

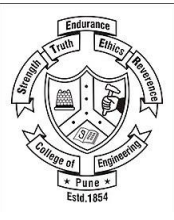
## Unit 5

# Water Chemistry

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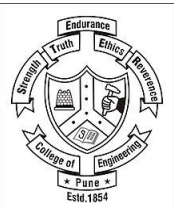
### Specifications for water:

- 1)** Water is important for the survival of life on the earth. Life has originated and evolved in water. Water acts as a solvent & medium for all the reactions taking place in living organisms. All the ancient civilization developed on the banks of rivers. The industrial revolution in Europe has started with the invention of steam engine by James Watt. The steam is generated from water. Water is an important component of Infra structure & Life activities. It is also very essential for the industrial development. Water plays an important role in the industries like:- Textile, Paper, Food processing etc in addition to Agriculture.
- 2)** Although, water is abundantly available on earth's surface, only a small quantity of it (4-5%) can be actually used for domestic and industrial purpose. The large portion ( $\approx 96\%$ ) is present in the seas and oceans, which is salty and cannot be used for domestic or industrial purpose directly. The remaining small quantity ( $\approx 4\%$ ) is present in the form of lakes, ponds, rivers, underground etc can be used.
- 3)** Sources Of Water: Water is mainly required for Domestic, Agricultural and Industrial purpose. The different sources of water can be mainly divided into following:
  - A) Rain Water
  - B) Sea water
  - C) Flowing Waters (Moorland Surface Drainage) present in rivers and streams etc.
  - D) Still Waters (Low Land Surface Drainage) present in ponds, lakes, reservoirs etc.
  - E) Underground Water from shallow deep wells and springs etc.
- 4)** From the point of view of Industrial application, it is not feasible to use Rain water and sea water.



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- Rain Water is irregular in supply and generally expensive to collect.
  - Sea water is too saline, containing 3-5% of dissolved salts. It can be used for cooling purpose in certain cases.
  - The main sources of water for Industrial purpose are therefore,
    - a) Flowing Waters (Moorland Surface Drainage) flowing through rivers, streams etc.
    - b) Still Water (Low Land Surface Drainage) present in lakes, ponds, reservoirs etc.
    - c) Underground Water from deep wells, springs etc.
- 5) General Composition of the Flowing water:**
- a) It is fairly constant in composition.
  - b) Generally clear but may have faint brownish colour due to dissolved CO<sub>2</sub> & weak organic acids.
  - c) Due to slightly acidic nature, it has corrosion tendency.
  - d) Have tendency to form Scales in Boiler.
  - e) For Drinking: may contain dissolved Pb and Cu (which are Toxic) & Pathogenic Organisms.
  - f) Rivers and Canals may get contaminated by sewage & Industrial waste released in it.
- 6) General Composition of the Still water:**
- a) Its composition is not constant but changes from place to place.
  - b) Usually colourless but may contain fine suspended mud.
  - c) Usually Hard and so can cause scales & corrosion in boilers and coolers.
- 7) General Composition of the Deep Well water:**
- a) Its composition is fairly constant.



b) It is colourless and clear.

c) May contain small amounts of  $\text{Fe}^{2+}$  salts, which get converted into hydrated  $\text{Fe}(\text{OH})_3$ .

Can have considerable amount of dissolved  $\text{CO}_2$ . So, corrosive for boilers.

### **Impurities in water:**

#### **I. Suspended impurities:**

When water is flowing in the river or present in the lake, then it appears turbid due to presence of fine particles of impurities suspended in the water. These are called Suspended Impurities. Such suspended impurities can be easily removed from water simply by filtration.

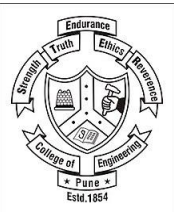
- The commonly occurring suspended impurities in the water are: clay particles, precipitates of iron hydroxide, calcium carbonate, bicarbonates, silicates etc. These impurities are of Inorganic type.
- Water may also contain Organic impurities in the form of decayed matter of dead or living organisms, pesticides etc.
- Underground water contains almost negligible amount of suspended impurities.
- As the size of suspended matter particles exceeds  $1\mu\text{m}$ , they are called Colloidal impurities.

#### **II. Biological (Microbial) impurities:**

When water is flowing through the river or gets accumulated in dams or lakes, it contains many micro-organisms, bacteria (aerobic or anaerobic) or fungi growing in it, pathogens, parasites etc are present in it. Their concentration increases with the time.

#### **III. Dissolved chemical impurities:**

Rain drops while down towards earth's surface, many gases like  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  present in the atmosphere get dissolved in it. If such water is directly used for industrial applications, it may cause corrosion of the metallic container in which it is stored or to some other metallic part it may come in contact with, during its application.



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- Underground and surface water, when comes in contact with surrounding soil, rock etc, then soluble inorganic compounds get dissolved and it shows presence of cations like:  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$  etc and anions like:  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{HCO}_3^-$  etc.
- In special industries like Sugar, Fertilizers, Pesticides, Agro-chemicals etc, alcohols, carbohydrates, carboxylic acids, aldehydes and ketones are also found to be present as impurities.

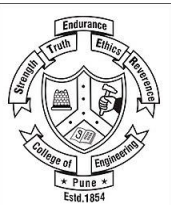
### Water quality parameters (physical, chemical, biological)

Water which contains excessive impurities cannot be used for Drinking or Industrial purpose. At the same time pure water is not available readily and economically.

- The acceptable Limits of impurities present in **Drinking water** are fixed by organizations like WHO (World Health Organization).
- The standards for **Drinking water** that is applicable in India is BIS (Bureau of Indian Standards) 10500-1991 standard. BIS used WHO standard as the basis and are amended from time to time.
- For the Industrial purpose, the purity levels required are much higher. They change from types of industry to industry.

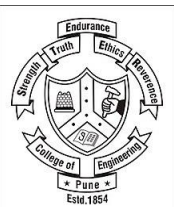
### Standard Drinking Water Specifications of BIS – 10500.

No	Characteristic / Parameter	Requirement  Desirable Limit	Permissible Limit in absence of an alternative source.
1	Colour (Hazes – Unit)	5	25
2	Odour	Unobjectionable	Unobjectionable
3	Taste	Agreeable	Agreeable
4	Turbidity (NTU unit)	5	10



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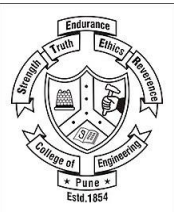
5	pH	6.5 to 8.5	No Relaxation
6	Total Hardness (ppm)	300	600
7	Iron as Fe (ppm)	0.3	1.0
8	Chloride as $\text{Cl}^-$ (ppm)	250	1000
9	Residual Free chlorine as Cl	0.2 ppm	- - -
10	Total Dissolve Solids (TDS)	500	2000
11	Calcium as $\text{Ca}^{2+}$ (ppm) (mg/L)	75	200
12	Manganese as $\text{Mn}^{2+}$ (ppm)	0.1	0.3
13	Copper as $\text{Cu}^{2+}$ (ppm)	0.05	1.5
14	Sulphate as $\text{SO}_4^{2-}$ (ppm)	200	400
15	Nitrates as $\text{NO}_3^-$ (ppm)	45	100
16	Fluorides as $\text{F}^-$ (ppm)	1.5	1.9
17	Phenolic compounds (ppm)	0.001	0.002
18	Mercury as $\text{Hg}^{2+}$ (ppm)	0.001	No Relaxation
19	Cadmium as $\text{Cd}^{2+}$ (ppm)	0.001	No Relaxation
20	Selenium as $\text{Se}^{2-}$ (ppm)	0.01	No Relaxation
21	Arsenic as $\text{As}^{3+}$ (ppm)	0.01	No Relaxation
22	Cyanide as $\text{CN}^-$ (ppm)	0.05	No Relaxation



23	Lead as $Pb^{2+}$ (ppm)	0.05	No Relaxation
24	Zinc as $Zn^{2+}$ (ppm)	5.0	No Relaxation
25	Anionic detergent (ppm)	0.2	1.0
26	Chromium as $Cr^{3+}$ (ppm)	0.05	No Relaxation
27	Pesticides (ppm)	Absent	0.001
28	Mineral oil (ppm)	0.01	0.03
29	Total Alkalinity (ppm)	200	600
30	Aluminium as $Al^{3+}$ (ppm)	0.03	0.2
31	Boron as $B^{3+}$ (ppm)	1.0	5.0

### Diseases caused by presence of Excess impurities in Drinking water

- A) Chloride ions (Desirable Limit: 250 ppm): Presence of Chloride ions is not proved to be very Harmful. But is in excess, leaves bad taste to water.
- B) Sulphate ions (Desirable Limit: 200 ppm): Presence of excess  $SO_4^{2-}$  ions, may produce a Laxative effect on the people consuming it.
- C) Nitrate ions (Desirable Limit: 45 ppm) Presence of excessive concentrations of  $NO_3^-$  ions is particularly Harmful to infant babies. It may cause, "Blue Baby Syndrome".
- D) Fluoride ions (Desirable Limit: 1.5 to 1.9 ppm): Less concentration of Fluoride ion may cause Dental Problems in children and excess concentration may cause "Fluorosis".
- E) Heavy Metals like Lead (Desirable Limit: 0.05 ppm) , Arsenic(Desirable Limit: 0.01 ppm) in the form of their salts are Toxic in nature.
- The presence of Pb in drinking water or food affects adversely. It is Toxic in nature.



