in the dissolved oxygen analysis and thus must be accounted for. Once the standard titer and blank have been determined, the samples can be titrated with thiosulfate delivered via the burette; the endpoint determined visually using the starch indicator solution. Below, the procedures for standardization, blank determination, and sample analysis are described. As mentioned above, the sodium thiosulfate solution will be standardized for you. You will make your own blank and sample determinations. If time allows, you may perform the standardization yourself.
- Standardization:** Label one clean, empty BOD bottle "KIO₃ standard"; add approximately 15 mL of milliwater and a stir bar.
 - Carefully add 10 mL of standard potassium iodate (0.00167 M = 0.01N) from an "A" grade pipette equivalent. Swirl to mix. immediately add 1 mL of the 50 % sulfuric acid sodium (Reagent 3). Rinse down sides of flask, swirling to mix, thus ensuring an acidic solution before the addition of reagents.
 - Add 1 mL of sodium iodide-sodium hydroxide reagent, swirl, then add 1 mL of manganese chloride reagent. Mix thoroughly after each addition. Once solution has been mixed, fill to the neck with deionized water.
 - From the "Standard" bottle, fill the 50 mL volumetric pipette with KIO₃ solution.
 - Empty the first 50 mL of solution into a waste container as a rinse.
 - Re-fill the 50 mL pipette with KIO₃ solution and empty into a clean 125-mL Erlenmeyer flask. Add a magnetic stir bar.
 - Check the 10 mL burette to ensure that it is full of thiosulfate working solution (0.01N). Place the Erlenmeyer flask under the burette and turn on the magnetic stirrer. Keep the speed of the stirrer moderate – do not create a vortex in the solution.
 - Slowly add thiosulfate to the solution until the solution turns a pale yellow color. Stop titrating.
 - Add three drops starch solution to the flask. Continue to titrate by adding thiosulfate drop by drop just until the solution becomes colorless.
 - Record the volume of thiosulfate added. Repeat steps (vi) through (ix) until you have three readings.

Determination:

Place approximately 15 mL Milli-Q water in a BOD bottle with a stir bar. Add 1 mL of the potassium iodate standard, mix thoroughly, then add 1 mL 50% sulfuric acid, again mixing the solution thoroughly.

Before beginning the titration, add the following reagents : 1 mL sodium iodite-sodium hydroxide reagent (1), rinse, mix, then add 1 mL manganese chloride reagent (2). Fill the BOD bottle to just below the neck with Milli-Q water. Titrate to the endpoint as described for the sample analysis procedure (below).

Pipette 1 mL of the standard solution into the same flask and again titrate to the end point.

The difference between the first and second titration is the reagent blank.

Sample Analysis:

Identify the sample you are working on by the number on the bottle and the corresponding data sheet; copy this information into your notebook.

i) Immediately prior to analysis, add 1 ml 50% H₂SO₄ (Reagent 3) below the water line in the sample bottle.

ii) Cover and invert the sample bottle several times to mix the solution. The precipitate should dissolve completely and the solution should turn a deep yellow color. If some precipitate remains add a few more drops of Reagent 3 (this reagent may be added in excess of 1 ml).

iv) Do not allow the sample to sit for any length of time after reagent 3 has been added – the sample must be run immediately.

v) Fill the 50 mL volumetric pipette with sample solution and empty into the waste container (this is your pipette rinse).

(vi) Re-fill the 50-mL volumetric pipette with sample and empty into a clean 125-ml Erlenmeyer flask (or beaker) and add a magnetic stir bar.

(vii) Check the 10 mL burette to ensure that it is full of thiosulfate solution. Place the Erlenmeyer flask (or beaker) under the burette and turn on the magnetic stirrer. Keep the speed of the stir bar moderate – do not create a vortex in the solution.

(viii) Slowly add thiosulfate to the sample until the solution turns a pale yellow color. Stop titrating.

(ix) Add three drops starch solution to the flask.

drop just until the solution turns clear and colorless.

- (x) Record the volume of thiosulfate added. Repeat steps (vi) – (ix) until there are three readings (of thiosulfate added) within 0.05 mL of each other.

