BHARTIYA INSTITUTE OF ENGINEERING & TECHNOLOGY SIKAR

DEPARTMENT OF CIVIL ENGINEERING

LAB MANUAL

6CE4-21: ENVIRONMENTAL ENGINEERING LAB

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LIST OF EXPERIMENTS

1. Physical Characterization of water: Turbidity, Electrical Conductivity, pH

2.Analysis of solids content of water: Dissolved, Settleable, suspended, total,volatile, inorganic etc.

3.Alkalinity and acidity, Hardness: total hardness, calcium and magnesium hardness

4.Optimum coagulant dose.

5.Chemical Oxygen Demand (COD)

6.Dissolved Oxygen (D.O) and Biochemical Oxygen Demand (BOD).

7.Break point Chlorination.

8. Bacteriological quality measurement: MPN,

1. Physical Characterization of water: Turbidity, Electrical Conductivity, pH

pH

Aim: To determine the pH of the given sample.

Theory: pH of aqueous solutions can be defined as negative logarithm of hydrogen ion concentration. pH values ranging from 0 to 7 are acidic, and from 7 to 14 are alkaline. The effect of pH on the chemical and biological properties of liquids makes its determination very important. It is used in several calculations in analytical work. The pH determination is usually done by electrometric method which is the most accurate method and free of interference.

Environmental Significance:

Determination of pH is one of the important objectives in biological treatment of the wastewater. In anaerobic treatment, if the pH goes below 5 due to excess accumulation of acids, the process is severely affected. Shifting of pH beyond 5 to 10 upsets the aerobic treatment of the wastewater. In these circumstances, the pH is generally adjusted by addition of suitable acid or alkali to optimize the treatment of the wastewater. pH value or range is of immense importance for any chemical reaction. A chemical shall be highly effective at a particular pH. Chemical coagulation, disinfection, water softening and corrosion control are governed by pH adjustment.

Dewatering of sludges, oxidation of cynides and reduction of hexavalent chromium into trivalent chromium also need a favorable pH range. It is used in the calculation of carbonate, bicarbonate, CO_2 corrosion, stability index and acid base equilibrium.

Lower value of pH below 4 will produce sour taste and higher value above 8.5 a bitter taste. Higher values of pH hasten the scale formation in water heating apparatus and also reduce the germicidal potencial of chlorine. High pH induces the formation of trihalomethanes, which are causing cancer in human beings.

Standard: pH of drinking water should be between 6.5 and 8.5

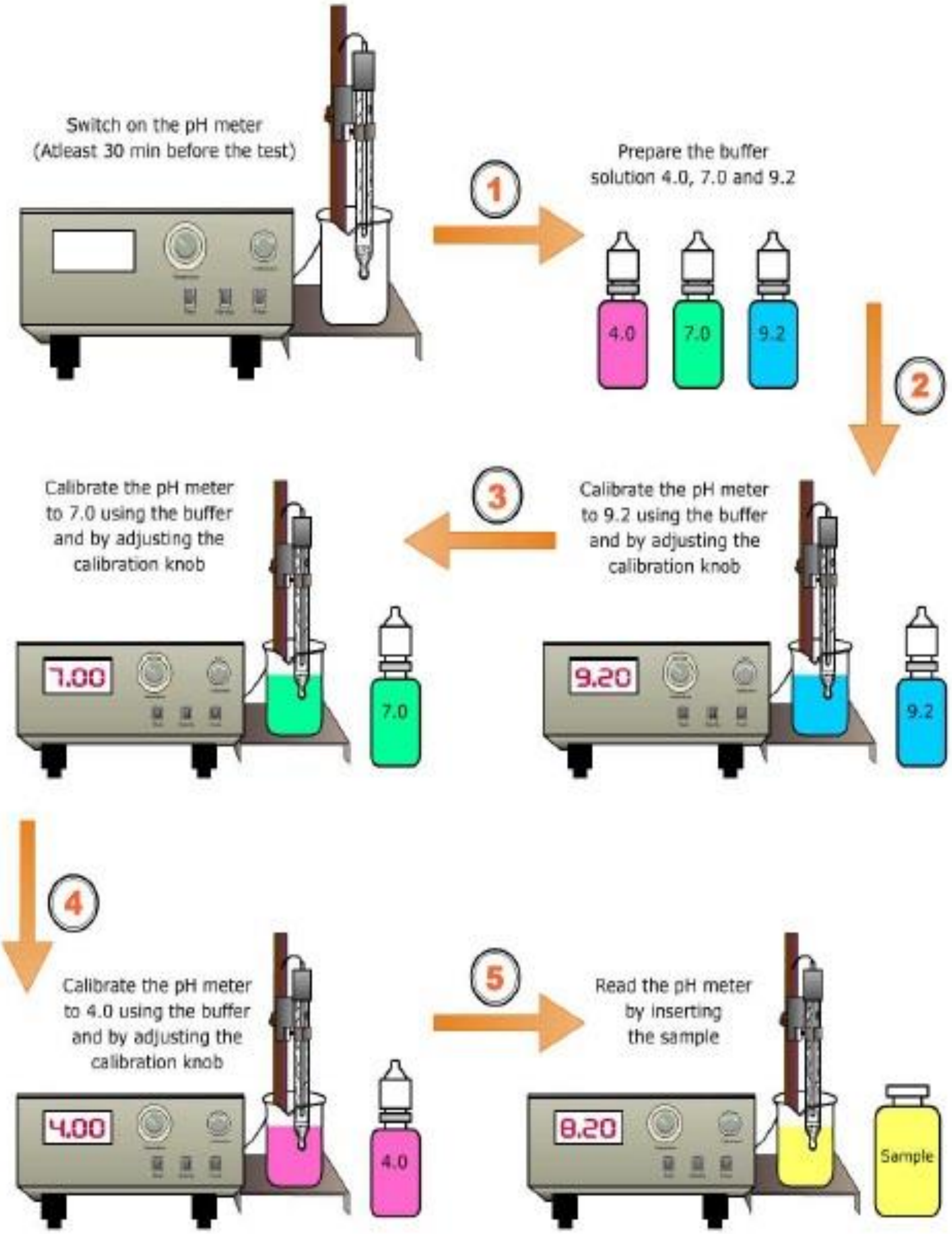
Requirements: pH Meter, Flask, Magnetic Stirrer, Funnel, Beaker, Wash Bottle

Electrometric Method:

The pH is determined by measurement of the electromotive force of a cell comprising an indicator electrode (an electrode responsive to hydrogen ions such as glass electrode) immersed in the test solution and a reference electrode or a combined electrode. The contact between the test solution and the reference electrode is usually achieved by means of a liquid junction. The emf of this cell is measured with pH meter. This is a high impedance electrometer calibrated in terms of pH.

Reagents: Calibrates the electrode system against standard buffer solution of known pH. Buffer tablets having pH 4.0, 7.0 and 9.2 are available.

PROCEDURE CHART



Reagents:

pH 4, pH7, pH 9.2 Buffer Solutions: Dissolve buffer tablet of pH 4 in 100 ml of distilled water to get pH 4 buffer solution. Similarly other buffer solutions can be prepared by dissolving corresponding buffer tablets.

Procedure:

1. Prepare buffers of pH 4, 7 and 9.2.
2. Rinse the electrode thoroughly with distilled water.
3. Standardize pH meter electrode with any two of these buffers.
4. Dip the electrode in the sample for test.
5. Let the reading on screen stabilize; note it as pH & temperature of your sample.

Results:

Sr. No.	Sample	pH	Temperature (°C)

CONDUCTIVITY

Aim: To determine the Conductivity of the given sample

Theory: Conductivity is the capacity of water to carry an electrical current and varies both with number and types of ions the solution contains, which in turn is related to the concentration of ionized substances in the water. Most dissolved inorganic substances in water are in the ionized form and hence contribute to conductance. Conductivity measurement gives rapid and practical estimate of the variations in the dissolved contents of water.

Environmental Significance:

Electrical conductivity measurements are often employed to monitor desalination plants. It is useful for detection of impurities in water. Used for quantitative measurement of ionic constituents dissolved in water, which are important for boiler feed water and cooling water etc.; Used for checking correctness of water analysis as there is a distinct relationship between conductivity and total dissolved solids (TDS).

Conductivity data is useful in determining the suitability of water and wastewater for disposal on land. Irrigation waters up to 2 millisiemens/cm conductance have been found to be suitable for irrigation depending on soils and climatic characteristics.

Requirements: Conductivity Meter, Flask, Beaker, Wash Bottle

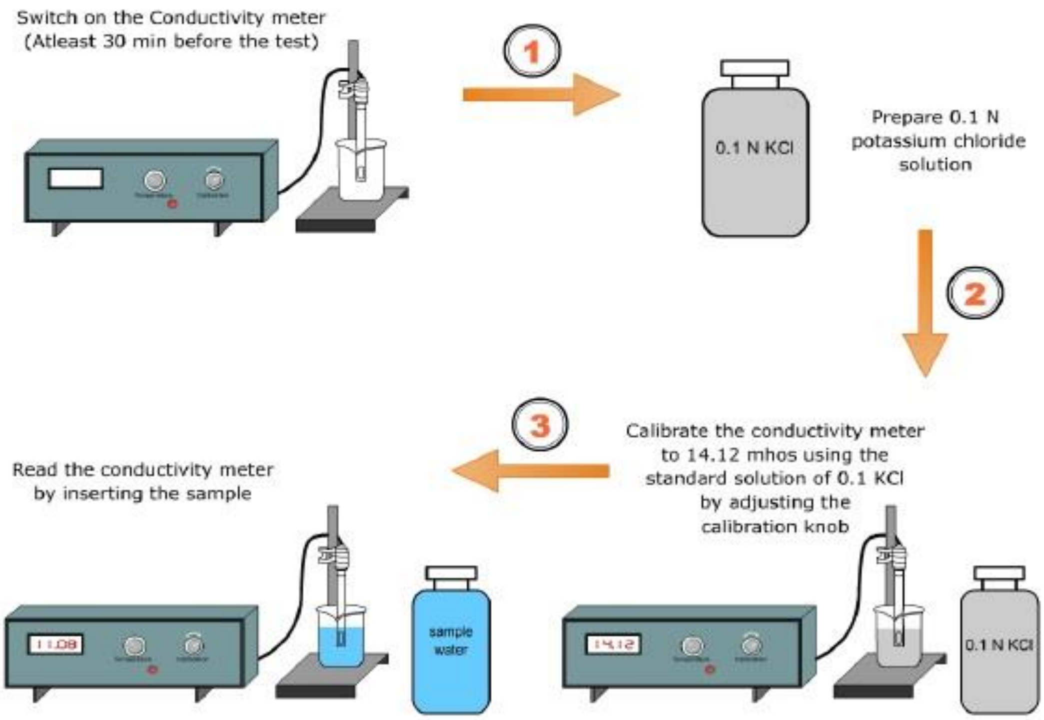
Reagents:

0.01 N, KCL solution: Dissolve 0.746 grams of potassium chloride in 1 liter of distilled water.

Procedure:

1. Rinse the electrode thoroughly blot and dry.
2. Immerse the electrode in 0.01 N KCL solution and the conductivity should be 1413 micro mhos at 25°C Temperature.
3. Now the instrument is calibrated.
4. Remove the cell from KCL solution and wash it thoroughly with distilled water.
5. Immerse the electrode/cell in the unknown sample whose conductivity is to be determined.
6. Note down the instrument reading. If the cell constant is given on the cell itself, then the measured value of conductivity = Cell Constant C X Screen reading

PROCEDURE CHART


Switch on the Conductivity meter (Atleast 30 min before the test)

Prepare 0.1 N potassium chloride solution

Calibrate the conductivity meter to 14.12 mhos using the standard solution of 0.1 KCl by adjusting the calibration knob

Read the conductivity meter by inserting the sample

Results:

Sr. No.	Sample	Conductivity (mS/cm)	Temperature (°C)

DETERMINATION OF TURBIDITY OF A GIVEN SAMPLE

Aim: To find out the turbidity of a given sample of water.

