J C BOSE UNIVERSITY OF SCIENCE AND TECHNOLOGY, YMCA, FARIDABAD

B.Tech (Civil Engineering)

ENVIRONMENTAL ENGINEERING LAB

LABORATORY MANUAL

SUBJECT CODE: PCCCE306P

Civil Engineering Department

LIST OF EXPERIMENTS

EXPERIMENT 01

AIM: To prepare a buffer solution and to determine pH of that buffer solution and other samples.

SIGNIFICANCE:

The pH level of water measures how acidic it is (pH stands for potential hydrogen, referring to how much hydrogen is mixed with the water.) 7 is a balanced pH for water. Anything below 7 indicates the water is acidic, and if it's above 7 it is alkaline. pH is really a measure of the relative amount of free hydrogen and hydroxyl ions in the water. Water that has more free hydrogen ions is acidic, whereas water that has more free hydroxyl ions is basic. Since pH can be affected by chemicals in the water, pH is an important indicator of water that is changing chemically.

THEORY

(I) PREPARATION OF BUFFER SOLUTION:

The resistance to change hydrogen ion concentration of a solution on addition of acid or alkali is known as Buffer action. The buffer solution is variably consists of a mixture of a weak acid or weak base and its salt .

The combination of weak acid, weak base and its salt suppress the dissociation of acid or base due to common ion effect so that the hydrogen ion or hydroxyl ion availability is lower than that in the pure solution at a comparable concentration.

(II) DETERMINATION OF pH OF BUFFER SOLUTION:

The ionic product of water and hydrogen ion concentration are related from the dissociation of water molecule as follows.

$H_2O = [H^+] + [OH^-]$

$Ka = [H^+] [OH^-] = 10^{-14}$

At neutral point, $[H^+] = [OH^-] = 10^{-7}$

The no. of gram ions of hydrogen present in 1 lit of solution is known as hydrogen ion concentration. If hydrogen ion concentration is more than 10^{-7} then the solution is acidic, if it is less than 10^{-7} then, it is basic. Sorenson (1909) introduced the term pH and suggested its use to express the acidity or alkalinity of solution which is defined as the negative logarithm of the hydrogen ion concentration.

$pH = - \log [H^+]$

For pure water, $pH = - \log [H^+] = - \log 10[10^{-7}] = 7$

For acidic solution, $pH < 7$

For basic solution $pH > 7$

APPARATUS

1. Buffer tablets/Buffer solutions
2. pH meter
3. Beaker (250ml)
4. Glass rod
5. Test tubes
6. Pipette (1ml)

PROCEDURE

1. Clean the electrode with distilled water and dry it with tissue paper
2. Calibrate the pH meter using buffer solutions of pH 4,7 and 9.2.
3. If buffer solutions are not available, they may be prepared using buffer tablets of respective pH
4. For preparing buffer solution, take 100ml of distilled water in a beaker and dissolve one tablet of pH 4. Stir well until the tablets dissolve s completely. Repeat he process to prepare Buffer solutions of pH 7 and pH 9.2.
5. First dip the combined electrode in buffer solution with pH 4.
6. Note the reading on the display. If it is not reading 4, then make it to 4 by using + and – keys on the pH meter.
7. Remove the electrodes , clean them with distilled water and dry with tissue paper.
8. Now dip the electrodes in buffer solution with pH 7 and adjust the meter to this pH.
9. Repeat the process of calibration using buffer of pH 9.2.
10. Once the instrument is caliberated , then clean the electrodes and dip in given sample.
11. Note the reading on the display.
12. Similarly record pH values of all the samples

OBSERVATIONS

S.No	Sample Name	pH
1		
2		
3		

RESULT: The pH of the given samples are found to be _____

PRECAUTIONS:

1. Handle the glass electrodes carefully to avoid breakage.
2. While calibrating the instrument always start from lower to higher pH buffer solutions.
3. Claen and wipe dry the electrodes before each reading.

EXPERIMENT 02

AIM: Determination of total hardness of water by EDTA method.

SIGNIFICANCE

Hard waters are generally considered to be those waters that require considerable amounts of soap to produce foam and that also produce scale in water pipes, heaters, boilers and other units in which the temperature of water is increased. Hard water are appropriate for human consumption similar to that as soft waters, however it produces adverse actions with soap and thus their use for cleaning purposes is unsatisfactory and thus their removal from water is required. Hardness of waters varies From place to place. In general, surface waters are softer than ground waters.

THEORY:

Hardness of water can be defined as that property of water, which prevents the lathering of soap. Hardness occurs mainly due to the presence of calcium and magnesium ions in the water. Heavy metal ions, and higher valent cations when present in water also cause hardness but to a lesser degree. Hence, in practice the hardness of water is taken as a measure of its Ca^{2+} and Mg^{2+} content. Mono-valent cations of alkali metals never produce hardness. Total hardness is due to the summation of permanent & temporary hardness. The Total hardness of water can be determined by complexo-metric titration. EDTA used as complexing agent & Eriochrome Black T (EBT) as indicator at a pH of 9—10.

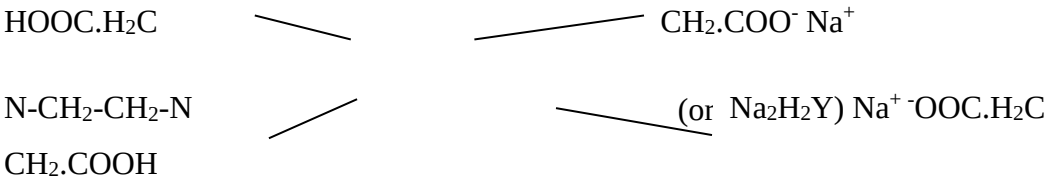
Unit of hardness:

Hardness of water is measured in parts **per million (**ppm) (w/v). All the hardness causing ions are expressed in terms of their respective weights equivalent to $CaCO_3$.

$1ppm \equiv 1mg / L \equiv 1g / 10^6 ml$

Ethylene diamine tetraacetic acid (**EDTA solution**

EDTA is a complexing agent (a remarkable ligand) which forms stable soluble complex with Ca & Mg ions having the following structure



The titration of EDTA with Ca or Mg ions is a 1:1ratio complex formation of cage like structure. The equilibrium is affected by the pH of the medium (p^H 9--10).

Indicator:

Eriochrome Black –T is an organic colouring substance that undergoes changes in colour while forming a less stable complex with Ca or Mg ions (compared to Ca or Mg-EDTA complex). Total reaction with colour changes may be represented as follows;

Ca^{2+} + EBT $\rightarrow$ Ca-EBT(unstable complex) (Blue)

(Pink)

$Ca^{2+} + EDTA^{2-} \rightarrow$ Ca- EDTA(Complex)

$Mg^{2+} + EDTA^{2-} \rightarrow$ Mg- EDTA(Complex)

Ca-EBT complex + EDTA $\rightarrow$ Ca-EDTA complex + EBT (Pink)

pH = 10 (Colourless) (Blue)

Similar reaction takes place for Mg^{2+} ion

Buffer solution:

The colour changes of the indicator are sensitive to pH of the medium. Hence to maintain the pH to appropriate range (9-10), ammonia buffer solution ($NH_4Cl + NH_4OH$) is added. At this pH of the medium, the complex between metal ions and EDTA is also stable.

APPARATUS: Burette (50 ml), Pipette (10ml), Measuring cylinder (10ml), Conical flask (100 ml)

PROCEDURE:

- Wash the burette with distilled water and rinse it with supplied EDTA solution.
- Fill the burette with EDTA solution.
- Remove air bubbles, if any and adjust to a level correctly.
- Fix the loaded burette to the burette stand.
- Wash & rinse the pipette with distilled water.
- Take 10 ml of the standard hard water with pipette into a 100ml conical flask previously washed with distilled water.
- To it, add 3 ml of ammonia buffer solution (pH ≈ 10) with measuring cylinder.
- Add 4 drops of the indicator {Eriochrome black-T (EBT)} solution & note the wine red colour.