- Lead is found to have adverse effects on the Human Nervous System, Renal System. In older people it may cause less hearing effect.

- Arsenic is well known for its Toxicity (Food Poisoning).

### Analysis of water:

#### I. Hardness:

Hardness of Water is basically defined as soap consuming capacity of a water sample. (or)

Depending upon the foam (froth or lather) produced by water when soap is dissolved in it, water is classified into: a) Soft Water and b) Hard Water.

- a) Soft Water: If good quantity of foam is produced on dissolving soap in it, then it is called Soft Water.
- b) Hard Water: If very less foam is produced or scum (curd like insoluble impurities are formed) on dissolving soap in it, then it is called Hard Water.
- Hardness of water is caused by presence of certain impurities in the water.
- If chlorides, Sulphates, Nitrates, bicarbonates, carbonates of bivalent cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  are present in water, water becomes Hard.
- Hard water is suitable for industrial applications.

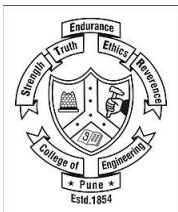
**Types of Hard Water:** Depending on the types of impurities present in water, it is mainly divided into following two types.

A) Temporary Hardness (or) Carbonate Hardness and

B) Permanent Hardness (or) Non-Carbonate Hardness.

Temporary Hardness (or) Carbonate Hardness: Hardness caused by Carbonates and/or bicarbonates of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  is called Temporary or carbonate Hardness.

- The salts responsible for causing Temporary or Carbonate Hardness are:
  - i.  $\text{Ca}(\text{HCO}_3)_2$ ,



- ii.  $\text{Mg}(\text{HCO}_3)_2$ ,
- iii.  $\text{CaCO}_3$ ,
- iv.  $\text{MgCO}_3$ , etc.
  - Carbonate hardness is also called Temporary Hardness because, it can be removed by simple methods like Boiling followed by Filtration.

Permanent Hardness (or) Non-carbonate Hardness: Hardness caused by Chlorides, Sulphates, Nitrates of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  is called Temporary or carbonate Hardness.

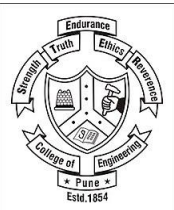
- The salts responsible for causing Temporary or Carbonate Hardness are:
  - i.  $\text{CaCl}_2$ ,
  - ii.  $\text{MgCl}_2$ ,
  - iii.  $\text{CaSO}_4$ ,
  - iv.  $\text{MgSO}_4$ ,
  - v.  $\text{Ca}(\text{NO}_3)_2$ ,
  - vi.  $\text{Mg}(\text{NO}_3)_2$ , etc.
- The salts of Fe and Mn if present in water cause Permanent Hardness.
- Non-Carbonate hardness is also called Permanent Hardness because it cannot be removed by simple methods. To remove Permanent Hardness some Chemical Treatment or other techniques are required.

$\text{Total Hardness} = \text{Temporary (Carbonate) Hardness} + \text{Permanent (Non-carbonate) Hardness}$
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**Units of Hardness:** Different Units are used to express Hardness of water. They are . . .

- i. ppm (parts per million) : It is defined as “the number of parts by weight of  $\text{CaCO}_3$  present in  $10^6$  (1 million) parts of water”.
- ii. Milligrams per liter (mg/L): It is defined as “The number of Milligrams (mg) of  $\text{CaCO}_3$  present in 1 Liter (L) of water”. (or) Number of parts of  $\text{CaCO}_3$  present in  $10^6$  parts of water.
- iii. Degree French ( $^\circ\text{Fr}$ ): It is defined as “The number of parts of  $\text{CaCO}_3$  present in  $10^5$  parts of water”.
- iv. Degree Clerk ( $^\circ\text{Cl}$ ): It is defined as “The Number of parts of  $\text{CaCO}_3$  present in 70,000 parts of water.



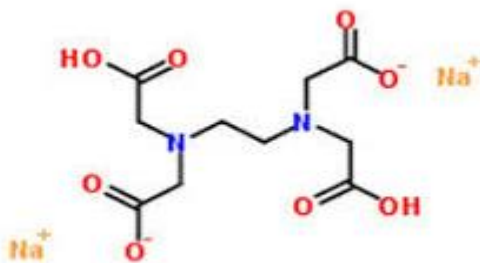


They can be related to each other by following relation:-

$$1 \text{ ppm Hardness} = 1 \text{ mg/L of CaCO}_3 \text{ equivalent} = 0.1^{\circ}\text{Fr} = 0.07^{\circ}\text{Cl}$$

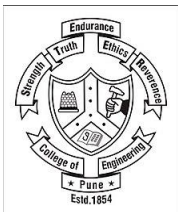
**Experimental Method to Determine Total Hardness of Water:** The most commonly used method to determine Total Hardness of water is Complexometry using EDTA (Ethylene Diamine Tetra Acetic Acid), as a Complexing agent.

- (In fact, in practice we use di-sodium salt of EDTA, indicated as  $\text{Na}_2\text{EDTA}$ .)
- The Volumetric Analysis is carried out using Erichrome Black-T (EBT) dye as an Indicator.
- The structure of  $\text{Na}_2\text{EDTA}$  can be given as under:



Disodium salt of EDTA ( $\text{Na}_2\text{EDTA}$ )

- We know that,  $\text{Na}_2\text{EDTA}$  forms a stoichiometric 1:1 complex with divalent cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  etc, which cause Hardness.
- By maintaining suitable conditions, this complexometric reaction can be used to measure the metal ion concentration causing Hardness to water.
- This reaction goes to completion at  $\text{pH} = 10$ , hence suitable Basic Buffer is used.
- The Buffer is usually the mixture of ( $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ ) solutions.

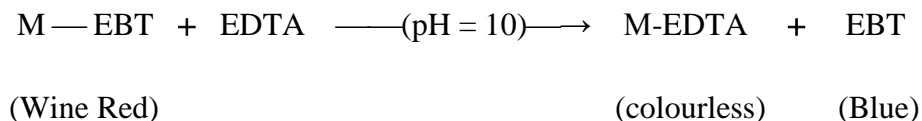


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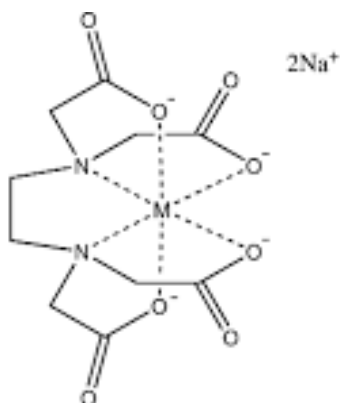
- Initially during the titration, the (blue) indicator (EBT) is added to water sample whose Hardness is to be determined along with the Buffer solution. The indicator reacts with the metal ions present in the water sample to undergo following reaction:

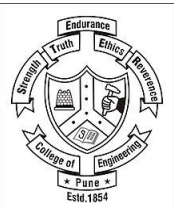


- This Wine Red solution of M-EBT is then titrated with standardized EDTA. This leads to the formation of colourless M-EDTA which is more stable than M-EBT, at pH = 10.



- A sharp colour change from Wine Red to Blue (Peacock Blue) indicates completion of the titration.
- Calculations are then carried out to find concentration of Metal ion/s causing Hardness, knowing concentration of EDTA and the volume of EDTA consumed during the Titration.
- The structure of M-EDTA complex can be given as under:-





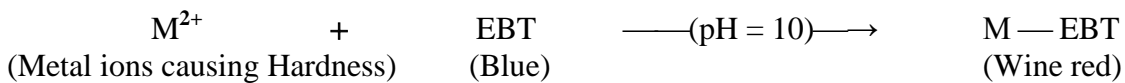
**EXPERIMENTAL PROCEDURE TO DETERMINE TOTAL HARDNESS OF WATER.**

- Principle:-

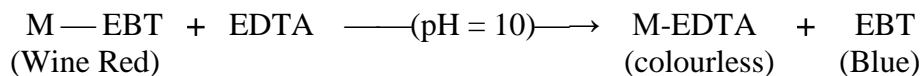
i) The  $\text{Na}_2\text{EDTA}$  forms a stoichiometric 1:1 complex with divalent cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  etc, which cause Hardness.

indicator Erichrome Black-T (EBT) is Blue coloured.

ii) When EBT reacts with any divalent cation like  $\text{M}^{2+}$ , it forms a complex which exhibits Wine Red Colour at  $\text{pH} = 10$ .



iii) This Wine Red coloured,  $\text{M} - \text{EBT}$  when titrated with standardized EDTA, The  $\text{M}^{2+}$  ion causing Hardness forms a colourless complex  $\text{M} - \text{EDTA}$  at  $\text{pH} = 10$ .



iv) As EBT is set free, it gives its original Blue colour, indicating completion of Titration.