Introduction:

Insoluble particles of soil, inorganic and organic materials and other micro-organisms impede (obstruct) passage of light by scattering and absorbing the light rays. The interference to passage of light is turbidity. It is usually caused by the finely dissolved and sometimes suspended particles of clay loam sand and microscopic organisms all in suspension.

Turbidity is measured photometrically by determining the quantity of light of given intensity absorbed / scattered.

Jackson turbidity meter and Nephlo turbidity meter in generally used to measure turbidity of water samples. Jacksons turbidity meter in generally is based on light absorption and nephlo turbidity meter is based on intensity of light scattered by the sample, taking a reference with standard turbidity meter suspensions.

Nephlometric turbidity meter is generally used for samples with low turbidity and expressed as NTU or mg/ltr. For portable water allowable turbidity is between 5 to 10 mg/ltr.

Apparatus:

1. Nephlo turbidity meter; 2. Sample Tubes

Procedure:

1. Switch on the instrument and allow sufficient warm-up period.
2. Take distilled water or bank solution in the test tube holder and close the lid. Make sure that the mark on the test tube coincides with mark on the panel.
3. Select required range for measurement.
4. Adjust the displayed to ‘000’ by adjusting set zero knob.
5. Remove the test tube containing distilled water and insert another test tube containing standard solution (say 100 NTU or 400 NTU). Place it in test tube holder.
6. Adjust the calibrate knob so that the display reach the standard solution value.
7. Again check ‘0’ display with distilled water. The instrument is now calibrated.

8. Place the given sample whose turbidity is to be determined in the test tube and take the reading in NTU.

Observations:

SN	Sample Details	Turbidity (NTU)	Remarks

Results:

The turbidity of the given sample is = ……………… NTU

Discussion:

Environmental Significance:

1. Turbidity is objectionable because of aesthetic and engineering considerations.
2. Disinfection of turbid water is difficult because of adsorptive characteristics of some colloids and their tendency to solid organisms from the disinfectant.
3. In natural water bodies, turbidity interferes with light penetrations and pathogenic reactions of aquatic plants.
4. Turbidity measurements are useful to determine whether a supply requires special treatment by chemical coagulation before public water supply. It is also used to determine the effectiveness of treatment produced with different chemicals and dosage needful.
5. Measurement of turbidity in settled water prior to filtration is useful in controlling the chemical dosage so as to excessive loading of rapid sand filters.
6. It is also useful to determine the optimum dosage of coagulants and to evaluate the performance of water treatment plants.

Questions:

1. What are the causes of turbidity in water?
2. What units are used for measuring turbidity?
3. What is the difference between visual method and instrumental method in turbidity measurement?
4. What is meant by coefficient of fineness? Mention its importance.
5. What is the basic difference in principle involved in Jackson turbid meter and Nephelo turbidity meter?
6. What is the general coagulant used for removal of turbidity in water?

2.Analysis of solids content of water: Dissolved, Settleable, suspended, total,volatile, inorganic etc.

SUSPENDED SOLIDS

Aim: To determine the Suspended solids present in water sample& waste water.

Theory: The term TSS applies to the dry weight of the material that is removed from a measured volume of water sample by filtration through a standard filter. To achieve reproducibility and comparability of the results close attention of procedural details, especially filter characteristics and time and temperature of drying is required.

Environmental Significance:

- They cut down light transmission through the water and so lower the rate of photosynthesis in aquatic flora.
- In less turbulent parts of river, some of the solids may sediment out, smothering life of the riverbed.
- The TSS determination is extremely valuable in the analysis of polluted water.
- It is a major parameter used to evaluate the strength of domestic wastewater and to determine the efficiency of treatment unit.

Apparatus: Suction Flask, Filtration Apparatus**,** Aluminum Weighing Dishes, Desiccator**,** Beakers, Weighing Balance, Hot Air Oven, Filter Paper, Graduated Cylinder etc.

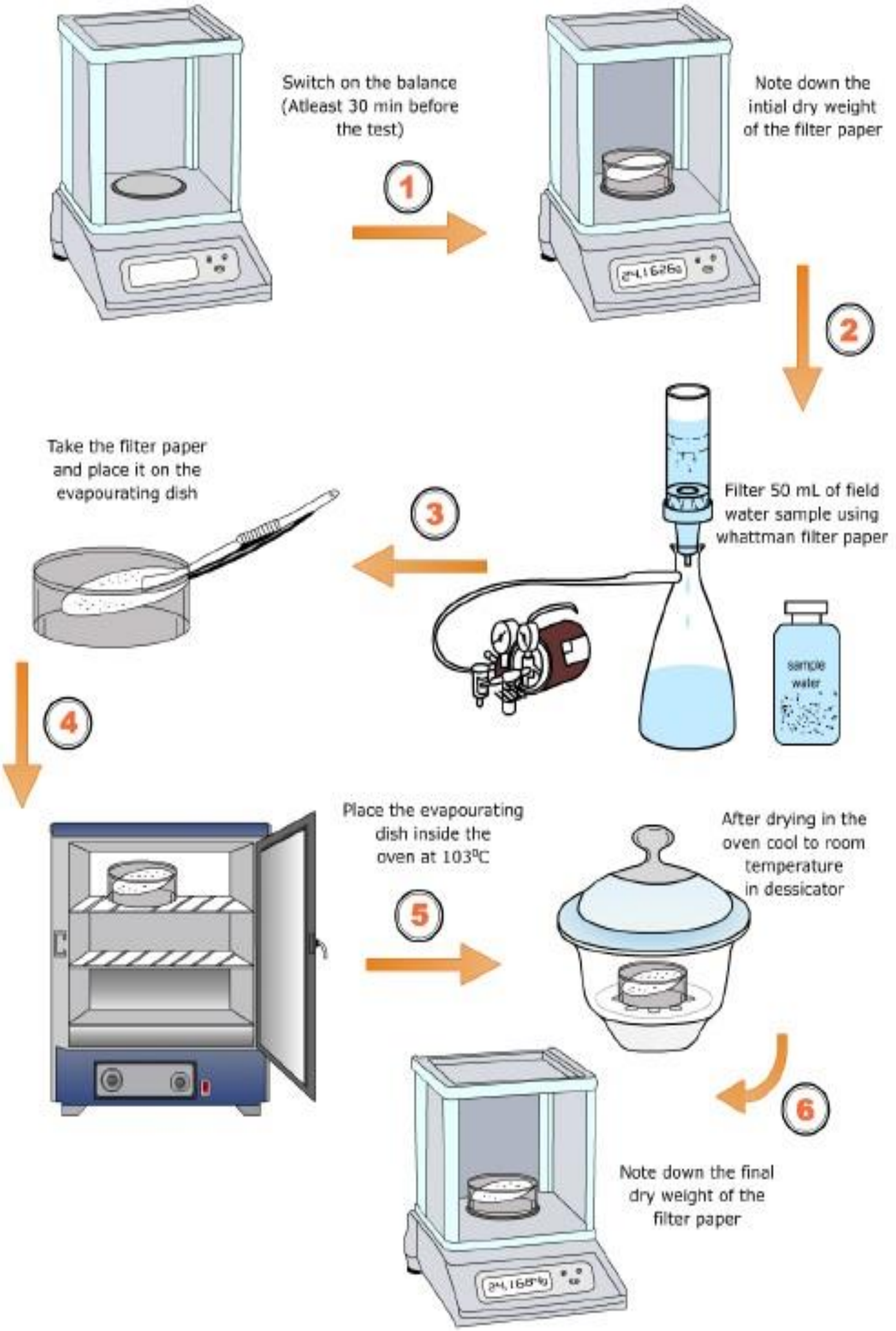
Procedure:

1. Measure the empty weight of filter paper and note down reading. (Wi)
2. Mix Sample well and pour into a graduated cylinder to the selected volume. (V)
3. Apply suction to filter flask and seat filter with a small amount of distilled water.
4. Pour selected volume into filtration apparatus.
5. Wash with 3-successive 10-mL volume of distilled water, allowing complete drainage between washing, and continue suction for about 3 minutes after filtration is completed.
6. Carefully remove the filter paper from filtration apparatus and transfer it to an weighing dish as a support.
7. Dry for at least 1 hour at 103-105°C in a hot air oven.
8. Cool in desiccator and weigh filter paper and record the reading (Wf)
9. Repeat cycle of drying, cooling, desiccating and weighing until a constant weight is obtained, or weight change is less than 4% of previous weight or 0.5 mg, whichever is less. Duplicate determination should be within 5% of their average

Observation:

Sr. No.	Particular	Water Sample	Waste water Sample
1.	Initial Wight of Filter Paper in gm, (W_i)		
2.	Final Wight of Filter Paper in gm, (W_f)		
3.	Total Wight of Filter Paper in gm, (W)		
4.	Volume of Sample in ml, (V)		

PROCEDURE CHART



Switch on the balance (Atleast 30 min before the test)

Note down the intial dry weight of the filter paper

Filter 50 mL of field water sample using whattman filter paper

Take the filter paper and place it on the evapourating dish

Place the evapourating dish inside the oven at 103^{0}C

After drying in the oven cool to room temperature in dessicator

Note down the final dry weight of the filter paper

Calculation:

$$\text{Suspended solids in mg/L} = \frac{(W_f - W_i) \text{ x } 1000000}{V}$$

TOTAL DISSOLVED SOLIDS

Aim: To determine the Dissolved solids present in water sample & waste water.

Theory: A well-mixed, measured portion of sample is filtered through a standard glass-fibre filter and the filtrate portion is evaporated to dryness at 180 ± 2 °C and that gives the amount of total dissolved solids. The reason for higher temperature used is to remove all mechanically occluded water. Where organic matter is generally very low in concentration, the losses due to higher drying temperature will be negligible.

Environmental Significance:

- They A high content of dissolved solids elevates the density of water, influences osmoregulation of freshwater organisms, reduces solubility of gases (like oxygen) and reduces utility of water for drinking, irrigation and industrial purposes.
- TDS concentration beyond 500 mg/L, decreases palatability and may cause gastrointestinal irritation.

Apparatus: Suction Flask, Filtration Apparatus**,** porcelain dish, Desiccator**,** Beakers, Weighing Balance, Hot Air Oven, Filter Paper, Graduated Cylinder etc.