- Titrate with EDTA solution of known strength until the colour turns sharply from wine red to blue indicating the end-point.
- Note the initial and final burette readings and enter it in the table-I.
- The titration process may be repeated to get the concordant reading.
- Similar titration will be done with supplied hard water and the values will be written in Table-II.

OBSERVATIONS:

In this titration the colour changes from **wine red to blue** sharply at the end-point

Tabulation-I:

No. of Obs.	**Vol. of standard hard water in ml**	**I.B.R.in ml**	**F.B.R.in ml**	**Diff. in ml**	**Volume of EDTA =X in ml**
1					
2					
3					
4					

Tabulation-II:

No. of Obs	**Vol. of hard water in ml**	**I.B.R.in ml**	**F.B.R.in ml**	**Diff.in ml**	**Volume of EDTA=Y in ml**
1					
2					
3					

4					

CALCULATION:

X= ml , Y= ml

X = amount of EDTA with SHW = Known hardness in ppm

Y amount of EDTA with hard water = Unknown hardness in ppm

Hence unknown hardness=(Y/X) x known hardness = =

ppm.

RESULT: Total hardness of water is found to be _____

EXPERIMENT 03

AIM: To determine the acidity of water supply

SIGNIFICANCE

Acids contribute to corrosiveness and influence chemical reaction rates, chemical speciation and biological processes. Acidity of water is its quantitative capacity to react with a strong base to a designated pH. The measured value may vary significantly with the end point pH used in the determination. Mmineral acids, weak acids such as carbonic and acetic and hydrolyzing salts such as iron or aluminum sulfate may contribute to the measured acidity according to the method of determination.

THEORY:

Measurement of acidity is important as acidic water are corrosive and corrosion producing substances have to be controlled or removed. If the acidic waters are used for stream generation in boilers, it results in corrosion & decreased efficiency of boiler. For mineral acids, the titration is carried to a pH of about 4.5 by using methyl orange indicator, giving a colour change from red to yellow. The acidity thus determined is called methyl orange acidity. Total acidity or phenolphthalein in acidity is determined by carrying the titration to phenolphthalein end point of 8.3 (measuring mineral acids, organic acids and free CO_2). The results are expressed as part of equivalent $CaCO_3$ per million parts of water.

END POINTS

1. Appearance of pink colour with NaOH in the burrete and a drop of phenolphthalein.
2. Change of red-orange colour to yellow with methyl orange as a indicator

APPARATUS:

1. Burette
2. Conical flask
3. Funnel

PROCEDURE:

1. Pipette out 100ml of the water sample into a conical flask.
2. Add 1 drop of N/10 $Na_2S_2O_2$ solution to destroy any residual chlorine
3. Add 2-3 drops of methyl orange indicator and titrate against N/50 NaOH solution until the red colour changes to yellow.

4. Take atleast 3 concordant readings and records the volume of NaOH (Sodium hydroxide) used as Y ml.

OBSERVATIONS

No. of obs	Vol. of water in ml	IBR in ml	FBR in ml	Difference in ml	Remark
1					
2					
3					

Volume of water sample taken for each titration = 100

Volume of N/50 NaOH used in presence of methyl orange indicator = Y ml Volume of N/10 NaOH used in presence of methyl orange as indicator = Z ml

METHYL ORANGE ACIDITY:

a) To calculate acid normality of the sample

$N_1V_1 = N_2V_2$

Sample = N/50 NaOH

$N_1 \times 100 = 1/50 \times Y$

$\rightarrow N_1 = \frac{Y}{50 \times 100}$

b) To calculate methyl orange acidity (in terms of $CaCO_3$)

Equivalent weight x Normality

Here Eq.Wt = 50

50 x N_1mg/L of $CaCO_3$

PHENOLPHTHALEIN ACIDITY:

1. Proceed as above 2-3 drops of Phenolphthalein indicator (in place of methyl orange) and titrate the sample against N/50 NaOH (from burette) until the solution is turned to pink colour and the colour persists for at least 30 second.

2. Repeat the titration to get atleast two concordant readings.

3. Record the volume of NaOH used as Z ml

In this titration, the colour changes from colourless to light pink.

a) To calculate acid normality of the sample

$N_1V_1 = N_2V_2$

Sample = N/50 NaOH

$N_1 \times 100 = 1/50 \times Z$

$\rightarrow N_1 = \frac{Z}{50 \times 100}$

b) To calculate Phenolpthalein acidity (in terms of $CaCO_3$)

Equivalent weight x Normality

Here Eq.Wt = 50

50 x N_1mg/L of $CaCO_3$

RESULT: The methyl orange acidity of the given water sample is found to be_____ppm

The phenolpthalein acidity of the given water sample is found to be_____ppm

EXPERIMENT 04

AIM: To determine the alkalinity of a given water sample.

SIGIFICANCE

Alkalinity can be defined as the ability of a water to neutralize acid or to absorb hydrogen ions. It is the sum of all acid neutralizing bases in the water. This ability to maintain the proper pH in the wastewater as it undergoes treatment is the reason why alkalinity is so important to the wastewater industry. Alkalinity values provide guidance in applying proper doses of chemicals in water treatment processes, particularly in coagulation, softening and operational control of anaerobic digestion.

Drinking natural alkaline water is generally considered safe, since it contains natural minerals. Artificial alkaline water, contains fewer minerals necessary for good health. So overuse of artificial alkaline water may lead to deficiency of minerals.

THEORY:

Alkalinity of water, which is a measure of the ability of water to neutralize the acids, is due to presence of bicarbonates, carbonates & hydroxides of Ca & Mg. Determination of alkalinity due to different ions is based on the titration of the water sample against a standard acid making selective use of indicators. The indicators used are phenolphthalein & methyl orange.

The reaction taking place is as follows:

1. $OH^- + H^+ \text{----------} \rightarrow H_2O$
2. $CO_3^{2-} + H^+ \text{----------} \rightarrow HCO_3^-$
3. $HCO_3^- + H^+ \text{----------} \rightarrow HCO$

A known volume of the sample is titrated against a standard acid using phenolphthalein as indicator to phenolphthalein end point [P] & continuing the titration using methyl orange as indicator to end point [M]. The volume of acid ran down upto phenolphthalein end point [P] corresponds to the completion of the equation (1) & (2) given above. Titration to pH 8.3 or decolorization of phenolphthalein indicator will indicate complete neutralization of hydroxide(OH^-) The volume of acid ran down after [P] corresponds to the completion of equation (3). This titration to pH 4.5 which is indicated by change in colour from yellow to orange using methyl orange as indicator indicates total alkalinity and complete neutralization of

OH^-, CO_3^{2-}, HCO_3^-. The total amount of acid used from the beginning of the experiment, i.e. → [M] corresponds to the completion of the reaction (1) to (3).

The result may be summarised in the following table from which the alkalinity due to different ions can be calculated.

ALKANITY DUE TO DIFFERENT IONS:

Titration result	OH^-	CO_3^{2-}	HCO_3^-
[P] = 0	NIL	NIL	[M]
[P] = [M]	[P] or [M]	NIL	NIL
$[P] = \frac{1}{2}[M]$	NIL	2 [P] or [M]	NIL
$[P] > \frac{1}{2}[M]$	2 [P] – [M]	2 { [M] – [P] }	NIL
$P < \frac{1}{2}[M]$	NIL	2 [P]	[M] – 2 [P]

Alkalinity is generally expressed as parts per million in terms of $CaCO_3$

APPARATUS:

1. Burette
2. Pipette
3. Conical flask
4. Glazed tile

PROCEDURE:

1. Take 50ml of water sample in a 250ml conical flask.
2. Add 2-3 drops of phenolphthalein indicator.
3. The colour of the solution will become pink.
4. Now titrate this solution against 0.02N Sulphuric acid taken in a burette till colour of the solution disappears

5. It shows all the carbonates have been converted in to bio-carbonates.
6. Note the titrate value of the phenolphthalein and point [P].
7. Add 2-3 drops of Methyl orange indicator to the same solution and continue the titration until the sharp colour changes from yellow to rose red takes place.
8. Note the total titre value from the beginning of the experiment as methyl orange end point [M].