- Experimental Procedure:- This experiment is performed in two parts.

Part – I : Standardization of EDTA:

- Prepare accurately 0.01 M  $\text{ZnCl}_2$  solution and approximately 0.01M  $\text{Na}_2\text{EDTA}$  solution.
- Fill the burette upto the mark with approximately 0.01 M  $\text{Na}_2\text{EDTA}$  solution.
- Pipette out 25 mL of 0.01 M  $\text{ZnCl}_2$  solution in a conical flask.
- Add 10 mL of Buffer having  $\text{pH} = 10$ , which is  $(\text{NH}_4\text{OH} + \text{NH}_4\text{Cl})$ .



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v) Add 2–3 mL of EBT (blue) indicator. The colour of reaction mixture becomes Wine Red.

- vi) Titrate this Wine Red reaction mixture with  $\text{Na}_2\text{EDTA}$  from burette till, Wine Red colour changes to Blue. This indicates End Point of the titration.
- vii) Record the amount (in mL) of  $\text{Na}_2\text{EDTA}$  consumed from the burette.
- viii) Calculate the accurate concentration of EDTA using following equation.

$$\begin{aligned}\text{ZnCl}_2 \text{ (Flask)} &= \text{Na}_2\text{EDTA (Burette)} \\ M_1 \times V_1 &= M_2 \times V_2 \\ 0.01 \times 25 &= M_2 \times \text{Burette Reading (known)} \\ M_2 \text{ (accurate conc of Na}_2\text{EDTA)} &\text{ can be calculated.}\end{aligned}$$

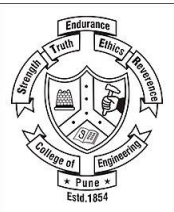
Part – II : To Find Total Hardness of Water.

- i) Fill Burette with accurately known concentration of  $\text{Na}_2\text{EDTA}$ . (Found in Part I)
- ii) Pipette out 25 mL of given Hard water sample in a conical flask.
- iii) Repeat all the steps of Part-I in the same sequence till step vii).
- iv) Calculate Total Hardness of water as under.

$$\begin{aligned}\text{Since, 1 M 1000 mL Na}_2\text{EDTA solution} &\equiv \text{1 M CaCO}_3 \text{ eq Hardness,} \\ \text{Hard Water (Flask)} &= \text{Na}_2\text{EDTA (Burette)} \\ M_1 \times V_1 &= M_2 \times V_2 \\ M_1 \times 25 &= (\text{known}) \times \text{Burette Reading (known)} \\ (\text{Since, 1 M 1000 mL Na}_2\text{EDTA solution} &\equiv \text{1 M CaCO}_3 \text{ eq Hardness}) \\ \text{Hardness of water} &= M_1 \text{ value.} \\ &\downarrow \times 100 \text{ (Mol wt of CaCO}_3\text{)} \\ \text{Hardness} &= ( \quad ) \text{ gms CaCO}_3\text{/L} \\ &\downarrow \times 1000 \text{ (so as to convert gm into mg)} \\ \text{Hardness} &= ( \quad ) \text{ mg CaCO}_3\text{/L} \\ \text{So, Hardness} &= ( \quad ) \text{ mg CaCO}_3\text{/L} = \text{ppm CaCO}_3 \text{ eq.}\end{aligned}$$

- If concentration of  $\text{Na}_2\text{EDTA}$  is known accurately (i.e. if it is a standard solution), directly Part II is done. Part I is not needed.

**II. Chloride content:**



Chloride ions ( $\text{Cl}^-$ ) are present in surface & underground water in significant concentration.

- Volumetric precipitation Titration methods are commonly carried out to determine concentration of Chloride ions present in a given water sample.

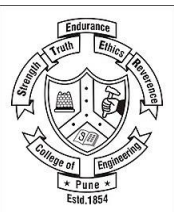
Experimental Determination (Mohr's Method) of  $\text{Cl}^-$  content in water:

- This is also called "Precipitation Titration" as formation of ppt of  $\text{Ag}_2\text{CrO}_4$  and  $\text{AgCl}$  takes place in this.

Principle: When there is possibility of two or more substances taking place during a reaction, that substance gets precipitated first which has least (smallest) value of its Solubility Product ( $K_{sp}$ ).

- In this case, there is a possibility of 2 substances ( $\text{Ag}_2\text{CrO}_4$  &  $\text{AgCl}$ ) getting precipitated as both of them are Sparingly Soluble Salts.
- Comparing the values, of their  $K_{sp}$ , it can be said,  $K_{sp}$  of  $\text{AgCl}$  is smaller than  $\text{Ag}_2\text{CrO}_4$ .
- So, till all  $\text{AgCl}$  does not get precipitated, precipitation of  $\text{Ag}_2\text{CrO}_4$  doesn't start. More over ppt of  $\text{Ag}_2\text{CrO}_4$  are Brick Red in colour, while  $\text{AgCl}$  gives White ppt.
- Experimental Procedure (Mohr's Method): The experiment is carried out in following steps:

- i) Fill Burette with standardized  $\text{AgNO}_3$  solution.
- ii) Take accurately measured volume of water sample. Record it.
- iii) Add 2 mL of Potassium chromate ( $\text{K}_2\text{CrO}_4$ ), which acts as an Indicator. The water sample turns Yellow as, it is the colour of the indicator.
- iv) Titrate this Yellow solution in the flask against standard  $\text{AgNO}_3$  from Burette.
- v) Continue titration, till white ppt (of  $\text{AgCl}$ ) is observed.
- vi) End Point: White to Brick Red. Stop the titration when End Point is reached.



vii) Record the  $\text{AgNO}_3$  consumed from the burette in mL.

- Reactions: Following reactions take place in the given sequence.
  - $\text{AgNO}_3(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow 2 \text{KNO}_3(\text{aq}) + \text{AgCl}(\text{s}) \downarrow$  (White)
  - $\text{AgNO}_3(\text{aq}) + \text{K}_2\text{CrO}_4(\text{aq}) \longrightarrow 2 \text{KNO}_3(\text{aq}) + \text{Ag}_2\text{CrO}_4(\text{s}) \downarrow$  (Brick Red ppt)

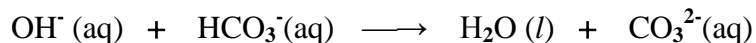
- Calculations:-

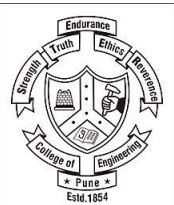
Burette	=	Flask		$N_2 = [\text{Cl}^-]$ (Chloride ion concentration) in N
(std $\text{AgNO}_3$ )	=	(Water sample)		$\downarrow \times 35.5$ (eq wt of chloride ion)
$N_1 \times V_1$	=	$N_2 \times V_2$		= ( ) gm/L of $[\text{Cl}^-]$ .
$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow \times 1000$ (to convert gm into mg)
(known)	(CBR)	=	$N_2 \times$	= ( ) mg/L Chloride ion.
(known)				= ( ) ppm. (Chloride content)
N2 is found out by calculations.				

### III. Alkalinity:

Pure water is neutral and so its pH = 7.00 But generally water in the lakes, ponds, rivers and underground water is slightly alkaline in nature.

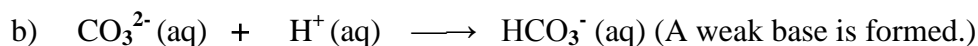
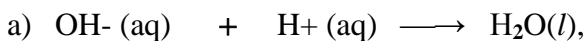
- The basic nature of water is due to the Hydrolysis of the dissolved basic salts present in the soil & surrounding earth's crust.
- The commonly occurring alkaline substances in the water are:- Hydroxides, Carbonates and Bi-carbonates of elements of Group 1 and 2. They are:  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{NH}_4\text{OH}$ ,  $\text{NaHCO}_3$ ,  $\text{KHCO}_3$ ,  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{Mg}(\text{HCO}_3)_2$  etc.
- In other words, the Basicity present in water is mainly due to free  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  ions present in the water.
- Both,  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions act as strong bases, but,  $\text{HCO}_3^-$  ion acts as a weak base.
- It should be noted that,  $\text{OH}^-$  and  $\text{HCO}_3^-$  ions can never exist together. This is because, if both these ions are present, they react with each other to form  $\text{CO}_3^{2-}$  ions as under-





Phenolphthalein Alkalinity (P):- The ions like  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  act as Strong Bases.