Procedure:

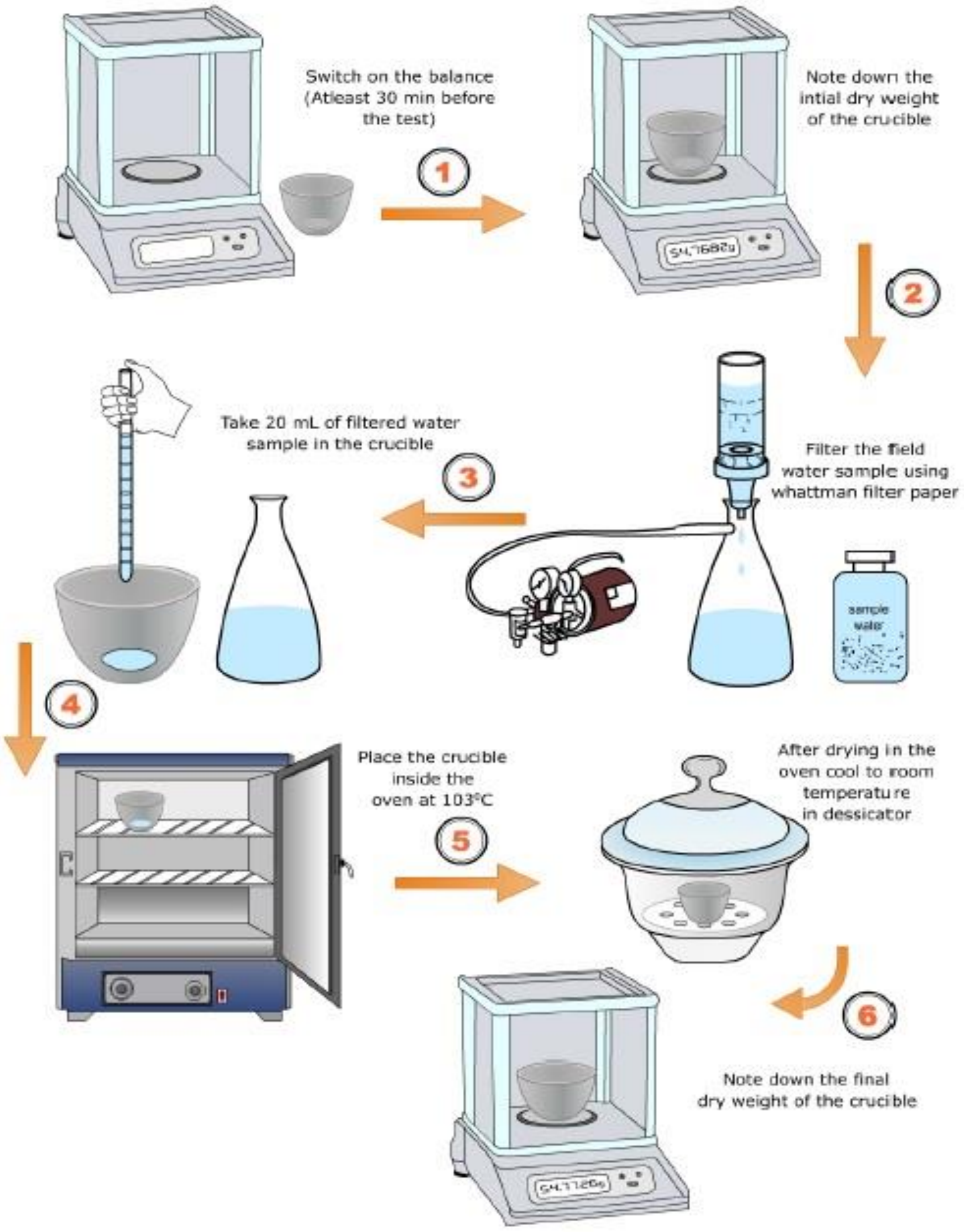
1. Take a clean porcelain dish/beaker which has been washed and dried in a hot air oven at 103-105 °C for one hour.
2. Now weigh the empty porcelain dish/beaker in analytical balance. (Wi)
3. Mix sample well and pour into a funnel with filter paper. Filter a known volume of a well-mixed sample in the above beaker. (i.e. 100 mL, 200 mL or 500 mL) (V)
4. Note: Choose the sample volume to yield 10 to 200 mg of dried residue. If more than 10 minutes are required for complete filtration, decrease the sample volume.

1. Evaporate the sample in a hot air over at180 ± 2 °C after the whole water is evaporated, cool the evaporating dish/beaker in a desiccator and take the final weight (Wf).
2. Total solids = (Suspended solids) + (Dissolved solids).

Observation:

Sr. No.	Particular	Water Sample	Waste water Sample
1.	Initial Wight of Beaker in gm, (W_i)		
2.	Final Wight of Beaker in gm, (W_f)		
3.	Total Wight of Beaker in gm, (W)		
4.	Volume of Sample in ml, (V)		

PROCEDURE CHART



Calculations:

$$\text{Total Dissolved solids in mg/L} = \frac{(W_f - W_i) \times 1000000}{V}$$

Sr. No.	Sample No.	Dissolved Solids (A)	Suspended Solids (B)	Total Solids (A+B)

SETTLEABLE SOLIDS

Aim: To determine the Settleable solid in given sample

Theory: The term settleable solids are applied to the solids in suspension that will settle, under quiescent conditions, because of the influence of gravity. Only the coarser suspended solids with a specific gravity sufficiently greater than that of water settle. Sludge is accumulation of settleable solids. Settleable solids may be determined and reported on either a volume (mL/L) or a weight (mg/L) basis.

Environmental Significance:

- To determine the need for and design of primary settling tank.
- To determine the efficiency of sedimentation units.
- To study the physical behaviour of waste streams entering natural water bodies.

Volumetric Method:

Apparatus: The volumetric test requires only an Imhoff cone

Procedure:

1. Fill an Imhoff cone to the l-L mark with a well-mixed sample).
2. Settle for 4S-min, gently agitate sample near the sides of the cone with a rod or by spinning, settle 15 min longer, and record volume of settleable solids in the cone as mL/L.
3. If the settled matter contains pockets of liquid between large settled particles, estimate volume of these and subtract from volume of settled solids.
4. The practical lower limit of measurement depends on sample composition and generally is in the range of 0.1 to 1.0 mL/L. where a separation of settleable and floating materials occurs, do not estimate the floating material as settleable matter.
5. Replicates usually are not required.

Results:

Report the results as mL of settleable solids/L (volumetric method).

: 3.Determination Acidity, Alkalinity and Hardness

ACIDITY

Aim: To determine the acidity present in water & Wastewater sample

Theory: Acidity of water is its quantitative capacity to neutralize a strong base to a designated pH. Acidity of water is significant in many water supply systems, because acidity influences certain chemical and biological process in water. Acidity of water is due to Hydrogen ions (H^+) present in a sample of water. As a result, dissociation of Hydrogen ions is neutralized by titration with standard solution of a strong base in presence of an indicator. Dissolved Carbon dioxide is usually the major acidic component of surface water. Acidity is usually determined by titration with 0.02N solution of Sodium Hydroxide. The amount of Sodium Hydroxide required for the sample to reach the pH 4.5 in a measure of Methyl orange acidity and amount to reach pH 8.3 is a measure of total acidity..

Environmental Significance:

- Acidity is interferes in the treatment of water. Carbon dioxide is of important considerations in determining whether removal by aeration or simple neutralization with lime / lime soda ash or NaOH will be chosen as the water treatment method.
- The size of the equipment, chemical requirements, storage spaces and cost of the treatment all depends on the carbon dioxide present.
- Aquatic life is affected by high water acidity. The organisms present are prone to death with low pH of water.
- High acidity water is not used for construction purposes. Especially in reinforced concrete construction due to the corrosive nature of high acidity water.
- Water containing mineral acidity is not fit for drinking purposes.
- Industrial wastewaters containing high mineral acidity is must be neutralized before they are subjected to biological treatment or direct discharge to water sources.

Apparatus: Titration Stand with Burette, Conical Flask, Beaker, Measuring Cylinder**,** Pipette, Funnel, Wash Bottle etc.

Reagents:

- **0.02 N NaOH Solution:** Dissolve 0.8 grams of NaoH in 1 liter of distilled water.
- **Phenolphthalein Indicator:** Dissolve 0.5 gm of Phenolphthalein Indicator in 500 ml95% of ethyl alcohol. Add 500 mL distilled water.
- **Methyl orange Indicator:** Dissolve 0.5 g of Methyl orange Indicator & dilute to 1000 ml with distilled water.

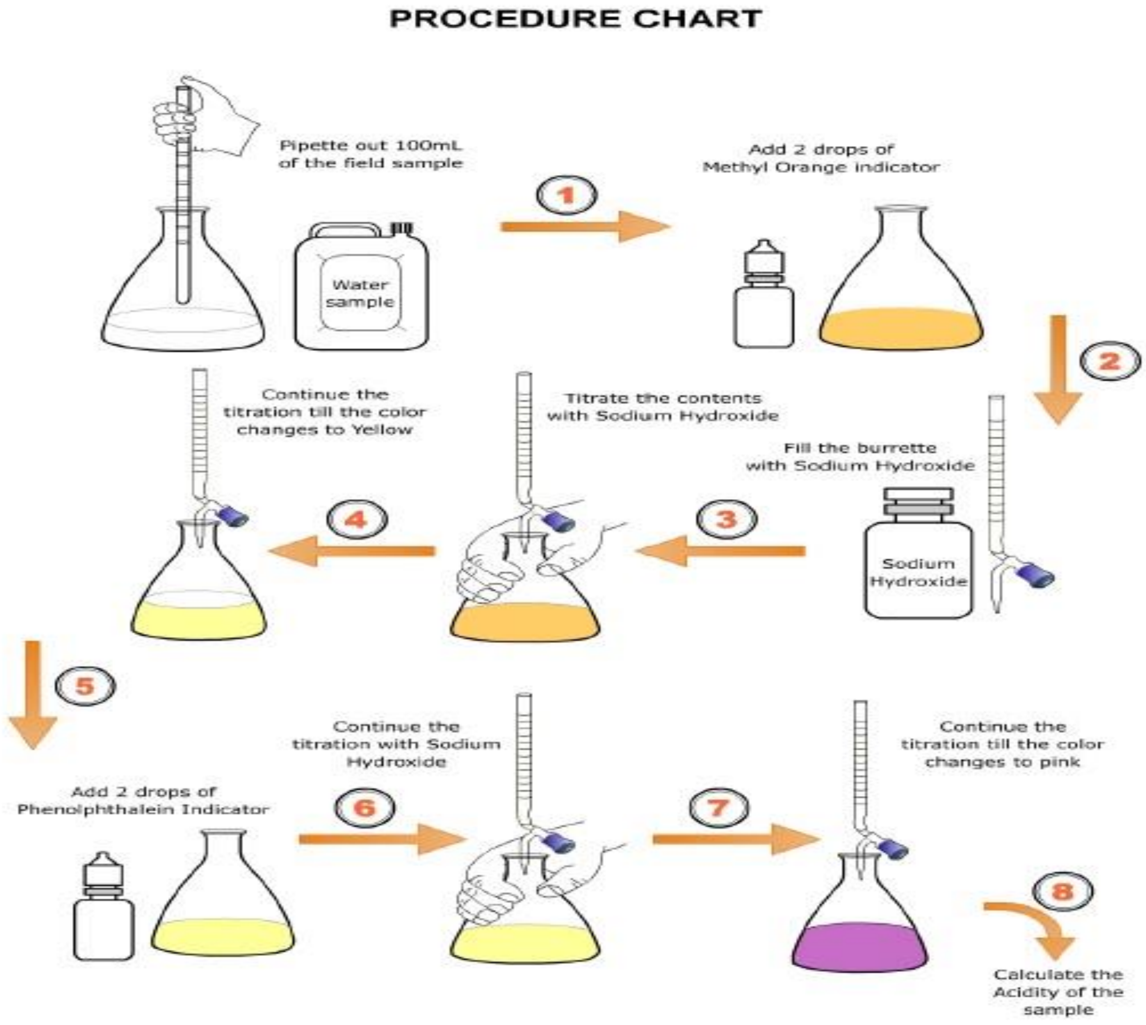
Procedure:

A. Methyl Orange Acidity

1. Take suitable volume of sample (25, 50 or 100 mL) in a Conical flask.(V)
2. Add 2 drops of methyl orange and see the colour. If color turns yellow, methyl orange acidity is absent. If colour turns orange, titrate with 0.02 N NaOH till colour changes to faint orange. Characteristic of pH 4.3-4.4. Note the volume of NaOH required (A).