OBSERVATIONS:

No. of obs	Volume of water	IBR	Titration with phenolphthalein		Titration with methyl orange.	
			FBR	Volume of H_2SO_4 used [P] = FBR-IBR	FBR	[M]=FBR-IBR
1						
2						
3						

In this titration, when phenolphthalein is used as indicator, the colour changes from light pink to colourless & when methyl orange is used as indicator, the colour changes from yellow to rose red colour.

RESULTS:

The supply water sample contains

$$\text{Total alkalinity} = \frac{M \times N \times 50000}{\text{ml of sample}}$$

$$\text{Phenolphthalein Alkalinity} = \frac{P \times N \times 50000}{\text{ml of sample}}$$

EXPERIMENT 05

AIM: To determine dissolved oxygen in a sample of water.

SIGNIFICANCE

Dissolved oxygen (DO) is one of the most important indicators of water quality. It is essential for the survival of fish and other aquatic organisms. Oxygen dissolves in surface water due to the aerating action of winds. Oxygen is also introduced into the water as a byproduct of aquatic plant photosynthesis. When dissolved oxygen becomes too low, fish and other aquatic organisms cannot survive.

The DO test tells how much oxygen is dissolved in the water. However, it does not tell you how much oxygen the water is capable of dissolving at the temperature at which it was measured. When water dissolves all of the oxygen it is capable of holding at a given temperature it is said to be 100% saturated. The colder the water is, the greater the amount of oxygen the water can hold. As the water becomes warmer, less oxygen can dissolve in the water. Salinity is also an important factor in determining the amount of oxygen a body of water can hold. As the amount of dissolved salts in the water increases, the amount of oxygen the water can hold decreases. Conversely, as the water becomes more fresh (lower salinity), more oxygen can dissolve into the water.

THEORY:

Oxygen present in water sample oxidize the dispersed divalent manganous hydroxide to ots higher valency which precipitates as a brown hydrated oxide on addition of NaOH and KI. Upon acidification, manganese reverts to divalent state and liberates iodine. The liberated iodine is titrated against standard hypo solution using starch as a final indicator. Since oxygen in water is in molecular state and not capable to react with KI, an oxygen carrier manganese hydroxide is used to bring about the reaction between KI and O_2. Manganous hydroxide is produced by the action of potassium hydroxide and manganous sulphate.

Chemical reaction

$2KOH+MnSO_4 \rightarrow Mn(OH)_2+K_2SO_4$

$2Mn(OH)_2+O_2 \rightarrow 2MnO(OH)_2$

$MnO(OH)_2+H_2SO_4 \rightarrow MnSO_4+2H_2O+[O]$

$2KI+H_2SO_4+[O] \rightarrow K_2SO_4+H_2O+I_2$

$I_2+2Na_2S_2O_3 \rightarrow 2NaI+Na_2S_4O_6$

Sodium tetrathionate

Starch+I_2→ Starch iodide complex (Blue in colour)

DO estimation in can also be done by membrane electrodes. A DO probe with a stirrer is used to determine DO. The semi permeable membrane provided in the DO probe acts as a diffusion barrier against impurities between sensing element and sample.

APPARATUS:

Burette, pipette, conical flask, beaker, measuring cylinder

PROCEDURE:

1. Take 500ml of water in a D.O/ Winkler's bottle.
2. Add 10ml of alkaline KI and 10 ml of $MnSO_4$ into it.
3. Stopper the bottle and shake it well.
4. Keep the bottle in dark for 5 min and add conc H_2SO_4 till the brown precipitates are dissolved.
5. Take 100 ml of the above solution in a conical flask. Titrate against hypo till the color changes to light Yellow.
6. Add 3-4 drops of starch in to it and the color changes to blue.
7. The blue color solution is titrated against hypo solution till blue color disappeared.
8. This is end point of the titration. Repeat this process till to get three concordant reading.

OBSERVATIONS:

No of obs	**Volume of water in ml**	**IBR in ml**	**FBR in ml**	**Diff in ml**	**Remark**
1					
2					
3					
4					

CALCULATION:

1000 ml of 1N $Na_2S_2O_3$=8 gm of O_2

100 ml of water sample contain=V/5 mg of O_2

1 lit of water sample contains =2V mg of O_2 = ppm

RESULT: The amount of dissolved oxygen in a sample of water is found to be_____ppm.

EXPERIMENT 06

AIM: To determine the optimum dose of coagulants for a water sample by jar test.

SIGNIFICANCE

Coagulants are used in water treatment plants

1) to remove natural suspended and colloidal matter
2) to remove material which do not settle in plain sedimentation, and
3) to assist in filtration

Alum [$Al_2S(SO_4)_3$. $18H_2O$] is the most widely used coagulant. When alum solution is added to water, the molecules dissociate to yield SO_4^{2-} and Al^{3+}. 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 mix 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 30 minutes 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

THEORY

A. Coagulant Solutions

Prepare your coagulant solution based on the information generated in item A and the size of the beakers you plan to use in your jar tests. For example, if your coagulant dosage is within the range of 5 to 100 ppm, you may want to make a 1% solution of the coagulant to add to your 1,000 ml beakers. This solution strength would result in you adding approximately 0.5 mls – 10 mls of your 1% solution to 1000 mls sample water. However, if your coagulant dosage is several hundred parts per million or greater, it would be better to make a 5 of 10% solution to be added to your 1,000 ml beakers.

B. Flocculent Solutions

Make the appropriate percent solution for the flocculants to be tested and the feed equipment to be used. If you cannot determine this information, a good starting point is a 0.1% solution. The calculations for determining the amount of emulsion flocculent product to use are the same as for coagulant; however, the mixing procedure requires much more agitation and mixing.

APPARATUS

1. Jar testing Equipment with multiple spindle stirrer

PROCEDURE:

Preparing Coagulant and Flocculent Solutions for Jar Testing:

For existing applications, determine the current feed rate of the coagulant and flocculants, if available. Additionally, if the coagulant is being diluted to a certain percent solution, it would be beneficial to know this information as well. Generally speaking, coagulant chemistries are fed neat and are not made down into solutions. Determine the flocculent solution prepared. Emulsion polymers require strong sheer force mixing and some age time to be inverted to full activity. Again, determine what the current make-down solution is for the existing application and dosage rate. Base the dosage of the flocculants aid on product dosage, not the make-down solution dosage. Make-down solution dosage for flocculants is normally 0.1 – 1% solutions.

Making a 1% Solution of a Coagulant with a Specific Gravity of 1.2

1. Determine the amount of solution to be made (200 mls).
2. Amount of coagulant product needed = mls of 1% solution to be made, multiplied by 1%, and divided by specific gravity of coagulant = 200 × .01 ÷ 1.2 = 1.67 mls. (2 grams)
3. Place amount of coagulant needed into approximately 198 mls (198 grams) of distilled water, for a 1% solution.

Note: If 10% solution is made, 16.7 mls (20 grams) of coagulant would be placed into 180 mls (180 grams) of distilled water.

4. The solution can be mixed by placing it in a clean sample bottle, securing a lid, and shaking it vigorously for 30 seconds to 1 minute.

Making an Emulsion Flocculent Solution:

1. Determine the amount of solution to be made (100 mls).

2. Amount of flocculent product needed = number of mls of solution to be made, multiplied by the percent solution to be made, divided by the specific gravity of the flocculent = 100 × 0.001 ÷ 1.05 = approximately 0.1 mls (0.1 grams) of flocculent product.