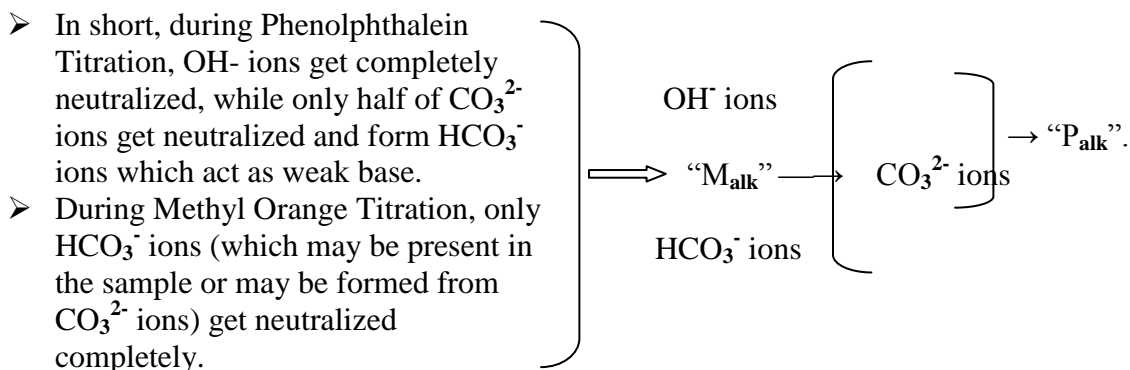
They are neutralized first by Strong acids. Their end point is indicated by using Phenolphthalein as an indicator. Phenolphthalein changes its colour from Colourless to Pink in the pH range of 8.5 to 10. ( $\text{pK}_{\text{in}} = 9.6$ ) This happens when strong Acid is taken in the Burette.



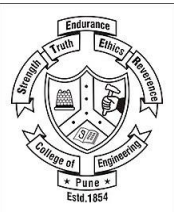
- Therefore, the Alkalinity due to presence of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions is called Phenolphthalein Alkalinity. It is indicated as " $\text{P}_{\text{alk}}$ " or just "P".

Methyl Orange Alkalinity (M):- The  $\text{HCO}_3^- (\text{aq})$  ion acts as a Weak Base. It is neutralized afterwards as mentioned above. The end Point of this is indicated by using Methyl Orange as an Indicator. Methyl Orange changes its colour from Orange to Yellow in the pH range of 3.5 to 5.5. ( $\text{pK}_{\text{in}} = 3.7$ ). This happens when strong Acid is taken in the Burette.

- $\text{HCO}_3^- (\text{aq}) + \text{H}^+ (\text{aq}) \longrightarrow \text{H}_2\text{O} (\text{l}) + \text{CO}_2 (\text{g}).$
- Therefore, the Alkalinity due to the presence of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions is called Phenolphthalein Alkalinity. It is indicated as " $\text{M}_{\text{alk}}$ " or just "M".
- It is interesting to note that, exactly half of  $\text{CO}_3^{2-}$  get neutralized during " $\text{P}_{\text{alk}}$ " and other half get neutralization during " $\text{M}_{\text{alk}}$ ".



Experimental Procedure to determine the ions present in water causing Alkalinity and their concentrations:



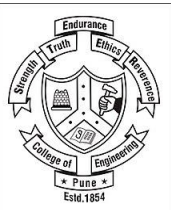
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- Principle: Alkalinity due to presence of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions is called

Phenolphthalein Alkalinity. It is indicated as " $\text{P}_{\text{alk}}$ " or just " $\text{P}$ ". Similarly, Alkalinity due to the presence of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions is called Phenolphthalein Alkalinity. It is indicated as " $\text{M}_{\text{alk}}$ " or just " $\text{M}$ ".

- Exactly half of  $\text{CO}_3^{2-}$  get neutralized (to  $\text{HCO}_3^-$ ) during " $\text{P}_{\text{alk}}$ " and these  $\text{HCO}_3^-$  or other which are present in the water from the beginning, get neutralization during " $\text{M}_{\text{alk}}$ ".
- Experimental Procedure: It is carried out in following steps –
  - a. Fill Burette with standard (known concentration/Normality) solution of strong acid.
  - b. Take 25 mL of water sample, whose Alkalinity is to be determined into a conical flask with the help of a pipette.
  - c. Add 1 to 2 drops of Phenolphthalein indicator. If  $\text{OH}^-$  and/or  $\text{CO}_3^{2-}$  ions are present in it, the water will develop pink colour.
  - d. Titrate it against Alkaline water in the conical flask till the colour changes from Pink to Colourless. Note the quantity in mL of Acid consumed from the burette. This is "P reading".
  - e. [If Pink colour is not developed after adding few drops of Phenolphthalein in water, it means that both  $\text{OH}^-$  &  $\text{CO}_3^{2-}$  are absent in water. In such case, P reading is 0.0 mL]
  - f. Add 2-3 drops of Methyl Orange into the titrating mixture present in the flask. The colour of the solution will become Yellow.
  - g. Continue its titration with the strong acid from the burette till the Yellow solution becomes Orange. [Do not top up the burette with strong acid. Do not disturb the burette reading] Record the burette reading when the colour becomes Orange. This is called "M reading".





Calculation: “P<sub>alk</sub>” is calculated from P reading and “M<sub>alk</sub>” is calculated from M reading.

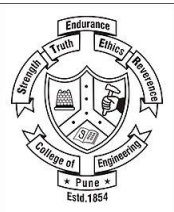
Part 1 : Calculation of P = P <sub>alk</sub> = P <sub>alkalinity</sub> .	Part 2 : Calculation of M = M <sub>alk</sub> = M <sub>alkalinity</sub> .
$\frac{\text{Acid}}{N_1 \times V_1} = \frac{\text{Alk}}{N_2 \times V_2}$ $\text{(Known)} \times (\text{P reading}) = N_2 \times 25$ $\text{So, } N_2 = \frac{(\text{Known } N_1 \times (\text{P reading}))}{25} N$ $\downarrow \times 50 \text{ (eq wt of CaCO}_3\text{)}$ $= ( ) \text{ gm/L CaCO}_3 \text{ eqv.}$ $\downarrow \times 1000 \text{ (to convert gm into mg)}$ $= ( ) \text{ mg/L (ppm) CaCO}_3 \text{ eqv.}$ $\therefore P = P_{\text{alk}} = ( ) \text{ mg/L ppm CaCO}_3 \text{ eqv.}$	$\frac{\text{Acid}}{N_1 \times V_1} = \frac{\text{Alk}}{N_2 \times V_2}$ $\text{(Known)} \times (\text{M reading}) = N_2 \times 25$ $\text{So, } N_2 = \frac{(\text{Known } N_1 \times (\text{M reading}))}{25} N$ $\downarrow \times 50 \text{ (eq wt of CaCO}_3\text{)}$ $= ( ) \text{ gm/L CaCO}_3 \text{ eqv.}$ $\downarrow \times 1000 \text{ (to convert gm into mg)}$ $= ( ) \text{ mg/L (ppm) CaCO}_3 \text{ eqv.}$ $\therefore M = M_{\text{alk}} = ( ) \text{ mg/L ppm CaCO}_3 \text{ eqv.}$

- Knowing the values of P<sub>alk</sub> & M<sub>alk</sub>, we can find out: Which ions are present in water causing Alkalinity & their concentrations in terms of mg/L (ppm) CaCO<sub>3</sub> equivalent. By following Table:-

Volume of Acid (mL)	Alkalinity (ppm)	[OH <sup>-</sup> ] ppm	[CO <sub>3</sub> <sup>2-</sup> ] ppm	[HCO <sub>3</sub> <sup>-</sup> ] ppm
P reading = 0	P = 0	0	0	M
P reading = M reading	P = M	M	0	0
P reading = ½ M reading	P = ½ M	0	2 P	0
P reading > ½ M reading	P > ½ M	(2 P) – M	2 x (M – P)	0
P reading < ½ M reading	P < ½ M	0	2 P	M – (2P)

### Dissolved Oxygen:

The dissolved oxygen content is an important index when considering its suitability for town supply. Good clean potable water will give dissolved oxygen value close to the theoretical value for the saturated solution of oxygen in water. When there is pollution from organic matter and other trade effluents, the dissolved oxygen is up in various biochemical oxidation processes and it is only slowly replaced through surface absorption. Such water will give a low dissolved oxygen content until oxidation is completed. Adequate dissolved oxygen is necessary for the life of fish and other aquatic organisms. The methods described below for the determination of oxygen in water is based on that devised by Winkler. When manganese hydroxide is precipitated



in the water sample it is quickly oxidized to higher hydrated oxides (probably in the four valent state) by the dissolved oxygen. Iodine, equivalent to the dissolved oxygen content, is then liberated on acidification in the presence of iodide, and it may be titrated with standard thio-sulphate.