B. Phenolphthalein Acidity

1. Take suitable volume of sample (25, 50 or 100 mL) in a Conical flask.(V)
2. Add 2-3 drops of phenolphthalein indicator, If the sample turns pinks color it means that, phenolphthalein acidity is absent and stop the experiment.
3. If there is no color change, the titrate with 0.02N Standard NaOH solution till faint pink color appears indicating pH 8.3. The end point is colorless to faint pink color.Note additional volume of NaOH required (B).



Observation:

1. Titrant :
2. Indicators : Phenolphthalein and Methyl Orange Indicator
3. End Point: a) Yellow to Faint Orange

   b) Colorless to Faint Pink Color

Table: 1 Mineral Acidity: (Methyl Orange Indicator)

Sr. No.	Volume of Sample (ml) (V)	Burette Reading (ml)		Volume of NaOH (ml) (A)
		Initial	Final	

Table: 2 Phenolphthalein Acidity: (Phenolphthalein Indicator)

Sr. No.	Volume of Sample (ml) (V)	Burette Reading (ml)		Volume of NaOH (ml) (B)
		Initial	Final	

Calculations:

$$\text{Mineral Acidity as } CaCO_3 \text{ in mg/L} = \frac{\text{Volume of NaOH (A)} \times N \times 50 \times 1000}{V}$$

$$\text{Phenolphthalein Acidity as } CaCO_3 \text{ in mg/L} = \frac{\text{Volume of NaOH (B)} \times N \times 50 \times 1000}{V}$$

$$\text{Total Acidity as } CaCO_3 \text{ in mg/L} = \frac{\text{Volume of NaOH (A)} + \text{(B)} \times N \times 50 \times 1000}{\text{ml of sample}}$$

Results:

Sample Used	Mineral Acidity (mg/L)	Phenolphthalein Acidity (mg/L)	Total Acidity (mg/L)

ALKALINITY

Aim: To determine the Alkalinity present in water sample

Theory: Alkalinity of water is its quantitative capacity to neutralize a strong acid to a designated pH. Alkalinity is significant in many uses and in treatment of natural acid and wastewater. It is significant in determining suitability of water for drinking as well as irrigation purpose. Alkalinity measurements are used in interpretation and control of water and wastewater treatment process. Alkalinity is primarily due to salts of weak acids and bicarbonates. Major part of alkalinity is because of the action of Carbon dioxide on basic materials.

Environmental Significance:

- Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. Higher alkalinity levels in surface waters will buffer acid rain and other acid wastes and prevent pH changes that are harmful to aquatic life.
- Large amount of alkalinity imparts bitter taste in water.
- The principal objection of alkaline water is the reactions that can occur between alkalinity and certain in waters. The resultant precipitate can corrode pipes and other accessories of water distribution systems.
- Wastewaters containing excess caustic (hydroxide) alkalinity are not to be discharged into natural water bodies or sewers.
- Alkalinity as carbonate and bicarbonate of saline water is very important in tertiary recovery processes for recovering petroleum. Alkaline water offers better wetting to the formation rock and improve oil release. As an additional benefit, ions that provide alkalinity absorb on rock surfaces occupying adsorption sites and decrease the loss of recovery chemical by adsorption.
- The alkalinity value is necessary in the calculation of carbonate scaling tendencies of saline waters.
- The alkalinity acts as a pH buffer in coagulation and lime-soda softening of water.
- In wastewater treatment, alkalinity is an important parameter in determining the amenability of wastes to the treatment process and control of processes such as anaerobic digestion, where bicarbonate alkalinity, and any fraction contributed by volatile acid salts become considerations.

Apparatus: Titration Stand with Burette, Conical Flask, Beaker, Measuring Cylinder**,** Pipette, Funnel, Wash Bottle etc.

Reagents:

- **0.02N H_2SO_4:** 3 mL. Conc. H_2SO_4 in 1 L distilled water toget 0.01 N H_2SO_4. Take 100 mL 0.01 N H_2SO_4 + 500 mL distilled water
- **Phenolphthalein Indicator:** Dissolve 0.5 gm of Phenolphthalein Indicator in 500 ml95% of ethyl alcohol. Add 500 mL distilled water.
- **Methyl orange Indicator:** Dissolve 0.5 g of Methyl orange Indicator & dilute to 1000 ml with distilled water.

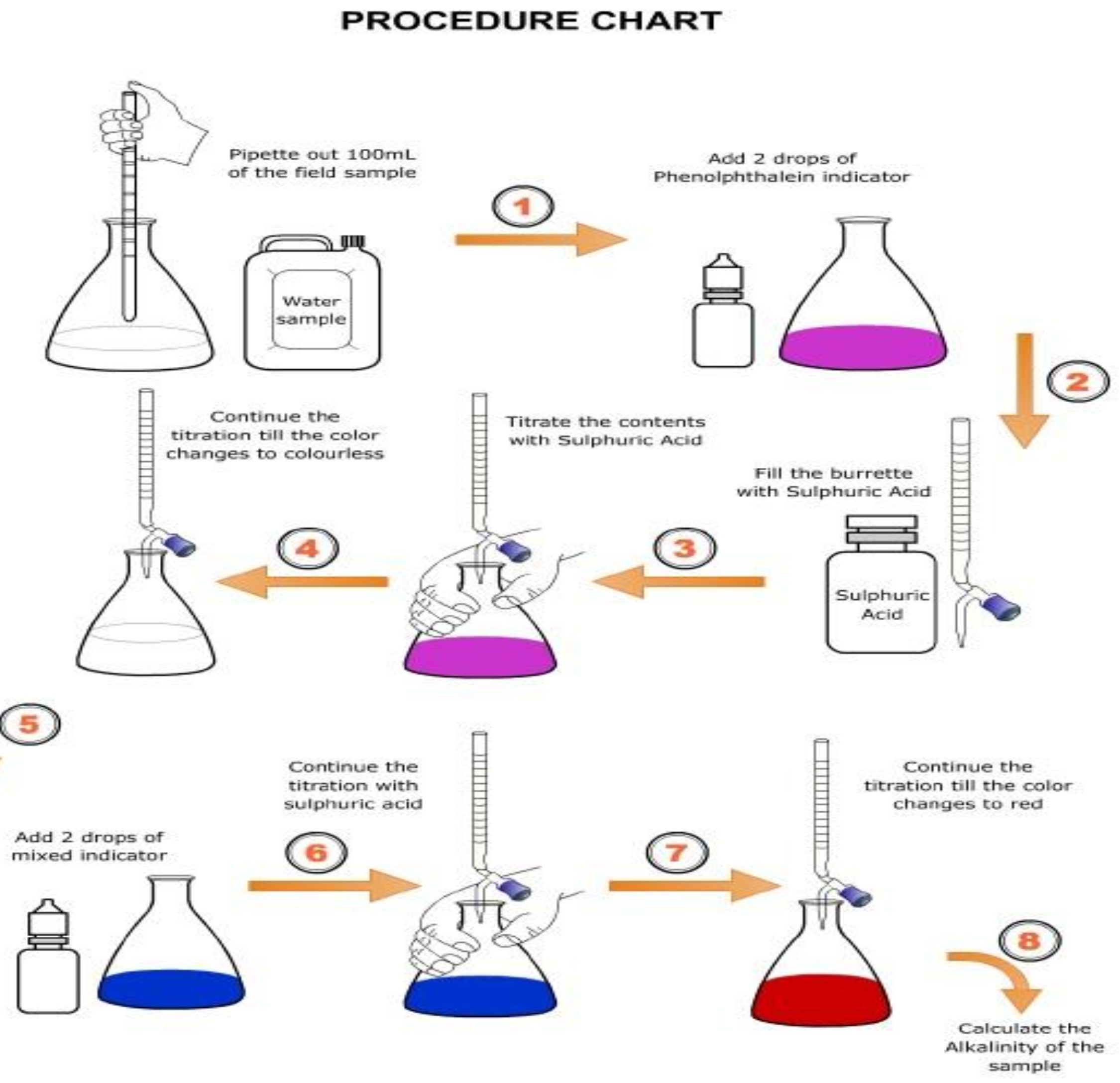
Procedure:

A. Phenolphthalein Alkalinity:

1. Take suitable volume of sample (25, 50 or 100 mL) in a conical flask.
2. Add 2-3 drops of phenolphthalein indicator.
3. If the sample turns pink in colour, then titrate with 0.02 NH_2SO_4, till the pink colour disappears. Note the volume of acid required as (A).
4. If the pink colour does not exist it indicates that, phenolphthalein Alkalinity is absent. Then continue the titration with Methyl Orange indicator.

B. Methyl Orange Alkalinity:

1. Add 2-3 drops of methyl orange to the same flask; continue titration till colour becomes orange. Note down volume of H_2SO_4 consumed as 'B'.
2. If there is no pink colour after adding phenolphthalein, continue according to step 3.
3. Calculate alkalinity in mg/l as;



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Observation:

1. Titrant :
2. Indicators : Phenolphthalein and Methyl Orange Indicator
3. End Point: a) Pink to Colourless

   b) Yellow to Faint Orange Color

Table: 1 Phenolphthalein Alkalinity: (Phenolphthalein Indicator)

Sr. No.	**Volume of Sample (ml) (V)**	**Burette Reading (ml)**		**Volume of H_2SO_4 (ml) (A)**
		Initial	**Final**	

Table: 2 Methyl orange Alkalinity: (Methyl Orange Indicator)

Sr. No.	**Volume of Sample (ml) (V)**	**Burette Reading (ml)**		**Volume of H_2SO_4 (ml) (B)**
		Initial	**Final**	

Calculations:

$$\text{Phenolphthalein Alkalinity as } CaCO_3 \text{ in mg/L} = \frac{\text{Volume of } H_2SO_4 \text{ (A) x N x 50 x 1000}}{V}$$

$$\text{Methyl Orange Alkalinity as } CaCO_3 \text{ in mg/L} = \frac{\text{Volume of } H_2SO_4 \text{ (B) x N x 50 x 1000}}{V}$$

$$\text{Total Alkalinity as } CaCO_3 \text{ in mg/L} = \frac{\text{Volume of } H_2SO_4 \text{ (A) + (B) x N x 50 x 1000}}{V}$$

Alkalinity Relationship (P and T)

The values obtained from Phenolphthalein and Total alkalinity determination for a given sample of water are used to estimate three forms of alkalinity shown below.

Results of Titration	**Hydroxide Alkalinity/Caustic Alkalinity as $CaCO_3$**	**Carbonate Alkalinity as $CaCO_3$**	**Bicarbonate Alkalinity as $CaCO_3$**
P=0	0	0	0
P<1/2 T	0	2P	T-2P
P=1/2T	0	2P	0
P>1/2 T	2P-T	2(T-P)	0
P=T	T	0	0

Where: P: Phenolphthalein Alkalinity, T: Total Alkalinity

Results:

Sample Used			
Phenolphthalein Alkalinity (mg/L)			
Methyl Orange Alkalinity (mg/L)			
Total Alkalinity (mg/L)			
Hydroxide Alkalinity			
Carbonate Alkalinity			
Bicarbonate Alkalinity			

HARDNESS

Aim: To determine the hardness of given sample of water or waste water.