3.Amount of water for solution = 100 grams – 0.1 gram flocculent product = 99.9 grams (99.9 mls) of water.

4. Place 99.9 mls of water into a plastic 200 ml mix cup

5. Using a Braun mixer (or similar), begin mixing the distilled water in the mix cup. A stir rate of 800-1000 rpm is desired.

6. Shake the emulsion sample for 5-10 seconds until the product is uniform.

7. Immediately add 0.1 mls of flocculent product into the vortex area of the water as it is mixing.

8. Mix for a total of approximately 1 minute while turning the mixer section from one side to the other side of the mix cup for approximately 20 second intervals.

9. Discontinue mixing. Allow emulsion flocculent mixture to drain from the Braun mixer into the cup and clean the mixer with a dry paper towel.

10. Ideally, turbulent mixing should continue for 30 minutes for most efficient unwinding of the polymer. At least 30 minutes should be provided with occasional mixing.

Note: If a mixer is not available, invert the emulsion polymer as follows. (This method will yield less efficient inversion and unwinding of the polymer).

a. Use a container with a lid. Measure the water out and add it to the container.

b. Rapidly shoot the emulsion into the water using a syringe. With this method, target a 0.1% solution.

c. Immediately cap the container and vigorously shake for 1 minute.

d. Provide additional occasional moderate shaking for 30 minutes. The resulting solution should be white, translucent to opaque, and homogenous.

Making a Flocculent Solution with Dry Polymers:

1. Determine the amount of solution to be made (100 mls).

2. Generally, 0.1% solution strength is a good amount, so weigh out 0.1 grams and add to 100 mls

3. Slowly add the flocculent particles into the vortex of water, mixing at 800-1000 rpm, then offset and continue turbulent mixing for 30 minutes. Alternatively, add slowly to a container, cap it, and vigorously shake for 1 minute, then provide additional moderate shaking for 30 minutes. The resulting solution should be clear and homogenous. If fisheyes or globs are present, continue additional mixing.

Testing

Using existing plant operating data, determine the range of coagulant dosage and flocculent dosage you would like to evaluate in your jar test. In the first iterations of jar tests, you will probably be changing the coagulant dosages while maintaining a constant flocculent dosage. The proper coagulant chemistry and dosage is what you want to determine first. Sometimes, you may not even apply flocculent until you have correctly identified the most effective coagulant chemistry.

Example: Plant is currently feeding a coagulant at 60 ppm and flocculent at 1 ppm. You have a 4-beaker gang stirrer and plan to dose the coagulants in the jars at 20 ppm increments, starting with 20 ppm. You will dose all the jars with 1 ppm of flocculent. Calculate the amount of 1% solution of coagulant added to 1,000 mls of water to achieve a dosage of 20 ppm.

Determine what 1 ml of a 1% solution into 1,000 mls sample is equal to in mg/L or ppm.

1 ml of a 1% solution = 0.01 grams.

Divide by 1,000 mls and 1 ml in 1000 mls = 0.00001 g/L. Multiply by

1,000,000 to get mg/L which is 10 mg/L (ppm) or a

1% solution = 10,000 ppm. Dilute a 1 ml 1% solution with 1,000 mls of water to be tested.

10,000 ÷ 1,000 = 10 ppm.

When using a 1% solution of coagulant and 1,000 ml jars, 1 ml of solution added = 10 ppm. For a 500 ml sample, 1 ml of a 1% solution = 20 ppm.

Therefore, for jar 1, you will add 2 mls, add 4 mls to jar 2, 6 mls to jar 3, and 8 mls to jar

4 to have respectively 20, 40, 60, and 80 ppm of coagulant.

Determine the amount of 0.1% flocculent solution added to 1,000 ml jars to achieve 1 ppm dosage.

1 ppm = (X mls of 0.1% solution multiplied by 0.001 divided by 1,000 mls of sample) multiplied by 1,000,000.

X = 1 ml of 0.1% flocculent solution, therefore, we are going to add 1 ml of the 0.1%

flocculent solution to achieve 1 ppm dosage to all four beakers.

RESULT: Optimum dose of coagulant is found to be_____

EXPERIMENT 07

AIM: To perform microbiological culture analysis of bacterial samples followed by MPN (*Most Probable Number*) test.

SIGNIFICANE

The bacteriological examination of water is performed routinely by water utilities and many governmental agencies to ensure a safe supply of water for drinking, bathing, swimming and other domestic and industrial uses. The examination is intended to identify water sources which have been contaminated with potential disease-causing microorganisms. Such contamination generally occurs either directly by human or animal feces, or indirectly through improperly treated sewage or improperly functioning sewage treatment systems. The organisms of prime concern are the intestinal pathogens, particularly those that cause typhoid fever and bacillary dysentery.

Since human fecal pathogens vary in kind (viruses, bacteria, protozoa) and in number, it would be impossible to test each water sample for each pathogen. Instead, it is much easier to test for the presence of nonpathogenic intestinal organisms such as *E. coli*. *E. coli* is a normal inhabitant of the intestinal tract and is not normally found in fresh water. Therefore, if it is detected in water, it can be assumed that there has been fecal contamination of the water.

THEORY

In order to determine whether water has been contaminated by fecal material, a series of tests are used to demonstrate the presence or absence of coliforms. The coliform group is comprised of Gram-negative, non spore-forming, and aerobic to facultative anaerobic rods, which ferment lactose to acid and gas. Two organisms in this group include *E. coli* and *Enterobacter aerogenes*; however, the only true fecal coliform is *E. coli*, which is found only in fecal material from warm-blooded animals. The presence of this organism in a water supply is evidence of recent fecal contamination and is sufficient to order the water supply closed until tests no longer detect *E. coli.*

There are three principal tests: the presumptive, confirmed and completed tests.

STANDARD WATER ANALYSIS

The Presumptive Test

In the presumptive test, a series of lactose broth tubes are inoculated with measured amounts of the water sample to be tested. The series of tubes may consist of three or four groups of three, five or more tubes. The more tubes utilized, the more sensitive the test. Gas production in any one of the tubes is presumptive evidence of the presence of coliforms. The most probable number (MPN) of coliforms in 100 ml of the water sample can be estimated by the number of positive tubes.

The Confirmed Test

If any of the tubes inoculated with the water sample produce gas, the water is presumed to be unsafe. However, it is possible that the formation of gas may not be due to the presence of coliforms. In order to confirm the presence of coliforms, it is necessary to inoculate EMB (eosin methylene blue) agar plates from a positive presumptive tube. The methylene blue in EMB agar inhibits Gram positive organisms and allows the Gram- negative coliforms to grow. Coliforms produce colonies with dark centers. *E. coli* and *E. aerogenes* can be distinguished from one another by the size and color of the colonies. E. coli colonies are small and have a green metallic sheen, whereas *E. aerogenes* forms large pinkish colonies.

If only *E. coli* or if both *E. coli* and *E. aerogenes* appear on the EMB plate, the test is considered positive. If only *E. aerogenes* appears on the EMB plate, the test is considered negative. The reasons for these interpretations are that, as previously stated, *E. coli* is an indicator of fecal contamination, since it is not normally found in water or soil, whereas *E. aerogenes* is widely distributed in nature outside of the intestinal tract.

The Completed Test

The completed test is made using the organisms which grew on the confirmed test media. These organisms are used to inoculate a nutrient agar slant and a tube of lactose broth. After 24 hours at 37°C, the lactose broth is checked for the production of gas, and a Gram stain is made from organisms on the nutrient agar slant. If the organism is a Gram- negative, non spore-forming rod and produces gas in the lactose tube, then it is positive that coliforms are present in the water sample.