Calculation and Expression of Results:

The calculation of oxygen concentration (mL O₂ L⁻¹) from this analysis follows in principle the procedure outlined by Carpenter (1965).

$$\text{O}_2 \left(\frac{\text{mL}}{\text{L}} \right) = \frac{((R - R_{\text{blank}}) \times V_{\text{IO}_3} \times N_{\text{IO}_3} \times E)}{(R_{\text{std}} - R_{\text{blank}}) \times (V_{\text{bottle}} - V_{\text{rgts}})} - \text{DO}_{\text{rgts}}$$

where,

R = Volume of thiosulfate used to titrate the sample (mL)

R_{std} = Volume of thiosulfate used to titrate the KIO₃ standard (mL)

R_{blank} = Volume of thiosulfate used to titrate the blank as measured above (mL)

N_{IO3} = Normality of standrd KIO₃ (equiv/L) – use 0.01 N

V_{IO3} = Volume of KIO₃ standard (mL) – use 10 mL

E = 5598 mL O₂ / equiv

V_{bottle} = Volume of sample bottle (mL) – use 250 mL

DO_{rgts} = Oxygen added in reagents – use 0.0017 mL O₂/L

V_{rgts} = Volume of reagents – use 2 mL

The additional correction for DO_{rgts} of 0.0017 mL oxygen added in 1 mL manganese chlorite and 1 mL of alkaline iodide has been suggested by Murray, Riley and Wilson (1968).

The appropriate range of O₂ values for fresh water and seawater is 0 – 10 m of O₂ / L of water.

The dissolved oxygen concentration can be calculated by substituting the values into the equation given above.

SUMMARY

- Water is a universal solvent widely used in industrial utility.
- Hardness is the undesired property of water which brings in lot of disadvantages in its industrial use.
- Hardness of water is a property which prevents the lathering of soap. It is imparted due to the presence of certain salts of multivalent cations like Ca²⁺, Mg²⁺, Fe²⁺, Mn²⁺ and Al³⁺ (heavy metals) dissolved in water. Unit: mg/L or ppm (parts per million) of CaCO₃ equivalent.
- Softening of water means removal of hardness causing salts from water.

ENGINEERING CHEMISTRY (BATU)

The water is softened methods mainly employed are the Zeolite Process, Ion Exchange Process and Hot Lime and Soda Process.

The dissolved oxygen (DO) is the oxygen dissolved in the water. DO is expressed as the number of oxygen (O_2) molecules in milligrams dissolved in 1000 mL of water. Unit: mg/L or ppm.

Chemical Oxygen Demand (COD) is defined as the amount in milligrams of oxygen required to oxidise the oxidisable material present in 1000 mL of water using a strong oxidising agent such as acidified potassium dichromate ($K_2Cr_2O_7$).

Biological Oxygen Demand (BOD) is defined as the amount in milligrams of oxygen required by micro-organisms to oxidize the organic matter present in 1000 mL of water over a period of 5 days under aerobic conditions.

EXERCISE

- What is hard water and what are its types? List its disadvantages.
- What is softening of water and discuss the various types?
- Discuss the process details of following water softening methods:
 - Zeolite method
 - Ion-Exchange method
 - Hot Lime-Soda method.
- Compare the Ion-Exchange method over the Zeolite method of water softening.
- List the advantages and limitations of :
 - Zeolite method
 - Ion-Exchange method
 - Hot Lime and Soda method of water softening.
- Explain the term Chemical Oxygen Demand (COD) and give its significance.
- Explain the term Biological Oxygen Demand (COD) and give its significance.

UNIVERSITY QUESTIONS**May 2017**

- Describe the determination of dissolved Oxygen in water by Iodometric method.
- How permanent hardness of water can be removed by hot lime-soda process?

December 2017

- Explain Ion Exchange process of softening of water with its advantages and disadvantages.
- How does the Hardness of water determined by EDTA complexometric method?
- Write note on Chemical Oxygen Demand (COD).

May 2018

- Explain Zeolite process of softening of water with its advantages and disadvantages.
- What are the types of water and explain methods to remove temporary hardness?
- Write note on: Dissolved Oxygen.

December 2018

- Explain Zeolite process of softening of water with its advantages and disadvantages.
- How does the Hardness of water determined by EDTA Complexometric method?
- Write note on : Dissolved Oxygen.

May 2019

- Explain Zeolite process with its advantages and disadvantages.
- Explain the determination of Dissolve Oxygen by Winkler's Method.
- Write a note on Ion exchange resins.