Theory: Originally hardness of water is a measure of soap consuming capacity to produce foam or lather. Also produce scale in hot water pipes, heaters, boilers and other units, precipitated chiefly by Calcium and Magnesium ions commonly present in water. Also may be precipitated by ions of other polyvalent metals such as Aluminium, Iron, Strontium, Zinc and by Hydrogen ions. Calcium and Magnesium ions are usually present in significant concentrations in natural water. Hardness of water varies from place to place. Surface waters are soften than the ground water, due to the dissolved salts of Carbonates, Bicarbonates, Chlorides, Sulphate, Nitrates of Calcium and Magnesium. Temporary hardness is mainly due to Carbonate and Bicarbonate of Calcium and Magnesium. Permanent hardness is mainly due to Sulphate and Chlorides.

A small amount of dye Eriochrome Black –T is added to hard water containing Calcium and Magnesium ion, the solution will become wine red. EDTA is then added as a titrant. Complexes of Calcium and Magnesium are formed after sufficient EDTA has been added. The solution turns from Wine Red to Blue. This is the end point of titration, a pH value of 10.2 is usually maintained.

The degree of hardness of drinking water has been classified in terms of the equivalent $CaCO_3$ concentration as follows:

Soft: 0 - 60 mg/L.
Medium: 60 - 120 mg/L.
Hard: 120 -180 mg/L
Very hard: > 180 mg/L.

Environmental Significance:

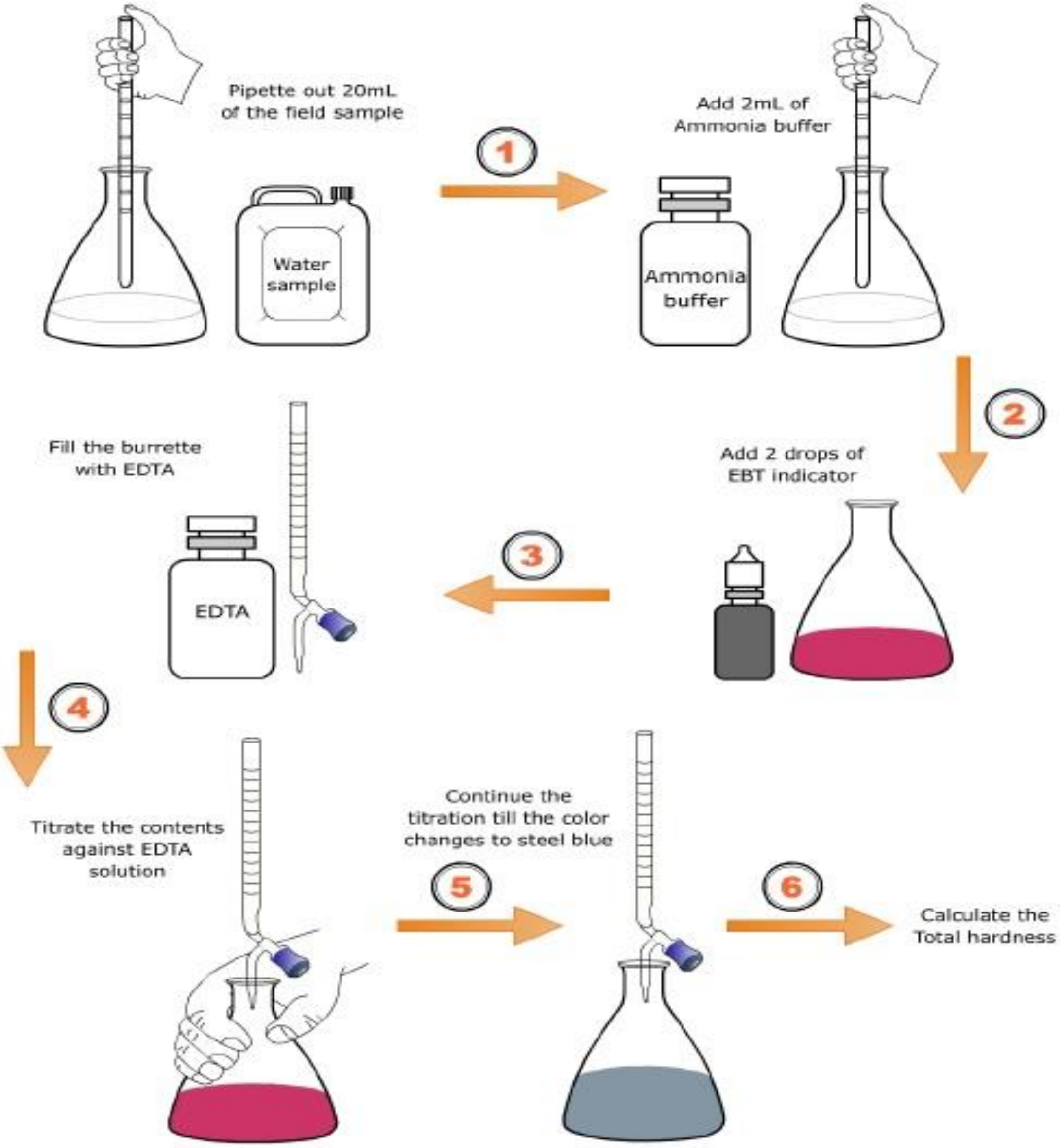
- Scales are formed as inner coating of the pipelines prevents corrosion.
- Absolutely soft waters are corrosive and dissolve the metals.
- More cases of cardio vascular diseases are reported in soft water areas.
- Hard water is useful to growth of children due to the presence of calcium.
- Hard waters cause excessive consumption of soap used for cleaning purpose. Sodium soaps react with multivalent metallic cations to form a precipitate, thereby lose their surfactant properties. Lathering doesn’t take place until all hardness ions precipitate out.
- This precipitate adheres to surfaces of tubes, sinks, dish washer and may stain clothing.
- Scales formed mainly due to carbonate hardness act as insulations and cause enormous loss of fuel in boiler.
- Scales deposited mainly due to increase in pH to 9 at which bicarbonates are converted as carbonates are formed in distribution mains reducing their carrying capacity.

Apparatus: Titration Stand with Burette, Conical Flask, Beaker, Measuring Cylinder**,** Pipette, Funnel, Wash Bottle etc.

Reagents:

- **Standard EDTA solution 0.01 M (0.02N):** Dissolve 3.723 gm EDTA disodium salt and dilute to 1000 ml distilled water.
- **Eri0chrome black T indicator:** Mix 0.5gm dye with 100 gm NaCI to prepare dry powder. or 0.5 gm of indicator in 100 ml of Ethyl Alcohol.
- **Ammonia Buffer solution:** Dissolve 16.9gmAmmonium Chloride (NH_4CI) in 143 ml of Ammonium Hydroxide (NH_4OH). Add 1.25 gm magnesium salt of EDTA and dilute to 250 ml with distilled water.

PROCEDURE CHART



Procedure:

1. Take well mixed suitable volume of sample (25, 50 or 100 mL) in a conical flask (V). Select a sample volume that requires less than 15 mL EDTA titrant and complete titration within 5 minutes, measured from time of buffer addition.
2. Add 1-2 ml of Ammonia buffer solution. Usually 1-2 mL buffer solution is sufficient to give a pH of 10.0 to 10.1 and mix well.
3. Add a pinch of Eriochrome black T and titrate with standard EDTA (0.01 M) till wine red colour changes to blue colour. Note down the Volume of EDTA required. (A).
4. Run a reagent blank with distilled water. Note the volume of EDTA consumed (B).
5. Calculate the volume of EDTA required by sample; C = (A-B)

Observation:

1. Titrant :
2. Indicators : Eriochrome Black T Indicator
3. End Point : Wine Red to Blue

Sr. No.	Volume of Sample; V (ml)	Burette Reading of Sample; A (ml)			Burette Reading of Blank; B (ml)			Volume of EDTA (ml) (C=A-B)
		Initial	Final	Total	Initial	Final	Total	

Calculations:

$$\text{Total Harness as } CaCO_3 \text{ in mg/L} = \frac{\text{Volume of EDTA (C) x N x 50 x 1000}}{V}$$

Results:

Sample No.	Total Hardness as $CaCO_3$ (mg/L)

4.DETERMINATION OF OPTIMUM DOSAGE OF COAGULANT

Aim: To determine the optimum dosage of coagulant

Introduction:

The solids may vary in size from 1 milli micron to 200 milli micron and broad in characteristics between suspended and dissolved solids. They are small enough to exhibit stability by virtue of slight residual electrical charge but large enough to interfere with passage of light and therefore cause turbidity. They will not settle physically unless destabilized, coagulated and flocculated into larger mass with sufficient greater densities than water.

Principle:

Metal salts hydrolyse in presence of the natural alkalinity to form metal hydroxides. The divalent cation can reduce the Zeta potential while the metal hydroxides are good adsorbents and hence remove the suspended materials. Alum [Al2(SO4)3. 18H2O] is the most widely used coagulant. When alum solution is added to water, the molecules dissociate to yield sulphate and aluminium ions. The +ve species combine with negatively charged colloidal to neutralise part of the charge on the colloidal particle. Thus, agglomeration takes place. Coagulation is a quite complex phenomenon and the coagulant should be distributed uniformly throughout the solution. A flash mixer accomplishes this.

Jar test is simple device used to determine this optimum coagulant dose required. The jar test, device consists of a number of stirrers (4 to 6) provided with paddles. The paddles can be rotated with varying speed with the help of a motor and regulator. Samples will be taken in jars or beakers and varying dose of coagulant will be added simultaneously to all the jars. The paddles will be rotated at 100 rpm for 1 minute and at 40 rpm for 20 to 30 minutes, corresponding to the flash mixing and slow mixing in the flocculator of the treatment plant. After 30minutes settling, supernatant will be taken carefully from all the jars to measure turbidity. The dose, which gives the least turbidity, is taken as the optimum coagulant dose.

Apparatus:

1. pH meter; 2. Turbidity meter; 3. Flash mixer; 4. Jar test apparatus; 5. Titration apparatus.

Reagents:

1. Alum Solution
2. H_2SO_4

3. Phenolphthalein indicator
4. Methyl orange

Procedure:

1. Take 6 beakers containing 1 ltr of sample
2. Check the initial pH, turbidity, alkalinity of the given sample. If pH is low add soda ash or lime make up the pH between 6.5 - 8.5.
3. Add the coagulant alum for the beakers in increasing order.
4. With the help of flash mixer go for the process of coagulation with the speed between 80-100 rpm for 15 minutes.
5. After 15 minutes, slow down the speed between 20-30 rpm and stir for 5-10 minutes.
6. After all the above process keep the beaker for a detention period of 20-30 min for efficient settling of flocks.
7. Take out the supernatant liquid without disturbing the sediment and check the final turbidity and alkalinity of all the beakers.

Observations and Calculations:

Raw water sample:

Initial pH = ...

Initial alkalinity = ...mg/L

Initial turbidity = ...NTU

Beaker No	Dosage of Coagulant (ml)	pH	Turbidity (NTU)	Alkalinity = VR * 1000/ ml of sample				% removal of turbidity.
				IBR	FBR	VR	Alkalinity (mg/lt)	
1	2							
2	4							
3	6							
4	8							
5	10							
6	12							

From the graph; we can conclude that whichever will give maximum turbidity removal, that dosage of alum will be the optimum dosage of coagulant.