FIRST PERIOD

APPARATUS:

1. Nine tubes of double-strength lactose broth
2. 10, 1.0 and 0.1 ml pipettes
3. Water samples

PROCEDURE:

Presumptive Test

1. Take a water sample (dilute as instructed in some cases) and inoculate three tubes of lactose broth with 10 ml, three tubes with 1.0 ml and three tubes with 0.1 ml.
2. Incubate all tubes at 37^{o}C for 24 hours.

SECOND PERIOD

APPARATUS:

1. EMB agar plates

PROCEDURE

Presumptive Test

1. Observe the number of tubes at each dilution that show gas production in 24 hrs. Record results
2. Reincubate for an additional 24 hours at 37°C.

Confirmed Test

1. Inoculate an EMB plate with material from a tube containing gas.
2. Invert and incubate the plate at 37°C for 24 hours.

THIRD PERIOD

APPARATUS:

1. Lactose broth tubes
2. Nutrient agar slants

PROCEDURE

Presumptive Test

1. Observe the number of tubes at each dilution that show gas. Record results and determine the most probable number index.

Confirmed Test

2. Observe EMB agar plates. A positive confirmed test is indicated by small colonies with dark centers and a green metallic sheen (*E. coli*). Record results.

Completed Test

3. Inoculate a lactose broth tube and a nutrient agar slant with organisms from the EMB plate.

4. Incubate the broth tube and agar slant at 37°C for 24 hours

FOURTH PERIOD

PROCEDURE

Completed Test

1. Check for gas production in the lactose broth tube.

2. Make a Gram stain from the organisms on the nutrient agar slant.

3. Record results.

RESULT: Recorded results are found to be_____

EXPERIMENT 08

AIM: To determine the turbidity of different water samples.

SIGNIFICANCE

Turbidity can be measured by its effect on the scattering light, which is termed as Nephelometry. Turbidimeter can be used for sample with moderate turbidity and nephelometer for sample with low turbidity. Higher the intensity of scattered lights higher the turbidity. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample.

THEORY

The standard method for the determination of turbidity has been based on the Jackson candle turbidity meter. However, the lowest turbidity value that can be measured directly on this instrument is 25 units. An indirect method is necessary to estimate the turbidity in the range of 0-5 units; the turbidities of treated water generally fall in this range. Most commercial turbidimeters available for measuring low turbidities give comparatively good indicators of the intensity of light scattered in one particular direction, predominantly at right angle to the incident light. These nephelometers are relatively unaffected by small changes in design parameters and are therefore specified as the standard instrument for measurement of low turbidities. Results from nephelometric measurements are expressed as nephelometric turbidity units(NTU).

APPARATUS:

1. Digital Turbidimeter
2. Volumetric flasks

REAGENTS:

1. Solution I. Dissolve 1.000g hydrazine sulphate, $(NH_2)_2.H_2SO_4$ in distilled water and dilute to 100 mL in a volumetric flask.
2. Solution II. Dissolve 10.00g hexamethylenetetramine, $(CH_2)_6N_4$, in distilled water and dilute to 100 mL in a volumetric flask.
3. 4000NTU suspension. In a flask mix 5.0 mL of Solution I and 5.0 mL of Solution II. Let stand for 24 h at 25 ±3°C. This results in a 4000 NTU suspension. Store in an amber glass bottle. The suspension is stable for up to 1 year.

4. Dilute 4000 NTU stock solution with distilled water to make 100ml. This suspension is 400NTU.
5. Dilute 10ml of 400NTU suspension to 100ml to get 40NTU suspension.
6. Prepare the standard suspension of 2, 4,6,8,16 and 32 NTU using 40NTU suspension for preparation of calibration curve just before use and discard after use.

PROCEDURE

Preparation of Calibration Curve:

1. Connect the nephelometer with electric supply. Insert a tube filled with distilled water in the sample holding compartment/cell. Close the lid and set 0 on the scale given on the instrument using knob marked as SET ZERO.
2. Next fill 2/3rd of nephelometer tube by standard suspension of 40NTU. Put it in sample holding compartment and set 40 on the scale using knob marked as SET 100.
3. Insert the nephelometer tube by filling 2,4,6,8,16 and 32 NTU and note their turbidity from the scale and draw the calibration graph.
4. Gently agitate sample. Wait until air bubbles disappear and pour sample into cell. Read turbidity directly from instrument display.
5. Find the value of turbidity of that sample from the standard curve with respect to the instrument reading.

Precision and Bias

For comparison of water treatment efficiencies, it may be desirable to estimate turbidity more closely. However, the uncertainties and discrepancies in turbidity measurements make it unlikely that two or more laboratories will duplicate results on the same sample more closely than specified. To maintain the precision, analyze the sample in duplicate.

RESULTS: Turbidity in sample is found to be____NTU.

EXPERIMENT 09

AIM: To find out amount of total solids and dissolved solids in water sample.

SIGNIFICANCE:

The term 'solid' refers to the matter either filterable or non-filterable that remains as residue upon evaporation and subsequent drying at a defined temperature. Further categorization depends upon depends upon the temperature employed for drying and ignition. Different forms of solids are defined on the basis of method applied for their determination. Solids may affect water or effluent quality adversely in number of ways. Water with high dissolved solids may include an unfavorable physiological reaction in the transient consumer and generally are of inferior palatability. Highly mineralized waters are unsuitable for many industrial applications. High suspended solids in waters may be aesthetically unsatisfactory for such purposes as bathing. Analysis of total solids is important to decide upon the various unit operations and processes in physical and biological wastewater treatment and to assess its performance evaluation. For assessing compliance with regulatory agency, wastewater effluent limitations for various forms of solids act as indicating parameters.

THEORY:

A. Total solids

Residue left after the evaporation and subsequent drying in oven at specific temperature 103-105°C of a known volume of sample are total solids. Total solids include "Total suspected solids" (TSS) and "Total dissolved solids" (TDS). Whereas loss in weight on ignition of the same sample at 500°C, 50°C, in which organic matter is converted to CO2 volatilization of

inorganic matter as much as consistent with complete oxidation of organic matter, are volatile solids.

APPARATUS:

a. Electrically heated temperature controlled oven

b. Monopan balance

c. Evaporating dish (200mL)

d. Pipettes

e. Measuring cylinder (100mL)

Sample collection, preservation and storage

The water samples may be collected in resistant glass or plastic bottle. Water has considerable solvent property. There is possibility of increase in mineral content of sample, if water is collected and stored in non-resistant glass bottle. The effect is pronounced with alkaline water. Exclude particles such as leaves, sticks, fish and lump of faecal matter in the sample. Begin analysis as soon as possible due to impracticality of preservation of sample.

Calibration

The oven thermometer and balance need to be properly calibrated regularly.

PROCEDURE

a. Take a known volume of a well-mixed sample in a tarred dish ignited to constant weight (W_1)

b. Evaporate the sample to dryness at 103-105°C for 24hrs. c.

Cool in desiccator, weigh and record the reading (W_2)

d. Ignite the dish for 15-20 minutes in a muffle furnace maintained at 550±50°C.

e. Cool the dish partially in air until most of heat has been dissipated, and then transfer to a desiccator for final cooling in a dry atmosphere and record final weight (W_3).

f. The concentration is to be calculated in percent by weight.

CALCULATION

The total and the volatiles solids are expressed as:

Total solids, mg/L = $(W_2 - W_1)$ x 1000 / mL of sample

And$(W_2 – W_3)$ x 1000 / mL of sample

Where W_1, W_2 and W_3 are recorded in mg

B. Total dissolved solids

The filterable residue is the material that passes through a standard glass filter disk and remains after evaporation and drying at 180°C.

APPARATUS

Evaporatory dish (porcelain) – 100/200mL

Drying oven – equipped with thermostatic control capable of maintaining the temperature within 2°C range.