Dissolved oxygen (DO) levels in environmental water depend on the physiochemical and biochemical activities in water body and it is an important useful in pollution and waste treatment process control. Two methods are commonly used to determine DO concentration: (1) The iodometric method which is a titration-based method and depends on oxidizing property of DO and (2) The membrane electrode procedure, which works based on the rate of diffusion of molecular oxygen across a membrane. In the Iodometric method, divalent manganese solution is added to the solution, followed by addition of strong alkali in a glass-stopper bottle. DO rapidly oxidizes an equivalent amount of the dispersed divalent manganese hydroxide precipitates to hydroxides of higher valence states. In the presence of iodide ions in an acidic solution, the oxidized manganese reverts to the divalent state, with the liberation of iodine equivalent of the original DO content. The iodine is then titrated with a standard solution of thiosulfate. The titration end point can be detected visually with a starch indicator. Some oxidizing and reducing agents present in solution can interfere with the iodometric method. Oxidizing agents liberate iodine from iodides (positive interference) and some reducing agents reduce iodine to iodide (negative interference). Also, organic matter present in solution can be oxidized partially in the presence of oxidized manganese precipitate, thus causing negative errors. Thus some modification of procedure is required.

### **Applications**

Dissolved oxygen analysis can be used to determine:

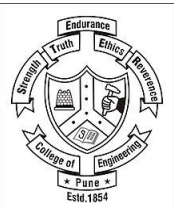
- the health or cleanliness of a lake or stream,
- the amount and type of biomass a freshwater system can support,
- the amount of decomposition occurring in the lake or stream.

### **Experimental method for determination of dissolved oxygen.**

#### **Aim**

The aim of the experiment is to determine the quantity of dissolved oxygen present in the given sample(s) by using modified Winkler's (Azide modification) method.

#### **Principle**



Dissolved Oxygen (D.O.) levels in natural and wastewaters are dependent on the physical, chemical and biochemical activities prevailing in the water body. The analysis of D.O. is a key test in water pollution control activities and waste treatment process control. Improved by various techniques and equipment and aided by instrumentation, the Winkler (or iodometric) test remains the most precise and reliable titrimetric procedure for D.O. analysis. The test is based on the addition of divalent manganese solution, followed by strong alkali to the water sample in a glass-stoppered bottle. D.O. present in the sample rapidly oxidises in equivalent amount of the dispersed divalent manganous hydroxide precipitate to hydroxides of higher valency states. In the presence of iodide ions and upon acidification, the oxidised manganese reverts to the divalent state, with the liberation of iodine equivalent to the original D.O. content in the sample. The iodine is then titrated with a standard solution of thiosulphate.

### Apparatus

1. 300 mL capacity bottle with stopper
2. Burette
3. Pipettes, etc.

### Reagents

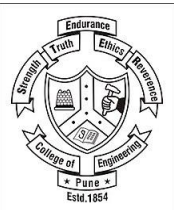
1. Manganous sulphate solution ( $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ )
2. Alkali-iodide azide reagent
3. Conc. sulphuric acid (36 N)
4. starch indicator
5. Standard sodium thiosulphate solution (0.025N)
6. Standard potassium dichromate solution (0.025N)

### Procedure

1. Add 2 mL of manganous sulphate solution and 2 mL of alkali-iodide azide reagent to the 300 mL sample taken in the bottle, well below the surface of the liquid.

(The pipette should be dipped inside the sample while adding the above two reagents.)

2. Stopper with care to exclude air bubbles and mix by inverting the bottle at least 15 times.
3. When the precipitate settles, leaving a clear supernatant above the manganese hydroxide floc, shake again.
4. After 2 minutes of settling, carefully remove the stopper, immediately add 3 mL



concentrated sulphuric acid by allowing the acid to run down the neck of the bottle.

5. Restopper and mix by gentle inversion until dissolution is complete.
6. Measure out 203 mL of the solution from the bottle to an Erlenmeyer flask. As 2 mL each of manganese sulphate and azide reagent have been added, the proportionate quantity of yellow solution corresponds to 200 mL of sample is

$$= \frac{200 \times 300}{300 - 4} = 203 \text{ mL}$$

7. Titrate with 0.025 N sodium thiosulphate solution to a pale straw colour.
8. Add 1–2 mL starch solution and continue the titration to the first disappearance of the blue colour and note down the volume of sodium thiosulphate solution added (V), which gives directly the D.O. in mg/L.

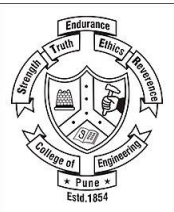
### Observation

Sample x Standard sodium thiosulphate solution (0.025N) (Starch indicator)

Description of sample	Trial no.	Volume of sample (mL)	Burette reading		Volume of titrant mL	D.O. in mg/L
			Initial	Final		
Sample I						
Sample II						
Sample III						

### Result

Description of sample	D.O. mg/L
Sample I	
Sample II	
Sample III	



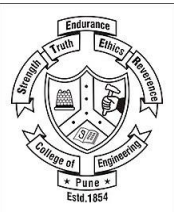
### **Biological Oxygen Demand:**

The Biochemical Oxygen Demand (BOD) is an empirical standardized laboratory test which measures oxygen requirement for aerobic oxidation of decomposable organic matter and certain inorganic materials in water, polluted waters and wastewater under controlled conditions of temperature and incubation period. The quantity of oxygen required for above oxidation processes is a measure of the test. The test is applied for fresh water sources (rivers, lakes), wastewater (domestic, industrial), polluted receiving water bodies, marine water (estuaries, coastal water) and also for finding out the level of pollution, assimilative capacity of water body and also performance of waste treatment plants

#### **Principle**

This test measures the oxygen utilized for the biochemical degradation of organic material (carbonaceous demand) and oxidation of inorganic material such as sulphides and ferrous ions during a specified incubation period. It also measures the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by an inhibitor. Temperature effects are held constant by performing a test at fixed temperature. The methodology of BOD test is to compute a difference between initial and final Do of the samples incubation. Minimum 1.5 L of sample is required for the test. DO is estimate by iodometric titration.

Since the test is mainly a bio-assay procedure, it is necessary to provide standard conditions of temperature, nutrient supply, pH (6.5-7.5), adequate population of microorganisms and absence of microbial-growth-inhibiting substances. The low solubility of oxygen in water necessitates strong wastes to be diluted to ensure that the demand does not increase the available oxygen. A mixed group of microorganisms should be present in the sample; otherwise, the sample has to be seeded. Generally, temperature is controlled at 20°C and the test is conducted for 5 days, as 70 to 80% of the carbonaceous wastes are oxidized during this period. The test can be performed at any other temperature provided the correlation between BOD<sub>5</sub> 20°C is established under same experimental condition (for example BOD<sub>5</sub>, 27°C) is equivalent to BOD<sub>3</sub>, 27°C) for Indian conditions. While reporting the results, the incubation period in days and temperature in °C is essential to be mentioned.



### Equipment and apparatus

- BOD bottles 300mL capacity (clean with a detergent, rinse thoroughly and drain before use) with a water seal.
- Incubator or water-bath to be controlled at 20°C or at any desired temperature 1°C. Exclude all light to prevent photosynthetic production of DO.

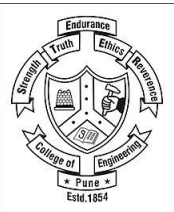
### Reagents and standards

All reagents listed in DO estimation are used for BOD. In addition following reagents are required:

- Phosphate buffer: Dissolve 8.5g  $\text{KH}_2\text{PO}_4$ , 21.75g  $\text{K}_2\text{HPO}_4$ , 33.5g  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  and 1.7g  $\text{NH}_4\text{C}$ ; in distilled water and dilute to 1000mL. The pH should be 7.2 without further adjustment. Discard reagent if there is any sign of biological growth.
- Magnesium sulphate: Dissolve 22.5g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in about 700mL of distilled water and dilute to 1 Litre.
- Calcium chloride: Dissolve 27.5g anhydrous  $\text{CaCl}_2$  in about 700mL of distilled water and dilute to 1 Litre.
- Ferric chloride: Dissolve 0.25g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in about 700mL of distilled water and dilute to 1 L.
- Sodium sulphate solution 0.025N: Dissolve 1.575g  $\text{Na}_2\text{SO}_3$  in distilled water and dilute to 1000mL. Solution should be prepared daily.
- Acid and Alkali solutions 1N: Prepare 1N  $\text{H}_2\text{SO}_4$  and 1N  $\text{NaOH}$  or neutralization of caustic or acidic samples.
- Nitrification inhibitor: 2-chloro-6-(trichloromethyl) pyridine [Nitrification inhibitor 2570-24 (2.2% TCMP), Hach Co. equivalent]
- Glucose-glutamic acid solution: Dry reagent grade glucose and glutamic acid at 103°C for 1h. Dissolve 150 mg glucose and 150mg glucose acid in distilled water and dilute to 1000mL. Prepare fresh immediately before use.

### Sample collection, preservation and storage

Grab or composite samples are collected. Keep composite samples at or below 4°C during compositing. Samples for BOD may degrade significantly during storage. Minimise reduction of BOD by analyzing samples promptly or by cooling it to near freezing temperature during storage. The maximum holding time recommended between collection and analysis is 48 hours. Warm chilled samples to 20-27°C  $\pm$  3°C before analysis. State storage time and condition as part of results.