Enclosure Graph sheet

Results:

Optimum dosage of coagulant to be added for the given water sample is ………… ml

Discussion:

Environmental Significance:

Coagulants are used in water treatment plants

(i) to remove natural suspended and colloidal matter,

(ii) to remove material which do not settle in plain sedimentation, and

(iii) to assist in filtration.

To maintain the cost of operation and maintenance, optimum dosage quantity is essential to be determined.

5.DETERMINATION CHEMICAL OXYGEN DEMAND (COD)

Aim: To determine chemical oxygen demand (COD) of a given waste water sample.

Introduction:

COD is the oxygen required for the oxidation (chemical) of organic matter by strong chemical oxidant ($K_2Cr_2O_7$) under acidic condition. In COD test the main disadvantage is that along with the organic matter, some inorganic substance like Nitrates, Chlorides, Sulphides also get oxidized (However some organic substances like Amino Acids, Benzene, Ketone, etc., do not get oxidized). Hence, this test does not give the exact measure of the strength of organic wastes. The main limitation of the test lies in its inability to differentiate between biologically oxidizable and biologically inert material.

COD determination has the advantage over BOD determination, in that, the result can be obtained within 3 hours, where as it takes 5 days in BOD test.

Principle:

The organic matter present in the sample gets oxidized completely by $K_2Cr_2O_7$ in the presence of H_2SO_4 to produce CO_2 and H_2O. The excess of $K_2Cr_2O_7$ remaining after the reaction is titrated with $F(NH_4)_2$, $(SO_4)_2$ i.e., Ferrous Ammonium Sulphate (FAS). The dichromate consumed gives the oxygen required for the oxidation of organic matter.

Apparatus:

1. Reflux apparatus; 2. Burner/Heating mantle; 3. Burette; 4. Conical flask; 5. Pipette

Reagents:

1. Standard Potassium Dichromate (0.25N)
2. Sulphuric Acid with Silver Sulphate
3. Standard Ferrous Ammonium Sulphate(0.1N)
4. Ferroin Indicator.
5. Mercuric Sulphate ($HgSO_4$)

Procedure:

1. Place 0.4g Mercuric Sulphate in the reflux flask and add 20ml of sample and mix.
2. Then add 10ml of standard $K_2Cr_2O_7$ solution and add slowly 30ml of concentrate H_2SO_4 containing Silver sulphate in it and mix it thoroughly.
3. Reflux this mixture for a minimum period of 1 hour. Cool and wash down the condenser with distilled water.
4. Dilute the sample to make up 150ml and cool. Transfer this solution to a conical flask And titrate excess $K_2Cr_2O_7$ with 0.1 N FAS using ferroin indicator
5. Sharp colour change from bluish green to reddish brown indicates the end point.
6. Reflux the blank in the same manner using distilled water instead of the sample.

Observations:

Burette: 0.1N Ferrous Ammonium Sulphate (FAS) solution.

Conical flask : 150ml of sample

Indicator: Ferroin indicator

End Point: Bluish green to reddish brown.

Sample Details	Volume of sample taken (ml)	IBR	FBR	Vol. of FAS, VR=FBR- IBR	COD of Sample (mg/L)
Water sample (B)					
Blank solution (A)					

Calculations:

$$\boldsymbol{COD\left(\frac{mg}{L}\right) = \frac{(A - B) * Normality\ of\ FAS * 8 * 1000}{Volume\ of\ sample\ (ml)}}$$

Where ;

Quantity of FAS added for blank solution = A (ml)

Quantity of FAS added for water sample = B (ml)

= ………………………….. mg/lt.

Results:

The COD of waste water is = ……………….. mg/lt

Discussion:

Environmental significance:

1. The COD test is used extensively in the analysis of industrial wastes.
2. It is widely used in place of BOD in assessing the operation of treatment facility because of the speed with which the result can be obtained.
3. It is useful to access strength of wastes which contain toxins and biologically resistant organic substances.

Questions:

1. What is the difference between BOD and COD?
2. What are the other methods to determine the chemical oxygen demand of water sample?

6.Dissolved Oxygen (D.O) and Biochemical Oxygen Demand (BOD).

Aim: To determine the quantity of dissolved oxygen present in the given sample(s) by using Winkler's (Azide modification) method.

Introduction:

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.

The presence of oxygen is essential for the survival of aquatic life in water. This oxygen is especially required by aerobic bacteria and other micro-organisms for degradation and stabilization of organic constituents in waste water. A rapid fall in DO level in river water is one of the first indications of organic pollution. Thus it is one of the important parameters for accessing the quality of water, water bodies and plays a key role in water pollution control activities.

The major inputs of DO to natural water are from atmosphere and photosynthetic reaction. The solubility to oxygen in water depends on pressure, temperature, altitude and chloride concentration etc.

The solubility of atmosphere oxygen in fresh water varies from 14.6 mg/lt at 0^o C to about 7 mg/lt at 35^o C under 1 atmospheric pressure. Low DO in water can kill fish and many other organisms in water. For example, fish requires 2 mg/lt to 5 mg/lt of DO in water.

Principle:

Improved by various techniques and equipment and aided by instrumentation, the Winkler (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. BOD Bottle- 300 ml Capacity; 2. Conical Flask; 3. Burette; 4. Measuring Jars

Reagents:

1. Manganous Sulphate

2. Alkali Iodide-Azide Solution
3. Starch Indictor
4. Standard Sodium Thio Sulphate (0.025 N)
5. Concentrated Sulphuric Acid

Procedure (Winkler Method):

1. Take the BOD bottle and fill it completely with the given sample of water.
2. Add 2 ml of Manganous sulphate and 2 ml of Alkali - Iodide – Azide solution to the BOD bottle. (The tip of the pipette should be below the liquid level while adding these agents).
3. Stopper with care to exclude air bubbles and mix by repeatedly inverting the bottle 15 times.
4. After shaking and allowing sufficient time for all oxygen to react, the chemical precipitates are allowed to settle leaving at least 100 ml of clear solution.
5. Add 2 ml of concentrate Sulphuric acid by allowing the acid to run down the neck of the bottle.
6. Restopper and mix by gentle invertion until the suspension is completely dissolved and yellow colour is uniform throughout the bottle.
7. 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 = $(200\times300/(300-4)$ =203mL
8. Titrate it against Sodium thio sulphate solution until dark yellow changes to pale yellow.
9. 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.

Observations:

Burette: 0.025N $Na_2S_2O_3$

Conical flask: 203ml prepared sample (water + 2ml MnSO4 + 2ml alkali iodide azide + 2ml concentrated H_2SO_4) titrated against burette solution until dark yellow changes to pale yellow. Indicator: Starch (solution is turned to blue colour); End point: Blue to Colourless

SN	Description of sample(volume)	Initial Burette reading	Final Burette Reading	Volume of titrant rundown (mL)

Results:

The Dissolved Oxygen present in the sample = …………….. mg/L

Discussion:

Environmental Significance:

- The oxygen remains in water in dissolved form depending upon the temperature of water. As the temperature increases, the solubility of D.O in water decreases. For example the maximum D.O at 20^{o}C is 9.17 mg/l where as at 25^{o}C it is 8.38 mg/l. A minimum of 4 mg/L D.O is essential for the aquatic life.
- The organic matter present in the waste water poses a Biochemical Oxygen Demand. This demand is met with the Dissolved Oxygen present in the fresh body of water. If the organic load (volume x BOD) of the waste water is more than the asset (volume x D.O) the whole of the oxygen is depleted. This causes the death of fish and other aquatic animals and plants and they being organic matter further increase the demand of oxygen for the degradation. So it is necessary to find out the D.O of water to maintain sanitary conditions. It can be achieved by the treatment of waste water. Treatment means the reduction of BOD below the allowable limits. The limit is 30 mg/l for disposal of wastewater (sewage) in water.
- Aerobic bacteria thrive when free oxygen is available in plenty. Aerobic conditions prevail when sufficient DO is available in water. End products of aerobic metabolism are stable and not foul smelling.
- Higher temperature, biological impurities, ammonia, nitrites, ferrous iron, chemicals such as hydrogen sulphide and organic matter reduces DO values.
- Algae group in water may release oxygen during its photosynthesis and DO may even shoot up to 300 mg/lt.
- Drinking water should be rich in DO for good taste. However higher value of DO in water may cause corrosion of iron and steel.
- DO test is necessary for all aerobic biological waste treatment process to control rate of aeration.
- DO test is used to evaluate the pollution strength of industrial and domestic waste.

Questions:

1. **The concentration of Dissolved Oxygen in water is mainly dependent on**
    1. The temperature
    2. Chloride concentration

DETERMINATION OF BIOCHEMICAL OXYGEN DEMAND (BOD) OF WASTE WATER

Aim: To determine the amount of BOD (Biochemical Oxygen Demand) exerted by a given sample of waste water.

Introduction:

The Biochemical Oxygen Demand (B.O.D.) of sewage or of polluted water is the amount of oxygen required for the biological decomposition of dissolved organic matter to occur under aerobic condition and at the standardised time and temperature. Usually, the time is taken as 5 days and the temperature 20°C as per the global standard. The B.O.D. test is among the most important method in sanitary analysis to determine the polluting power, or strength of sewage, industrial wastes or polluted water. It serves as a measure of the amount of clean diluting water required for the successful disposal of sewage by dilution. The test has its widest application in measuring waste loading to treatment plants and in evaluating the efficiency of such treatment systems.

Principle:

The test consists in taking the given sample in suitable concentrations in dilute water in B.O.D. bottles. Two bottles are taken for each concentration and three concentrations are used for each sample. One set of bottles is incubated in a B.O.D. incubator for 5 days at 20°C; the dissolved oxygen (initial) content (D1) in the other set of bottles will be determined immediately. At the end of 5 days, the dissolved oxygen content (D2) in the incubated set of bottles is determined.

$$\text{Then, mg/L B.O.D.} = \frac{D1-D2}{P}$$

where, P = decimal fraction of sample used.

D1 = dissolved oxygen of diluted sample (mg/L), immediately after preparation.

D2 = dissolved oxygen of diluted sample (mg/L), at the end of 5 days incubation.

Among the three values of B.O.D. obtained for a sample select that dilution showing the residual dissolved oxygen of at least 1 mg/L and a depletion of at least 2 mg/L. If two or more dilutions are showing the same condition then select the B.O.D. value obtained by that dilution in which the maximum dissolved oxygen depletion is obtained.

Apparatus:

1. BOD bottles; 2. Pipette; 3. Burette; 4. Conical Flask; 5. BOD Incubator; 6.Measuring Jar

Reagents:

1. 0.025N Sodium Thio - Sulpahte

2. Manganous Sulphate
3. Alkali- Iodide- Azide Solution
4. Concentrated Sulphuric Acid
5. Starch Indicator
6. Phosphate Buffer Solution
7. Magnesium Sulphate Solution
8. Ferric Chloride Solution
9. Calcium Chloride Solution

Procedure:

1. Preparation of aerated distilled water: Place desired volume of distilled water in a 5 litre flask. Aeration is done by bubbling compressed air through water.
2. Add 1 ml each of phosphate buffer, magnesium sulphate solution, calcium chloride solution and ferric chloride solution for every litre of distilled water.
3. In the case of waste water which is not expected to have sufficient bacterial population, add seed to the diluted water. Generally 2 ml of settled domestic sewage is sufficient for 1000 ml of dilution water.
4. Highly acidic or alkaline sample are to be neutralized to a pH of 7.
5. Take the sample and dilute it with distilled water and mix contents well.
6. Take diluted sample into 2 BOD bottles.
7. Fill the other two BOD bottles with dilution water alone.
8. Find DO of diluted waste water and dilution water and note them down.
9. Incubate the other two BOD bottles in a BOD Incubator for 5 days at 20^0C. They are to be tightly stoppered to prevent any air entry into the bottles.
10. Determine DO content in the incubated bottles at the end of 5 days.
11. Calculate the B.O.D. of the given sample.