Desiccator – provided with desiccants

Analytical balance – 200mg capacity of weighing to 0.1mg Filter holder – Gooch crucible adapter or membrane filters Suction flask – 500mL capacity

Sample collection, preservation and storage

Begin analysis as soon as possible due to impractically of preservation of sample.

PROCEDURE

Filter the well-mixed sample under vacuum through membrane filter or Gooch Crucible. Transfer 100mL or more, depending upon the concentration of dissolved solids, in a weighed evaporating dish.

Evaporate to dryness on steam bath. Dry the evaporated sample for at least 1 hour in an oven at 180±2°C. Cool in a desiccator and weigh. Repeat the drying until constant weigh is obtained or weight loss is less than 0.5mg.

CALCULATION

mg/l total filterable residue at 180°C = (A –B) x 1000 / C

Where:

A = weight of dried residue + dishB = weight of dish

C = ml of filtrate used

RESULTS: Total solid and Dissolved solid in the sample is found to be____ and respectively

EXPERIMENT 10

AIM: To determine the Biological Oxygen Demand (BOD) of water sample.

SIGNIFICANCE:

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

THEORY

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 20ºC 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_5 20ºC is established under same experimental condition (for example BOD_5, 27ºC) is equivalent to BOD3, 27ºC) for Indian conditions. While reporting the results, the incubation period in days and temperature in ºC is essential to be mentioned.

APPARATUS:

a. BOD bottles 300mL capacity (clean with a detergent, rinse thoroughly and drain before use) with a water seal.

b. Incubator or water-bath to be controlled at 20ºC or at any desired temperature 1ºC. 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:

a. Phosphate buffer: Dissolve 8.5g KH_2PO_4, 21.75g K_2HPO_4, 33.5g $Na_2HPO_4.7H_2O$ and 1.7g NH_4C; in distilled water and dilute to 1000mL. The pH should be 7.2without further adjustment. Discard reagent if there is any sign of biological growth.

b. Magnesium sulphate: Dissolve 22.5g $MgSO_4.7H_2O$ in about 700mL of distilled water and dilute to 1 Litre.

c. Calcium chloride: Dissolve 27.5g anhydrous $CaCl_2$ in about 7000mL of distilled water and dilute to 1 Litre.

d. Ferric chloride: Dissolve 0.25g $FeCl3.6H_2O$ in about 700mL of distilled water and dilute to 1 L.

e. Sodium sulphate solution 0.025N: Dissolve 1.575g Na_2SO_3 in distilled water and dilute to 1000mL. Solution should be prepared daily.

f. Acid and Alkali solutions 1N: Prepare 1N H_2SO_4 and 1N NaOH for neutralization of caustic or acidic samples.

g. Nitrification inhibitor: 2-chloro-6-(trochloromethyl) pyridine [Nitrification inhibitor 2570-24 (2.2% TCMP), Hach Co. equivalent]

h. Glucose-glutamic acid solution: Dry reagent grade glucose and glutamic acid at 103ºC 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 4ºC 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 20-27ºC ± 3ºC before analysis. State storage time and condition as part of results.

PROCEDURE

Preparation of dilution water:

a. 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.

b. 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 20ºC/27ºC. Before use stabilize the water at 20ºC/27ºC.

c. 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 20ºC for 3 days at 27ºC. DO uptake of dilution water should not be more than 0.2 mg/L and preferable not more than 0.1mg/L.e

d. 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/Lof

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.

e. 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 Na_2S2O_3 solution as described below.

c. Take 50mL of the sample and acidify with addition of 10mL 1 + 1 acetic acid. Add about 1g Kl. Titrate with 0.025N $Na_2S_2O_3$, using starch indicator. Calculate the volume of $Na_2S_2O_3$ 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 ± 1ºC 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, DO ≥ 9mg/L should be treated to reduce the DO content to saturation at 20ºC. 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 20ºC for 5 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_2 consumption in dilution water.

d. Also prepare a seed blank in triplicate to measures BOD of seed for correction of actual BOD.

e. Determine DO in a BOD in the blank on initial day and end of incubation period by Winkler method as described for DO measurement.

CALCULATIONS

Calculate BOD of the sample as follows:

a. When dilution water is not seeded

BOD as O_2 mg/L = $(D_1 - D_2) \times 100 / \%$ dilution

b. When dilution is seeded

BOD O_2 mg/L = $[(D_1 - D_2) - (B_1 - B_2)] \times 100 / \%$ dilution

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

BOD O_2 mg/L = $[(D1 - D2) - (B_1' \times B_2')] \times F \times 100 / \%$ dilution

where,

D_1 = DO of sample immediately after preparation, mg/L D_2 = DO of sample after incubation period, mg/L

B_1 = DO of blank (seeded dilution water) before incubation, mg/L

B_2 = 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)

B_1, = DO of seed control before incubation, mg/L

B_2, = DO of seed control after incubation, mg/L

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

RESULT: The BOD of sample is found to be_____

EXPERIMENT 11

AIM: To determine the Chemical Oxygen Demand (COD) of the water sample.

SIGNIFICANCE

Chemical Oxygen Demand (COD) test determines the oxygen requirement equivalent of organic matter that is susceptible to oxidation with the help of a strong chemical oxidant. It is important, rapidly measured parameters as a means of measuring organic strength for streams and polluted water bodies. The test can be related empirically to BOD, organic carbon or organic matter in samples from a specific source taking into account its limitations. The test is useful in studying performance evaluation of wastewater treatment plants and monitoring relatively polluted water bodies. COD determination has advantage over BOD determination. COD results can be obtained in 3-4 hrs as compared to 3-5days required for BOD test. Further, the test is relatively easy, precise, and is unaffected by interferences as in the BOD test. The intrinsic limitation of the test lies in its inability to differentiate between the biologically oxidisable and biologically inert material and to find out the system rate constant of aerobic biological stabilization.

THEORY:

The open reflux method is suitable for a wide range of wastes with a large sample size. The dichromate reflux method is preferred over procedures using other oxidants (e.g. potassium permanganate) because of its superior oxidizing ability, applicability to a wide variety of samples

and ease of manipulation. Oxidation of most organic compounds is up to 95-100% of the theoretical value. The organic matter gets oxidized completely by potassium dichromate ($K_2Cr_2O_7$) with silver sulphate as catalyst in the presence of concentrated H_2SO_4 to produce CO_2 and H_2O. The excess $K_2Cr_2O_7$ remaining after the reaction is titrated with ferrous ammonium sulphate [Fe $(NH_4)_2(SO_4)_2$]. The dichromate consumed gives the oxygen (O_2) required for oxidation of the organic matter. The chemical reactions involved in the method are as under:

a. $2K_2Cr_2O_7 + 8\ H_2SO_4$ ® $2\ K_2\ SO_4 + 2Cr_2(SO_4)_3 + 8\ H_2O + 3O_2$

b. $C_6H_{12}O_6 + 6O_2$ ® $6CO_2 + 6H_2O$

c. $Cr_2O_7 + 6Fe^{++} + 14H^+ +$ ® $6Fe^{+++} + 2Cr^{3+} + 7H_2O$

APPARATUS:

a. 250 or 500mL Erlenmeyer flask with standard (24/40) tapered glass joints

b. Friedrich's reflux condenser (12 inch) with standard (24/40) tapered glass joints

c. Electric hot plate or six-unit heating shelf

d. Volumetric pipettes (10, 25, and 50mL capacity)

e. Burette, 50mL with 0.1mL accuracy f.

Burette stand and clamp

g. Analytical balance, accuracy 0.001g h.

Spatula

i. Volumetric flasks (1000mL capacity)

j. Boiling beads, glass

k. Magnetic stirrer and stirring bars.