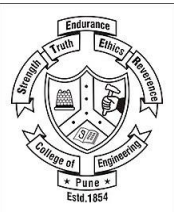
## Procedure

### Preparation of dilution water:

- i. The source of dilution water may be distilled water, tap or receiving-stream water free of biodegradable organics and bio inhibitory substances such as chlorine or heavy metals.
- j. Aerate the required volume of dilution water in a suitable bottle by bubbling clean-filtered compressed air for sufficient time to attain DO saturation at room temperature or at 20°C/27°C. Before use stabilize the water at 20°C/27°C.
- k. Add 1mL each of phosphate buffer, magnesium sulphate, and calcium chloride and ferric chloride solutions in that order for each Litre of dilution water. Mix well. Quality of dilution water may be checked by incubating a BOD bottle full of dilution water for 5 days at 20°C for 3 days at 27°C. DO uptake of dilution water should not be more than 0.2mg/L and preferable not more than 0.1mg/L.
- l. For wastes which are not expected to have sufficient microbial population, seed is essential. Preferred seed is effluent from a biological treatment system. Where this is not available, supernatant from domestic wastewater (domestic sewage) settled at room temperature for at least 1h but not longer than 36hours is considered sufficient in the proportion 1-2mL/L of dilution water. Adopted microbial population can be obtained from the receiving water microbial population can be obtained from the receiving water body preferably 3-8 km below the point of discharge. In the absence of such situation, develop an adapted seed in the laboratory.
- m. Determine BOD of the seeding material. This is seed control. From the value of seed control determine seed DO uptake. The DO uptake of seeded dilution water should be between 0.6mg/L and 1mg/L.

### Sample preparation:

- a. Neutralize the sample to pH 7, if it is highly acidic or alkaline.
- b. The sample should be free from residual chlorine. If it contains residual chlorine remove it by using  $\text{Na}_2\text{S}_2\text{O}_3$  solution as described below.



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- c. Take 50mL of the sample and acidify with addition of 10mL 1 + 1 acetic acid. Add about 1g KI. Titrate with 0.025N  $\text{Na}_2\text{S}_2\text{O}_3$ , using starch indicator. Calculate the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  required per Litre of the sample and accordingly add to the sample to be tested for BOD.
- d. Certain industrial wastes contain toxic metals, e.g. planting wastes. Such samples often require special study and treatment.
- e. Bring samples to  $20 \pm 1^\circ\text{C}$  before making dilutions.
- f. If nitrification inhibition is desired, add 3mg 2-chloro-6-(trichloromethyl) pyridine (TCMP) to each 300mL bottle before capping or add sufficient amount to the dilution water to make a final concentration of 30mg/L. Note the use of nitrogen inhibition in reporting results.
- g. Samples having high DO contents,  $\text{DO} \geq 9\text{mg/L}$  should be treated to reduce the DO content to saturation at  $20^\circ\text{C}$ . Agitate or aerate with clean, filtered compressed air.

Dilution of sample: Dilutions that result in a residual DO of at least 1mg/L and DO uptakes of at least 2mg/L produce reliable results. Make several dilutions of the pre-treated sample so as to obtain about 50% depletion of DO or DO uptake of 2mg/L. Prepare dilutions as follows:

Siphon out half the required volume of seeded dilution water in a graduated cylinder or volumetric flask without entraining air. Add the desired quantity of mixed sample and dilute to the appropriate volume by siphoning dilution water. Mix well with plunger type mixing rod to avoid entraining air.

General guidelines for dilution range are as follows:

0.1% to 1% : Strong trade waste

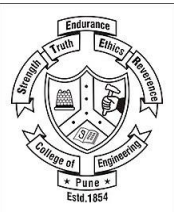
1% to 5% : Raw or settled sewage

5% to 25% : Treated effluent

25% to 100% : River water

Sample processing:





- a. Siphon the diluted or undiluted sample in three labeled bottles and stopper immediately.
- b. Keep 1 bottle for determination of the initial DO and incubate 2 bottles at 20°C for 3 days. See that the bottles have a water seal.
- c. Prepare a blank in triplicate by siphoning plain dilution water (without seed) to measure the O<sub>2</sub> consumption in dilution water.
- d. Also prepare a seed blank in triplicate to measure BOD of seed for correction of actual BOD.
- e. Determine DO in a BOD test can in the blank on initial day and end of incubation period by Winkler method as described for DO measurement.
- f. DO estimation in a BOD test can also be done by membrane electrodes. A DO probe with a stirrer is used to determine initial and final DO after incubation in BOD samples. The semi-permeable membrane provided in the DO probe acts as a diffusion barrier against impurities between sensing element and sample.

### Calculations

Calculate BOD of the sample as follows:

- a. When dilution water is not seeded

$$\text{BOD as O}_2 \text{ mg/L} = (D_1 - D_2) \times 100 / \% \text{ dilution}$$

- b. When dilution is seeded

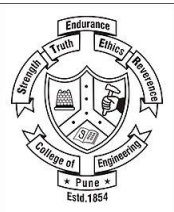
$$\text{BOD O}_2 \text{ mg/L} = [(D_1 - D_2) - (B_1 - B_2)] \times 100 / \% \text{ dilution}$$

- c. When material is added to sample or to seed control

$$\text{BOD O}_2 \text{ mg/L} = [(D_1 - D_2) - (B_1' \times B_2')] \times F \times 100 / \% \text{ dilution}$$

where,

D1 = DO of sample immediately after preparation, mg/L



D2 = DO of sample after incubation period, mg/L

B1 = DO of blank (seeded dilution water) before incubation, mg/L

B2 = DO of blank (seeded dilution water) after incubation, mg/L

F = ratio of seed in diluted sample to seed in seed control (Vol. Of seed in diluted sample / Vol. of seed in seed control)

B1' = DO of seed control before incubation, mg/L

B2' = DO of seed control after incubation, mg/L

In calculations, do not make corrections for DO uptake in dilution water.

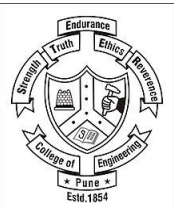
### **Result:**

### **Precision and Bias**

For reliable results following conditions are essential:

- Minimum depletion of DO of 2mg/L
- Minimum residual DO of 1mg/L at the end of test period
- 5days 20°C or 3days 27°C BOD value of 5mg/L can be measured directly without dilution
- For reproducible and accurate results, perform the test in duplicate
- Check the quality of reagents and dilution water
- Perform glucose-glutamic acid check to get the value of BOD for known synthetic chemical.

Minimum detection limits is 1mg/L. Because BOD test is bioassay, the results are influenced by many factors, viz. operating conditions like pH, nutrients, buffers, toxicants, seed material, etc. The standard check with the Glucose-glutamic acid (GG) is intended for evaluating reliability of analytical technique adopted. For 300mg/L mixed primary standard of GG, average BOD would



be 198 mg/L with a standard deviation of 30.5 mg/L. There is no measurement of establishing bias of the BOD procedure.

### **Chemical Oxygen Demand:**

The chemical oxygen demand gives information on the oxygen required by a water of oxidation of almost all water-soluble organic substance, the exceptions being a number of compounds containing nitrogen and only very slightly soluble hydrocarbons. The following method is used to determine the quantity of organic material in a sample which may be oxidised chemically. The sample is refluxed with an accurately known amount of a potassium dichromate in a large excess of sulphuric acid for definite time. Most organic substances are completely oxidised and the remaining dichromate is determined by titration with ferrous ammonium sulphate. Silver sulphate is added as a catalyst for the oxidation and mercuric sulphate is added to overcome chloride interference.

The methods has a theoretical range of 0-500 mg dm<sup>-3</sup> chemical oxygen demand (COD) when using a 5 cm<sup>3</sup> sample and is suitable for highly polluted water. It should be noted that if a larger sample is used organic matter may not be oxidised to the same extent by the more dilute reagents.

### **Experimental method for determination of chemical oxygen demand.**

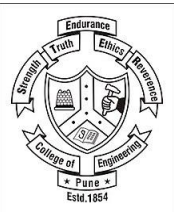
*(All apparatus should be washed in chromic acid before used and should be free of dust. The ground glass joints should free grease).*

#### **Collection of Sample**

Collect the sample in a narrow necked 200-300 cm<sup>3</sup> glass bottle having an accurately fitting ground glass stopper. When sampling stream water, displace the water in the bottle several times before collecting the sample. Avoid contamination.

### **Procedure for Determination of Chemical Oxygen Demand**

Introduce 10.0 cm<sup>3</sup> of the water sample into 100 cm<sup>3</sup> round-bottomed flask, and add 2 cm<sup>3</sup> potassium dichromate, 2.5 cm<sup>3</sup> mercuric sulphate solution, 10-15 ml concentrated sulphuric acid containing silver sulphate, and an anti-bumping rod. Heat gentle with steady boiling over an



electric hot plate or heating mantle, under a reflux condenser. After exactly 45 minutes boiling, allow cooling briefly, wash 20 cm<sup>3</sup> distilled water through the condenser into the flask and the cool completely in cold water. Add 2 drops of ferroin solution and titrate the excess potassium dichromate with ammonium iron (II) sulphate until the colour changes from bluish-green to reddish brown.