Note: The procedure for determining the dissolved oxygen content is same as described in the experiment under “Determination of dissolved oxygen”.

Observations:

Sample	DO of 0th day				DO of 5th day			
	IBR	FBR	VR	$(DO)_0$	IBR	FBR	VR	$(DO)_5$
Sewage sample								
Blank solution								

Calculations:

$$B.O.D.\,in\,\frac{mg}{L} = \left(\frac{(DO_0 - DO_5) * volume\ of\ bottle}{mL\ of\ sample\ taken}\right) - (B_0 - B_5)$$

Where:

D_O = DO of diluted wastewater sample on 0th day

D_5 = DO of diluted waste water sample on 5th day

B_O = DO of blank solution before incubation

B_5 = DO of blank solution after incubation of 5 days

Results:

The BOD of sample is __________________mg/L

Discussion:

Environmental Significance:

- The most widely used test indicating organic pollution of both wastewater and surface water is the 5-day BOD (BOD_5). This determination involves the measurement of the dissolved oxygen used by microorganisms in the biochemical oxidation of organic matter. BOD_5 is the total amount of oxygen consumed by microorganisms during the first five days of biodegradation. Oxygen demand is associated with the biodegradation of the carbonaceous portion of wastes and oxidation of nitrogen compounds such as ammonia. The following equations simplify the process of biodegradation:

  - *Organic matter* + O_2 + *microorganisms* → CO_2 + H_2O + *new microbial cells*
  - *Ammonia* + O_2 + *microorganisms* → NO_3 + H_2O + *new microbial cells*

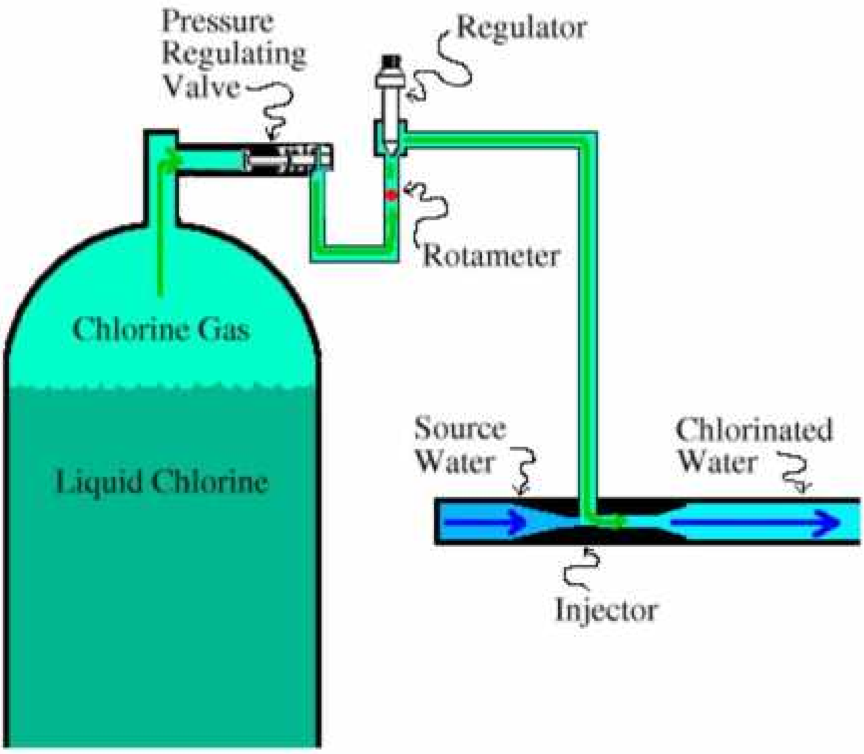
- The determination of BOD is used in studies to measure the self purification capacity of streams and help the regulatory authorities to check the quality of effluents discharged into such waters.
- It is useful in determination of strength of domestic and industrial sewage.
- BOD of wastewater is helpful in the design of treatment facilities and to evaluate the efficiency of various treatment units.
- It is a factor considered in choice of treatment method and is used to determine the size of certain units, particularly trickling filters and activated sludge units.
- It is the only parameter which gives an idea of the biodegradability of any sample and self purification capacity of rivers and streams.
- Drinking water usually has a BOD of less than 1 mg/L and water is considered fairly well up to 3 mg/L of BOD. But when BOD value reaches 5 mg/L, the purity of water is doubtful.
- Any effluent to be discharged into natural bodies of water should have BOD less than 30 mg/L as per CPCB Guidelines.

Questions:

1. What use is made of the B.O.D. test in water pollution control?
2. What are the three methods that can be used to control nitrification in the 5 days B.O.D. test at 20°C?
3. What are the factors affecting the rate of biochemical oxidation in the B.O.D. test?
4. What purpose or purposes are served by each of the following in BOD dilution water: (a) $FeCl_3$, (b) $MgSO_4$, (c) K_2HP0_4, (d) NH_4C1 and (e) $CaCl_2$
5. What justification does the engineer have for using first-order reaction kinetics to describe the complex biochemical processes occurring in the BOD test?
6. What is carbonaceous and nitrogenous BOD?
7. Draw and explain the BOD curve.

Experiment 7

Break Point Chlorination



Introduction:

Chlorination of public water supplies and polluted waters serves primarily to destroy or deactivate disease-producing microorganisms. Disinfection with chlorine is widely practiced. Chlorination may produce some adverse effects including taste and odor problem. in recent years, chlorination has been found to produce trihalomethanes (THMs) and other organics of health concern (THMs are suspected human carcinogens). Thus, use of alternative disinfectants, such as chlorine dioxide and ozone that do not cause this particular problem, is increasing.

Theory:

Disinfectant capabilities of chlorine depend on its chemical form in water, which in turn is dependent on pH, temperature, organic content of water, and other water quality factors. Chlorine is used in the form of free chlorine [e.g., chlorine gas] or as hypochlorites [e.g., NaOCl and $Ca(OC1)_2$]. Chlorine applied to water either as free chlorine or hypochlorite initially undergoes hydrolysis to form free chlorine consisting of aqueous molecular chlorine, hypochlorous acid and hypochlorite ion.

Chlorine gas rapidly hydrolyzes to hypochlorous acid according to:

$Cl_2 + H_2O = HOCl + H^+ + Cl^-$ **11.1**

Aqueous solutions of sodium or calcium hypochlorite hydrolyze too:

$Ca(OCl)_2 + 2H_2O = Ca^{2+} + 2HOCl + 2OH^-$ **11.2**

$NaOCl + H_2O = Na^+ + HOCl + OH^-$ **11.3**

Hypochlorous acid is a weak acid and will disassociate according to:

$HOCl \Leftrightarrow H^+ + OCl^-$ **11.4**

The two chemical species formed by chlorine in water, hypochlorous acid (HOCl) and hypochlorite ion (OCl^-), are commonly referred to as —free‖ or —available‖ chlorine.

In waters with pH between 6.5-8.5, the reaction is incomplete and both species (HOCl and OCl^-) will be present. Hypochlorous acid is the more germicidal of the two.

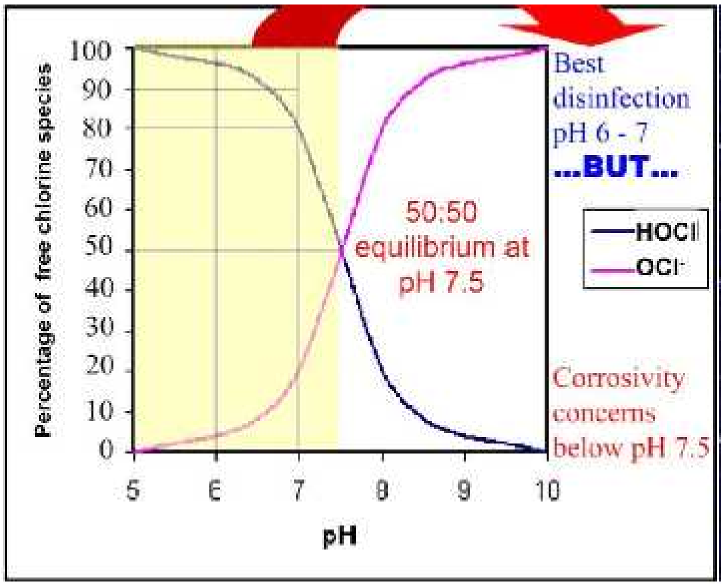


Figure 11.1: Free Chlorine Distribution with pH

Reactions of Chorine with Impurities in Water:

Reactions with Ammonia:

Free chlorine reacts readily with ammonia and certain nitrogenous compounds to form what are collectively known as "combined chlorine". The inorganic chloramines consist of three species: monochloramine (NH_2CI), dichloramine ($NHCl_2$) and trichloramine or nitrogen trichloride (NCI_3). The presence and concentrations of these combined forms depend on a number of factors including the ratio of chlorine to ammonia-nitrogen, chlorine dose, temperature, pH and alkalinity.

$NH_3 + HOCI = NH_2C1 + H_2O$; pH 4.5 to 8
$NH_2CI + HOCI = NHCl_2 + H_2O$; pH 4.5 to 8
$NHCl_2\ HOCI = NCI_3 + H_2O$; $pH < 4.5$

In addition to chlorinating ammonia, chlorine also reacts to oxidize ammonia to chlorine-free products (e.g., nitrogen gas and nitrate) as shown below.

$3\ Cl_2 + 2\ NH_3 = N_2\ (g) + 6H^+ + 6\ CI^-$
$4C1_2 + NH_3 + 3H_2O = 8C1^- + NO_3^- + 9H^+$

The mono- and dichloramines have significant disinfecting power and are therefore of interest in the measurement of chlorine residuals. Combined chlorine in water supplies may be formed in the treatment of raw waters containing ammonia; chlorinated wastewater effluents, as well as certain chlorinated industrial effluents normally contain only combined chlorine.

Reactions with Other Impurities:

Chlorine combines with various reducing agents and organi$_c$ compounds thus increasing the chlorine demand which must be satisfied before chlorine is available to accomplish disinfection.

Fe^{2+}, Mn^{2+}, NO_2^-, and H_2S are examples of inorganic reducing agents present in water supplies that will react with chlorine. Chlorine can react with phenols to produce mono-, di-, or trichlorophenols, which can impart tastes and odors to waters, Chlorine also reacts with humic substances present in water to form trihalomethanes (THMs, e.g., chloroform, brornoform, etc.) which are suspected human carcinogens (Note: According to USEPA, maximum allowable level of THMs in drinking water is 100 µg/L).

Break Point Chlorination

If chlorine is added to water containing reducing agents and ammonia (either naturally present or added to water to produce combined chlorine), a hump-shaped breakpoint curve is produced as shown in Fig. The different segment of the curve is described below:

a. If the water is free of ammonia and other compounds that may react with chlorine, the application of chlorine will yield free available chlorine residual of same concentration. This is denoted by the ‗no demand line‘ or the "zero demand line" (see Fig.).
b. Chlorine first reacts with reducing agents such as H_2S, Fe^{-2+}, Mn^{2+} and develops no measurable residual as shown by the portion of the curve from Origin up to point A.