Reagents and standards

a. Standard potassium dichromate solution, 0.25N (0.04167 M): Dissolve 12.259g $K_2Cr_2O_7$ dried at 103°C for 24h in distilled water and dilute to 1000mL. Add about 120 mg sulphamic acid to take care of 6 mg/L NO2 – N.

b. Sulphuric acid reagent: Add 10g of Ag_2SO_4 to 1000mL concentrated H_2SO_4 and let stand for one to two days for complete dissolution.

c. Standard ferrous ammonium sulphate approx. 0.25N (0.25M): Dissolve 98g $Fe(NH_4)2(SO_4)2.6H_2O$ in about 400mL distilled water. Add 20mL concentrated H_2SO_4 and dilute to 1000mL.

d. Ferroin indicator: Dissolve 1.485g 1, 10-phenanthroline monohydrate and 695mg $FeSO_4.7H_2O$ in distilled water and dilute to 100mL.

e. Mercuric Sulphates: $HgSO_4$, crystals, analytical gradef. Potassium hydrogen phthalate (KHP) Standard: Dissolve 425mg lightly crushed dried potassium hydrogen phthalate ($HOOC.C_6H_4.COOK$) in distilled water and dilute to
1000mL. This solution has a theoretical COD of 500µg O_2/ml. This solution is stable when refrigerated, up to 3 months in the absence of visible biological growth.

Sample collection, preservation and storage

Preferably collect samples in glass bottles. Homogenize samples containing settleable solids. If there is delay in collection and analysis, preserve sample by acidification to pH≤2 using concentrated H_2SO_4. Samples can be preserved for maximum 7 days.

Calibration

Since the procedure involves chemical of organic matter by potassium dichromate as oxidizing agent, which is a primary standard, calibration is not applicable. For standardization of ferrous ammonium sulphate, dilute 10ml standard $K_2Cr_2O_7$ to about 100mL. Add 10mL concentration of H_2SO_4 and allow it to cool. Titrate with ferrous ammonium sulphate (FAS) to be standardized using 2-3 drops of ferroin indicator. Calculate normally.

Normality of FAS = (ml $K_2Cr_2O_7$) (0.25) / ml FAS required

The deterioration of FAS can be decreased if it is stored in a dark bottle.

PROCEDURE

Sample preparation:

All samples high in solids should be blended for 2 minutes at high speed and stirred when an aliquot is taken for analysis. Select the appropriate volume of sample based on expected COD range, e.g. for COD range of 50-500 mg/l take 25-50mL of sample. Sample volume less than 25ml should not be pipetted directly, but serially diluted and then a portion of the diluted sample taken. Dilution factor should be incorporated in calculations.

a. 500mL of sample diluted to 1000mL = 0.5mL sample/ml of diluent, 50mL = 25mL of sample.

b. 100mL of sample diluted to 1,000mL = 0.1mL sample/ml diluent, 50mL of diluent =

5mL of sample.

Reflux of samples:

a. Place 0.4g HgSO4 in a 250mL reflux sample

b. Add 20mL sample or an aliquot of sample diluted to 20mL with distilled water. Mix well.

c. Add clean pumic stones or glass beads.

d. Add 10mL 0.25N (0.04167M) $K_2Cr_2O_7$ solution and mix.

e. Add slowly 30mL concentrated H_2SO_4 containing Ag_2SO_4 mixing thoroughly. This slow addition along with swirling prevents fatty acids to escape due to generation of high temperature. Alternatively attach flask to condenser with water flowing and then add H_2SO_4 slowly through condenser to avoid escape of volatile organic substance due to generation of heat.

f. Mix well. If the colour turns green, either take fresh sample with lesser aliquot or add more potassium dichromate and acid.

g. Connect the flask to condenser. Mix the contents before heating. Improper mixing will result in bumping and blow out of flask content.

h. Reflux for a minimum of 2 hours. Cool and then wash down condenser with distilled water.

i. Disconnect reflux condenser and dilute the mixture to about twice its volume with distilled water. Cool to room temperature and titrate excess $K_2Cr_2O_7$ with0.1M FAS using 2-3 drops of ferroin indicator. The sharp colour change from blue green to reddish brown indicates endpoint or completion of the titration. After a small time gap, the blue- green colour may reappear. Use the same quantity of ferroin indicator for all titrations.

j. Reflux blank in the same manner using distilled water instead of sample.

Alternate procedure for low COD samples less than 50mg/L:

Follow similar procedure with two exceptions (i) use standard 0.025N (0.004167M) $K_2Cr_2O_7$ and (ii) titrate with standardize 0.025M FAS. The sample volume should be 5.mL. Exercise extreme care with this procedure because even a trace of organic matter on the glassware or from the atmosphere may cause gross errors. Compute amount of HgSO4 to be added based on chloride concentrations. Carry blank reagent through the same procedure.

CALCULATIONS:

COD as mg/L = (a –b) x N x 8000 / mL sample

Where, a = mL FAS used for blank

b = mL FAS used for sample

N = normality of FAS

8000 = Milieq. wt. of O2 x 1000

RESULT: The COD of sample is found to be_____

EXPERIMENT 12

AIM: To determine total residual chlorine in a water sample.

SIGNIFICANCE

Chlorine and chlorine-based disinfectants are used worldwide to destroy germs in drinking water and swimming pools. One of the reasons for the widespread use of chlorine disinfectants is that they provide a "residual" level of protection against waterborne pathogens. A chlorine residual is a low level of chlorine remaining in water after its initial application. It constitutes an important safeguard against the risk of subsequent microbial contamination after treatment—a unique and significant benefit for public health

THEORY:

Living organism such as algae, fungi and bacteria are more abundant in surface drainage water, while in deep well water, the bacterial count is often low. The growth of these organisms in water used for industrial purpose may have serious consequences. The slime surrounding, these organisms causes them to add here to metal surface and the film of slime thus formed serves as a base to which suspended matter present in the water can add here. This leads to reduce the heat transfer rate and table blockages in boiler. The growth of marine organisms such as mussels may leads to serious reduction in the carrying capacity of pipe lines and culverts. Thus to prevent the development of living organisms, chlorine is primarily added to the water. Chlorine, hypochlorous acid and hypochlorites ions are commonly referd as free residual chlorines.

APPARATUS:

1. Burette
2. Pipette
3. Measuring flask
4. Watch glass
5. Weighing bottle
6. Glass rod

PROCEDURE:

1. Transfer 50ml of a given water sample in a conical flask.
2. Add 10ml of KI solution and about 3ml of glacial acetic acid to maintain 3-4 pH.
3. Cover the flask with stopper and mix the solution by shaking the flask.
4. After some time wash the sides of the flask with distilled water.
5. Titrate against standard $Na_2S_2O_3$ solution using 1ml starch as indicator.
6. At the end point the blue colour solution changes to colourless.
7. Note down the concordant volume of hypo solutions as V ml.

OBSERVATIONS:

S.NO	Sample size (g)	Titration volume (ml)	Results (Cl_2mg/L)

CALCULATION:

Residual chlorine (Cl_2 mg/L) = (A1 – f) × (1000/S) × 0.3545

A1: Titration volume of 0.01mol/L-sodium thiosulfate solution until the end point (ml)

F: Factor of 0.01mol/L-sodium thiosulfate solution (1.000)

S: Sample volume (ml)

RESULT: Amount of total residual chlorine in a given sample of water = ppm

EXPERIMENT 13

AIM: To determine chloride ion in a given water sample by Argentometric method (Mohr's Method)

SIGNIFICANCE:

Chlorides are present in water usually as NaCl, M_gCl_2 and $CaCl_2$. Although chlorides are not harmful as such, their concentration over 250ppm imparts a peculiar taste to the water thus rendering the water unacceptable for drinking purpose. Further existence of unusually high concentrations of chloride in a water sample indicates pollution from domestic sewage or from industrial waste waters. Salts like M_gCl_2 may undergo hydrolysis under the high pressure and temperature prevailing in the boiler, generating hydrochloric acid which causes corrosion in boiler parts chlorides in the form of M_gCl_2 and $CaCl_2$ cause Permanent hardness & area source of trouble not only at our house hold but also in industries.