Determine a blank with 10.0 cm<sup>3</sup> distilled water under exactly the same conditions.

### Standardization of Ammonium Iron (II) Sulphate

Add 10 cm<sup>3</sup> concentrated sulphuric acid carefully to 20 cm<sup>3</sup> water and cool. Add 2 cm<sup>3</sup> potassium dichromate and titrate with ammonium iron(II) sulphate using drops of ferroin as indicator. The colour changes from bluish-green to reddish-brown.

### Reagents

Standard Potassium Dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) (0.025 mol dm<sup>-3</sup>)

Dissolve 7.3548g AR potassium dichromate in distilled water, and make up to 1 litre. Dry the potassium dichromate for two hours in a drying chamber at 105<sup>0</sup>C before weighing out.

Ammonium Iron (II) Sulphate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·FeSO<sub>4</sub>·6H<sub>2</sub>O (0.0125 mol dm<sup>-3</sup>)

Carefully add 20 cm<sup>3</sup> concentrated sulphuric acid to 200 cm<sup>3</sup> water, mix, and cool. Dissolve 4.902g ammonium iron(II) sulphate in the cooled acid and make up to 1 litre.

Mercuric sulphate

Dissolve 5 gm mercuric sulphate in a mixture of 25 cm<sup>3</sup> concentrated sulphuric acid and 225 cm<sup>3</sup> water.

Silver Sulphate/ Sulphuric acid

Dissolve 5g silver sulphate in 500 cm<sup>3</sup> AR concentrated sulphuric acid by mixing.

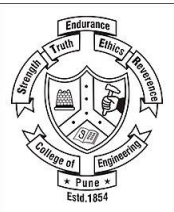
Ferroin Indicator

Dissolved 0.695g FeSO<sub>4</sub>·7H<sub>2</sub>O in distilled water (100 cm<sup>3</sup>), add 1,10-phenanthroline monohydrate (1.485g) and shake until dissolved.

### Ion transport:

Ion transport is the movement of ions across a membrane, passively through ion channels or actively through ion pumps such as symporters and antiporters.

The transport of ions across the membranes of cells and organelles is a prerequisite for many of life's processes. Transport often involves very precise selectivity for specific ions. Recently, atomic-resolution structures have been determined for channels or pumps that are selective for sodium, potassium, calcium, and chloride: four of the most abundant ions in biology. From these



structures we can begin to understand the principles of selective ion transport in terms of the architecture and detailed chemistry of the ion conduction pathways.

### Conductivity:

Conductivity of a substance is defined as '*the ability or power to conduct or transmit heat, electricity, or sound*'. Its units are Siemens per meter [S/m] in SI and millimhos per centimeter [mmho/cm] in U.S. customary units. Its symbol is  $\kappa$  or  $s$ .

Pure water is not a good conductor of electricity. Ordinary distilled water in equilibrium with carbon dioxide of the air has a conductivity of about  $10 \times 10^{-6} \text{ W}^{-1} \cdot \text{m}^{-1}$  (20 dS/m). Because the electrical current is transported by the ions in solution, the conductivity increases as the concentration of ions increases. Thus conductivity increases as water dissolved ionic species.

Typical conductivity of waters:

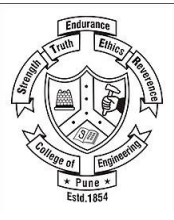
Ultra pure water  $5.5 \cdot 10^{-6} \text{ S/m}$

Drinking water 0.005 – 0.05 S/m

Sea water 5 S/m

Conductivity is a measure of water's capability to pass electrical flow. This ability is directly related to the concentration of ions in the water. These conductive ions come from dissolved salts and inorganic materials such as alkalis, chlorides, sulfides and carbonate compounds. Compounds that dissolve into ions are also known as electrolytes. The more ions that are present, the higher the conductivity of water. Likewise, the fewer ions that are in the water, the less conductive it is. Distilled or deionized water can act as an insulator due to its very low (if not negligible) conductivity value. Sea water, on the other hand, has a very high conductivity.

Ions conduct electricity due to their positive and negative charges. When electrolytes dissolve in water, they split into positively charged (cation) and negatively charged (anion) particles. As the dissolved substances split in water, the concentrations of each positive and negative charge remain equal. This means that even though the conductivity of water increases with added ions, it remains electrically neutral.

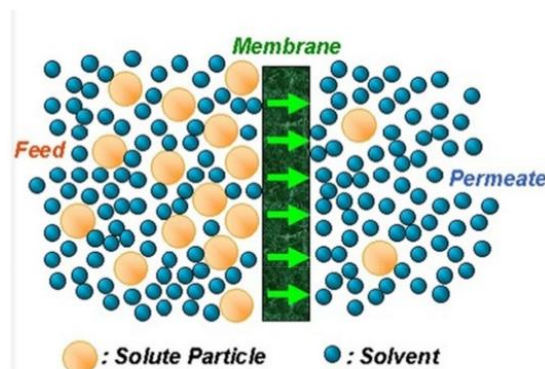


## Treatment of drinking water-

### I. Membrane filtration

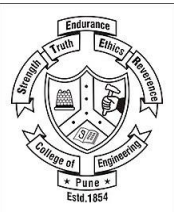
The Membrane Filter (MF) Technique was introduced in the late 1950s as an alternative to the Most Probable Number (MPN) procedure for microbiological analysis of water samples. The MF Technique offers the advantage of isolating discrete colonies of bacteria, whereas the MPN procedure only indicates the presence or absence of an approximate number of organisms (indicated by turbidity in test tubes).

The MF Technique was accepted by the U.S. EPA for microbiological testing of potable water in the 11<sup>th</sup> edition of *Standard Methods for the Examination of Water and Wastewater*. In the 1978 publication, *Microbiological Methods for Monitoring the Environment*, the U.S. EPA stated that the MF Technique is preferred for water testing because it permits analysis of larger samples in less time.



**Fig. Membrane filtration**

A membrane is a thin layer of semi-permeable material that separates substances when a driving force is applied across the membrane. Membrane processes are increasingly used for removal of bacteria, microorganisms, particulates, and natural organic material, which can impart color, tastes, and odors to water and react with disinfectants to form disinfection by products.



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As advancements are made in membrane production and module design, capital and operating costs continue to decline. The membrane processes discussed here are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO).

Municipal water treatment plants monitor drinking, waste, and surface water for the presence of coliform bacteria by the MF Technique. The key organism monitored in water treatment facilities is *E. coli*. The U.S. EPA considers this organism the leading indicator of fecal contamination.

In addition to its use by government labs for monitoring drinking water, the MF Technique is also used for microbial monitoring in the pharmaceutical, cosmetics, electronics, and food and beverage industries.

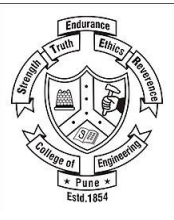
The MF Technique is used in these industrial labs to monitor the presence of microorganisms in process waters and final product.

The pharmaceutical and cosmetics industries typically focus on monitoring their process water for *Pseudomonas* species. The electronics industry monitors for any and all microorganisms because they must keep their process water free from even the smallest organisms. Microbial monitoring in the food and beverage industry typically employs several types of techniques because of the variety of samples that are encountered. Beverage samples can typically be monitored for microorganisms by the MF Technique, but when solid samples cannot be liquefied, alternative methods must be used.

The MF Technique is an effective, accepted technique for testing fluid samples for microbiological contamination. It involves less preparation than many traditional methods, and is one of a few methods that will allow the isolation and enumeration of microorganisms. The MF Technique also provides presence or absence information within 24 hours.

### **Advantages:**

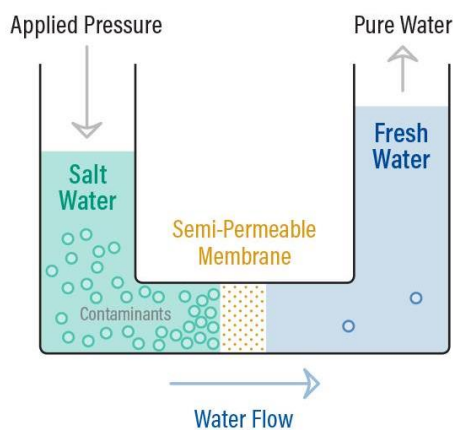
- Permits testing of large sample volumes.
- Reduces preparation time as compared to many traditional methods.
- Allows isolation and enumeration of discrete colonies of bacteria.
- Provides presence or absence information within 24 hours.
- Effective and acceptable technique. Used to monitor drinking water in government laboratories.



- Useful for bacterial monitoring in the pharmaceutical, cosmetics, electronics, and food and beverage industries.
- Allows for removal of bacteriostatic or cidal agents that would not be removed in Pour Plate, Spread Plate, or MPN techniques.