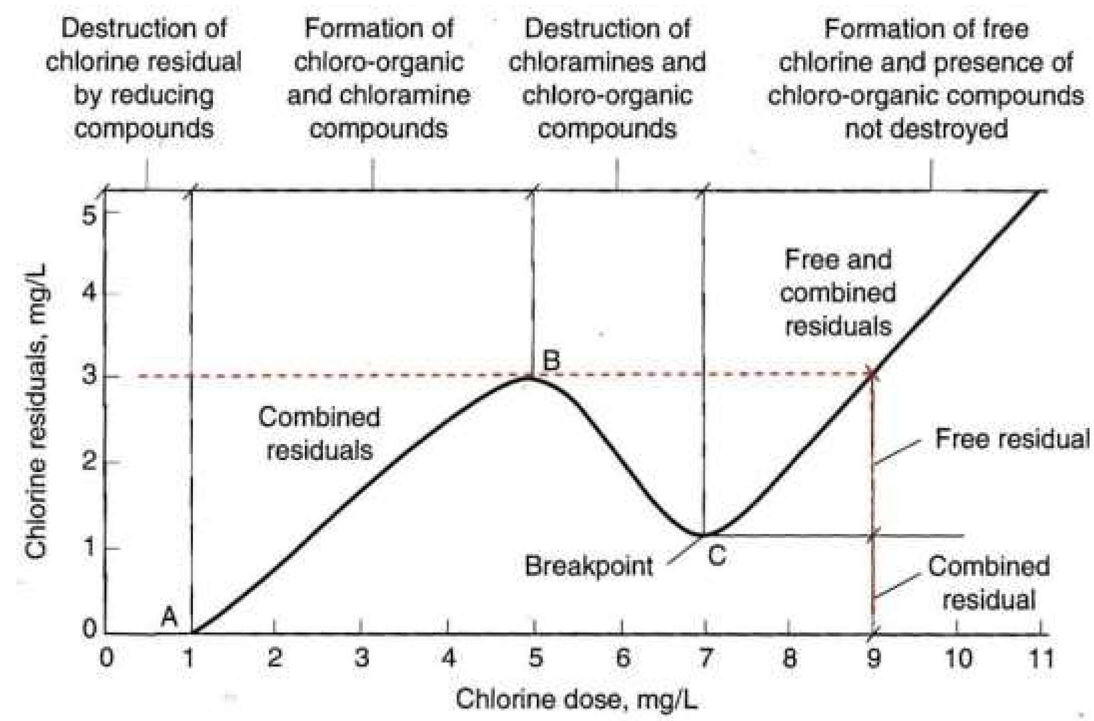


Figure 11.2: Generalized curve obtained during breakpoint chlorination of a water sample containing ammonia (Source: Peavy et al., 1985).

c. Addition of chlorine beyond point A results in forming mainly mono- and di-chloramines. With mole ratios of chlorine to ammonia up to 1:1 [i.e., $C1_2$:NH_3-N = 1:1], both mono and di-chloramines are formed. Chloramines thus formed are effective disinfectants and are shown as combined available chlorine residual in Fig. (From A to B).

d. Further increase in the mole ratio of chlorine to ammonia result in formation of some trichloramine and oxidation of part of ammonia to N_2 and NO_3^-. These reactions are essentially complete when 1.5 mole of chlorine has been added for each mole of ammonia nitrogen originally present in water [i.e., $C1_2$:NH_3-N = 1.5:1]. This is represented by the portion of the curve from B to C.

e. Addition of chlorine beyond point C would produce free chlorine residuals and is referred to as *"breakpoint chlorination"*. In other words, chlorination of water to the extent that all ammonia is converted to N_2 or higher oxidation state is referred to as *"breakpoint chlorination'.*

f. Addition of chlorine beyond point C would produce free chlorine residuals and is referred
to as *"breakpoint chlorination"*. In other words, chlorination of water to the extent that all ammonia *is* converted to N_2 or higher oxidation state is referred to as *"breakpoint chlorination"*.

Environmental Significance:

Breakpoint chlorination is required to obtain a free chlorine residual for better disinfection if ammonia is present in a water supply. While free chlorine residuals have good disinfecting powers, they are usually dissipated quickly in the distribution system. For this reason, final treatment with ammonia if often practiced to convert free chlorine residuals to longer-lasting combined chlorine residuals. The difference between the amount of chlorine added to the water and the amount of residual chlorine (i.e., free and combined available chlorine remaining) at the end of a specified contact period is termed as *"chlorine demand'.*

Materials required:

Reagents:

- Starch Indicator
- Standard 0.025 N Sodium thiosulfate
- Potassium Iodine crystal
- Concentrated Acetic Acid
- Chlorine water

Apparatus:

- Erlemeyer flask (250 mL)
- Bottle
- Beaker (250 mL)
- Measuring cylinder
- Dropper
- Stirrer

Procedure:

1. Place 200-mL portion of the water to be chlorinated in each of six 250-mL flasks.

2, Add required quantity (as instructed by your teacher) of "chlorine water" (stock solution of bleaching powder in water) in each of the flasks. The chlorine content of the "chlorine water" (determined earlier in the laboratory) would be provided to you by your teacher. Calculate the chlorine dose for each of the six flasks.

3. Shake each flask gently and allow to stand for 30 minutes.
4. Determine residual chlorine of water from each flask by the starch-iodine method as described below:

Starch-Iodine Method:

The starch-iodine method is based on the oxidizing power of free and combined chlorine residuals to convert iodide ion into free iodine at pH 8 or less, as shown below.

$Cl_2 + 2I^- = I_2 + 2\ Cl^-$

In the starch-iodine method, the quantity of chlorine residuals is determined by measuring the quantity of iodine by titration with a reducing agent sodium thiosulfate ($Na_2S_2O_3$). The end point of titration is indicated by the disappearance of blue color, produced by the reaction between iodine and starch (which is added as indicator during the titration),

$I_2 + 2\ Na_2S_2O_3 = Na_2S_4O_6 + 2\ NaI$
or, $I_2 + 2S_2O_3^{2-} = S_4O_6^{2-} + 2I^-$
I_2 + starch = blue color
(Qualitative test for the presence of iodine/chlorine)

The titration is carried out at pH 3 to 4, because the reaction with thiosulfate is not stoichiometric at neutral pH due to partial oxidation of the thiosulfate to sulphate.

Procedure for determination of Chlorine concentration in water:

a. Place 200 mL of the sample in an Erlenmeyer flask.
b. Add 'about 1g of potassium iodide (estimated on a spatula) and 2 mL of concentrated Acetic acid to the water.

c. Add 0.025 N sodium thiosulfate drop by drop from a burette until the yellow color almost disappears.
d. Add 1 mL of starch solution to the water.
e. Continue addition of standard sodium thiosulfate ($Na_2S_2O_3$) solution until the blue color just disappears.
f. Record the quantity (in mL) of sodium thiosulfate ($Na_2S_2O_3$) solution used.

Calculation:

Residual chlorine (mg/L) = mL of 0.025N sodium thiosulfate used x M.F.

M.F. = $\frac{\text{Normality of } N_2S_2O_3 \text{ X Equivalent wt.of } Cl_2 \text{ X } 1000}{\text{mL of sample taken}}$

Assignment:

1. What are the major disadvantages 'of chlorination? Name some of the alternate disinfectants.
2. You would like to perform chlorination to a water sample with pH 7.5. At this pH, what would be the relative proportions of HOC! and OCI^- (see Fig.- 1). What kind of change in pH would you propose in order to increase the relative proportion of HOCL, which is a better disinfectant?
3. Schematically draw a —chlorine residual" versus "chlorine dose" curve for a water sample with no ammonia or organic matter.

DATA SHEET

Table:

Observation No.	pH (initial)	Chlorine Dose (mg/L)	Residual Chlorine (mg/L)
1			
2			
3			
4			
5			
6			

Practical No. 8 : Presumptive Test for coliform bacteria

Aim: To find the Most Probable Number (MPN) of bacterial density by Presumptive test.

Theory: Coliforms are used as indicator organisms for fecal pollution in water. MPN is used to measure the optimum possibility of occurance of coliforms in the sample. Water is considered potable only if number of coliforms is not more than 3 per 100 ml of sample

Reagent: Lauryl tryptose broth -

Beef extract 3 g, peptone 5 g, lactose 5 g and reagent grade distilled water 1 litre. Add these ingredients to reagent grade distilled water, mix thoroughly and heat to dissolve. pH should be 6.87.0 after sterilisation

Computation of MPN:

The number of positive finding of coliform group organisms resulting from the multiple portion decimal dilution planting should be computed as the combination of positives and recorded in terms of the Most Probable Number (MPN). The MPN for the variety of planting series are presented in table. The values are at the 95% confidence limit for each of the MPN determined. These values are prepared for 10, 1 and 0.1 mL combination. If the combination is 100, 10, 1mL, the MPN is 0.1 times the value in the table. If on the other hand a combination corresponding to 1, 0.1, and 0.01 mL is planted, record MPN as 10 times the value shown in the table.

The MPN for combination not appearing on the table or for other combinations of tubes and dilutions, may be estimated by Thomas' simple formula:

$$\text{MPN/100mL} = \frac{No.\ of + ve\ tubes\ X\ 1000}{\sqrt{ml\ of\ sample\ in - ve\ tubes\ X\ ml\ of\ sample\ in\ all\ tubes}}$$

Sample Collection: Sample Bottle – use sterilised bottles of glass or plastic of any suitable size and shape (preferably use 250 mL capacity). Plastic bottles are sterilised in autoclave at 121^0C for 15 minutes. The non plastic bottles (glass) sterilised in hot air oven at 170^0 C for 1 hour.

Sample Presentation: If sample can not be analysed within 14 after collection use an ice cooler for storage during transport to the laboratory. In any case, the time elapsed between collection and analysis should not exceed 24 hr.

Procedure:

General: Clean and sterilise all the glasswares.

Presumptive Test:

1. Set up three separate series in a test rack, for each tubes three tubes marked as double strength (DS) and filled with 10 mL of double strength medium. Rest six tubes as single strength and added 10 mL of each single strength (SS) medium.
2. Sterlise the medium at 120°C.
3. Inoculate 10 ml aliquot of water sample to three tubes labelled double strength. Then 1 ml in 3 single strength tubes and lastly 0.1 mL in rest three single strength tubes.
4. Incubate all tubes for 48 hrs at 37°C, examine and if no gas is formed, repeat this test at the end of 48±3 hrs.
5. Record the presence or absence of gas formation at each examination of the tubes. Formation within 48±3 hrs of gas in any amount in the inverted fermentation tubes constitutes a positive presumptive test. Active fermentation may be shown by the continued appearance of small bubbles of gas throughout the medium outside the inner vial in the fermentation tubes.

Observations and Results for Presumptive Test:

Sr. No.	**Gas /Tubes showing +Ve result**			
	Sample	**Double strength (10 mL)** **1 2** **3**	**Single strength**	
			1 mL **1 2** **3**	**0.1 mL** **1 2** **3**

Calculation:

- **Case I:** For three each of 10 mL, 1 mL and 0.1 mL sample concentration combinations
  MPN from the MPN table (Table 1) = ...--

- **Case II:** For other combinations and dilutions

$$\text{MPN/100mL} = \frac{No.\ of + ve\ tubes\ X\ 1000}{\sqrt{ml\ of\ sample\ in - ve\ tubes\ X\ ml\ of\ sample\ in\ all\ tubes}}$$