## I. Reverse Osmosis (RO)

Reverse Osmosis is a technology that is used to remove a large majority of contaminants from water by pushing the water under pressure through a semi-permeable membrane.



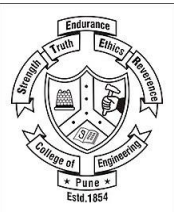
**Fig. Reverse Osmosis**

**Reverse Osmosis**, commonly referred to as **RO**, is a process where you demineralize or deionize water by pushing it under pressure through a semi-permeable Reverse Osmosis Membrane.

Reverse osmosis (RO) is a special type of filtration that uses a semi-permeable, thin membrane with pores small enough to pass pure water through while rejecting larger molecules such as dissolved salts (ions) and other impurities such as bacteria. Reverse osmosis is used to produce highly purified water for drinking water systems, industrial boilers, food and beverage processing, cosmetics, pharmaceutical production, seawater desalination, and many other applications. It has been a recognized technology for more than a century and commercialized since the 1960's.

Reverse osmosis can effectively remove nearly all inorganic contaminants from water. RO can also effectively remove radium, natural organic substances, pesticides, cysts, bacteria and





viruses. RO is particularly effective when used in series with multiple units. Disinfection is also recommended to ensure the safety of water.

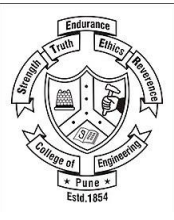
Some of the advantages of RO are:

- Removes nearly all contaminant ions and most dissolved non-ions,
- Relatively insensitive to flow and total dissolved solids (TDS level and suitable for small systems with a high degree of seasonal fluctuation in water demand,
- RO operates immediately, without any minimum break-in period,
- Low effluent concentration possible,
- Bacteria and particles are also removed, and
- Operational simplicity and automation allow for less operator attention and make RO suitable for small system applications.
- Some of the limitations of RO are:
  - High capital and operating costs,
  - Managing the wastewater (brine solution) is a potential problem,
  - High level of pretreatment is required in some cases,
  - Membranes are prone to fouling
  - Produces the most wastewater at between 25-50 percent of the feed.



## Treatment of wastewater

**Wastewater treatment** is a process used to remove contaminants from wastewater or sewage and convert it into an effluent that can be returned to the water cycle with minimum impact on the environment, or directly reused. The latter is called water reclamation because treated wastewater can then be used for other purposes. The treatment process takes place in a wastewater treatment plant (WWTP), often referred to as a Water Resource Recovery Facility (WRRF) or a sewage treatment plant. Pollutants in municipal wastewater (households and small industries) are removed or broken down.



The treatment of wastewater is part of the overarching field of sanitation. Sanitation also includes the management of human waste and solid waste as well as storm water (drainage) management. By-products from wastewater treatment plants, such as screenings, grit and sewage sludge may also be treated in a wastewater treatment plant.

Wastewater treatment is the process of converting wastewater – water that is no longer needed or is no longer suitable for use – into bilge water that can be discharged back into the environment. It's formed by a number of activities including bathing, washing, using the toilet, and rainwater runoff. Wastewater is full of contaminants including bacteria, chemicals and other toxins. Its treatment aims at reducing the contaminants to acceptable levels to make the water safe for discharge back into the environment.

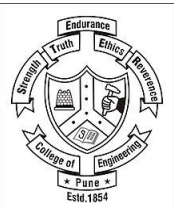
There are two wastewater treatment plants namely chemical or physical treatment plant, and biological wastewater treatment plant. Biological waste treatment plants use biological matter and bacteria to break down waste matter. Physical waste treatment plants use chemical reactions as well as physical processes to treat wastewater. Biological treatment systems are ideal for treating wastewater from households and business premises. Physical wastewater treatment plants are mostly used to treat wastewater from industries, factories and manufacturing firms. This is because most of the wastewater from these industries contains chemicals and other toxins that can largely harm the environment.

### **Step by Step Wastewater Treatment Process**

The following is a step by step process of how wastewater is treated:

#### **1. Wastewater Collection**

This is the first step in waste water treatment process. Collection systems are put in place by municipal administration, home owners as well as business owners to ensure that all the wastewater is collected and directed to a central point. This water is then directed to a treatment plant using underground drainage systems or by exhauster tracks owned and operated by business people. The transportation of wastewater should however be done under hygienic conditions. The pipes or tracks should be leak proof and the people offering the exhausting services should wear protective clothing.



## **2. Odor Control**

At the treatment plant, odor control is very important. Wastewater contains a lot of dirty substances that cause a foul smell over time. To ensure that the surrounding areas are free of the foul smell, odor treatment processes are initiated at the treatment plant. All odor sources are contained and treated using chemicals to neutralize the foul smell producing elements. It is the first wastewater treatment plant process and it's very important.

## **3. Screening**

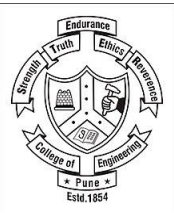
This is the next step in wastewater treatment process. Screening involves the removal of large objects for example nappies, cotton buds, plastics, diapers, rags, sanitary items, nappies, face wipes, broken bottles or bottle tops that in one way or another may damage the equipment. Failure to observe this step, results in constant machine and equipment problems. Specially designed equipment is used to get rid of grit that is usually washed down into the sewer lines by rainwater. The solid wastes removed from the wastewater are then transported and disposed off in landfills.

## **4. Primary Treatment**

This process involves the separation of macrobiotic solid matter from the wastewater. Primary treatment is done by pouring the wastewater into big tanks for the solid matter to settle at the surface of the tanks. The sludge, the solid waste that settles at the surface of the tanks, is removed by large scrappers and is pushed to the center of the cylindrical tanks and later pumped out of the tanks for further treatment. The remaining water is then pumped for secondary treatment.

## **5. Secondary Treatment**

Also known as the activated sludge process, the secondary treatment stage involves adding seed sludge to the wastewater to ensure that is broken down further. Air is first pumped into huge aeration tanks which mix the wastewater with the seed sludge which is basically small amount of sludge, which fuels the growth of bacteria that uses oxygen and the growth of other small microorganisms that consume the remaining organic matter. This process leads to the production



of large particles that settle down at the bottom of the huge tanks. The wastewater passes through the large tanks for a period of 3-6 hours.

## **6. Bio-solids handling**

The solid matter that settle out after the primary and secondary treatment stages are directed to digesters. The digesters are heated at room temperature. The solid wastes are then treated for a month where they undergo anaerobic digestion. During this process, methane gases are produced and there is a formation of nutrient rich bio-solids which are recycled and dewatered into local firms. The methane gas formed is usually used as a source of energy at the treatment plants. It can be used to produce electricity in engines or to simply drive plant equipment. This gas can also be used in boilers to generate heat for digesters.

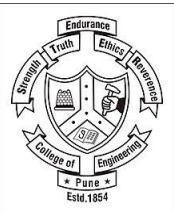
## **7. Tertiary treatment**

This stage is similar to the one used by drinking water treatment plants which clean raw water for drinking purposes. The tertiary treatment stage has the ability to remove up to 99 percent of the impurities from the wastewater. This produces effluent water that is close to drinking water quality. Unfortunately, this process tends to be a bit expensive as it requires special equipment, well trained and highly skilled equipment operators, chemicals and a steady energy supply. All these are not readily available.

## **8. Disinfection**

After the primary treatment stage and the secondary treatment process, there are still some diseases causing organisms in the remaining treated wastewater. To eliminate them, the wastewater must be disinfected for at least 20-25 minutes in tanks that contain a mixture of chlorine and sodium hypochlorite. The disinfection process is an integral part of the treatment process because it guards the health of the animals and the local people who use the water for other purposes. The effluent (treated waste water) is later released into the environment through the local water ways.

## **9. Sludge Treatment**



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The sludge that is produced and collected during the primary and secondary treatment processes requires concentration and thickening to enable further processing. It is put into thickening tanks that allow it to settle down and later separates from the water. This process can take up to 24 hours. The remaining water is collected and sent back to the huge aeration tanks for further treatment. The sludge is then treated and sent back into the environment and can be used for agricultural use.

Wastewater treatment has a number of benefits. For example, wastewater treatment ensures that the environment is kept clean, there is no water pollution, makes use of the most important natural resource; water, the treated water can be used for cooling machines in factories and industries, prevents the outbreak of waterborne diseases and most importantly, it ensures that there is adequate water for other purposes like irrigation.

In summary, wastewater treatment process is one of the most important environmental conservation processes that should be encouraged worldwide. Most wastewater treatment plants treat wastewater from homes and business places. Industrial plant, refineries and manufacturing plants wastewater is usually treated at the onsite facilities. These facilities are designed to ensure that the wastewater is treated before it can be released to the local environment. Some of the water is used for cooling the machines within the plants and treated again. They try to ensure that nothing is lost. It is illegal for disposing untreated wastewater into rivers, lakes, oceans or into the environment and if found culpable one can be prosecuted.