THEORY:

By Argentometric method, chlorides in a water sample which is neutral or slightly acidic can be determined by it against standard silver nitrate solution using potassium chromate.

The pH should be in between 7-8

$Ag^+ + OH^- = AgOH$.

$KHCrO_4$ is weak in nature. Concentration of CrO_4^- decreases & therefore higher concentration of Ag^+ is needed for the soluble Ag reacts with Cl^- and CrO_4^+ when $AgNO_3$ solution is released from the burette to the sample solution which as Cl^-.

$Ag^+ + Cl = AgCl$ (white ppt)

$2\ Ag^+ + CrO_4 = Ag_2CrO_7$ (red ppt)

Red colour formed because of formation of silver chromate disappears as the solution contains high concentration of Cl^-.

$Ag_2\ CrO_7 + 2\ Cl = 2AgCl + CrO_4^{2-}$

When the concentration of chloride ions decreases the red colur starts disappearing slowly and slowly on shaking and a stage is reached when all the chloride ions forms AgCl. One extra drop of $AgNO_3$ at this point reacts with potassium chromate and reddish coloured silver chromate is formed.

$2\ AgNO_3 + K_2CrO_4 = Ag_2CrO_4 + 2KNO_3$

APPARATUS:

1. Burette
2. Pipette
3. Conical flask
4. Measuring flask

PROCEDURE:

(i) Titration with distilled water:

1. Transfer 50ml of distilled water in a conical flask and add 3-4 drops of potassium chromate indicator.
2. Slowly add standard solution at $AgNO_3$ solution from the burette and the volume of titrant is noted down as an end point when yellow colour starts changing to red colour.
3. The titration is repeated until concordant volume V_1 is obtained.
4. The blank correction for the indication should be deducted from the volume of the titrants obtained after titrating the sample solution in steps 2.

(ii) Titration with the Sample solution:

1. Transfer 50ml of given water sample in a conical flask. Add 3-4 drops of freshly prepared potassium chromate solution.

2. Titrate it against $AgNO_3$ solution and shake the solution. At the end point light yellow colour starts changing to red colour and red colour persists.
3. Repeat the titration until the concordant volume is obtained.
4. Say the volume of N/50 $AgNO_3$ consumed is V_2 ml.

OBSERVATIONS

S.NO	Vol. of Sample	Vol. of $AgNO_3$		Vol. Consumed
		Initial	Final	
1. 2. 3.				

RESULT: From the above experiment the amount of chloride ion in a given water sample is_____ppm

EXPERIMENT 14

AIM: To determine the conductivity of the given sample water.

SIGNIFICANCE

Conductivity is a numerical expression of the ability of an aqueous solution to carry the electric current. This ability depends on the presence of ions, their mobility, valence, relative concentrations and on the temperature of measurement. The inorganic acids, bases, and salt solutions are relatively good conductors. On the contrary, molecules of organic compounds that do not dissociate in aqueous solution have a poor conductivity.

THEORY

The conductivity is measured in the laboratory in term of resistance measured in ohms. The electric resistance of a conductor is inversely proportional to its cross-sectional area and directly proportional to its length. The magnitude of the resistance measured in an aqueous solution therefore depends on the characteristics of the conductivity cell used. Specific resistance is the resistance of a cube of 1cm. In aqueous solutions such a measurement is seldom made because of the difficulties in fabrication of electrode. Actually the electrodes measure a given fraction of the specific resistance known as the cell constant C

$$C = \frac{\text{Measured resistance, } R_m}{}$$

Specific resistance, R_S

The reciprocal of resistance is conductance. It measures the ability to conduct a current and is expressed in reciprocal of ohms i.e. mhos. In water analysis generally micromhos is used. Knowing the cell constant the measured conductance is converted to the specific conductance or conductivity, K_S, as the reciprocal of the specific resistance.

$$K_S = 1/R_S = C/R_m$$

The term conductivity is preferred and usually reported in micromhos per centimeter (µ mhos/cm). Freshly made distilled water has a conductivity of 0.5 to 2 .0 µ mhos/cm that increases after some days due to the absorption of CO_2 from atmosphere. The conductivity of potable waters varies generally from 50 to 1500 µ mhos/cm. The conductivity of municipal waste waters may be near to that of the potable water. However the industrial waste waters may have conductivities above10000 µ mhos/cm.

Measurement of conductivity with lesser accuracy than laboratory analysis is done continuously by the field recorders. These automatic recorders give idea about any sudden drastic change in the quality of raw water or the waste water, so that required precautions may be taken.

Actually the total dissolved solids in water can be estimated by measuring its conductivity and multiplying it by an empirical factor. This factor varies from 0.55 to 0.9 depending upon the soluble components of water and the temperature. This factor can be obtained for a system by observing the conductivity and the dissolved solids and then it can be used for continuous monitoring.

Reagents

Conductivity water: Pass distilled water through a mixed bed deionizer and discard first liter. Conductivity should be less than 1 µ mhos/cm.

Standard Potassium Chloride Solution (KCl, 0.01M), Dissolve 745.6 mg of anhydrous KCl in conductivity water and dilute to 1000 ml at 25^oC. This is the standard reference solution having a conductivity of 1413 µ mhos/cm at 25^oC, useful for the cell constants between 1 and 2.

APPARATUS:

1. Conductivity meter

2. Conductivity Cell

PROCEDURE

(i) Determination of Cell Constant

Wash the conductivity cell with 0.01 M KCl solution. Adjust the temperature of the standard KCl at 25± 0.1^{O}C. Measure resistance of the KCl and note the temperature.

The Cell Constant, C = (0.001413) (RKCL) [1+0.0191(t-25)

(ii) Conductivity Measurement

Rinse cell with the sample. Adjust temperature of the sample to 25± 0.1^{O}C. Measure sample resistance or conductivity and the temperature

OBSERVATIONS AND CALCULATIONS

Water sample no.	**Temperature**	**Electrical conductivity µ mhos / cm**	**Total dissolved solids in mg/l= EC x 'K'(selecte**

RESULT: The electrical conductivity of the given water sample is_____µmhos/ cm

EXPERIMENT 15

AIM: To determine the fluoride content in the given water sample.

SIGNIFICANCE

Fluoride levels are monitored in drinking water supplies to achieve the required safety. Absence of fluoride and excessive quantities in water, both create problems. .Fluoride ion in traces in drinking water helps in growth and development of healthy, resistant teethes and bones. It has been scientifically established that 0.8-1.0mg/l of fluoride is essential in potable water. Consumption of drinking water with an elevated level of fluoride leads to a chronic disease that manifests as dental and skeletal fluorosis. WHO has established guideline value of 1.5 mgl^{-1} in drinking water based on the health hazards estimates. Bureau of Indian Standards is 1.0mgl^{-1} as permissible and 1.5 mgl^{-1} as the maximum permissible limit. Prevention of fluorosis requires the screening of drinking water. Moreover, knowledge of fluoride level in potable water is important for health-care personnel and policymakers.

THEORY:

Fluorides are analysed by a method that involves the bleaching of a preformed colour by fluoride ions. The preformed colour is result of reaction of Zirconyl chloride octahydrate and SPADNS dye. The colour produced is referred to as lake and the intensity of colour is reduced if Zirconium present is reduced. Fluoride ions present in the sample reacts with the zirconium

dye to form stable complex ZrF_6^-. The dye becomes progressively lighter as fluoride concentration increases. The bleaching action is the function of the fluoride ion concentration and is directly proportional to it. Thus, Beer's law is satisfied and in and inverse manner.

APPARATUS

Spectrophotometer

Reagents:

Standard fluoride solution 1ml=10μgF

Zirconyl- alizarin reagent

Mixed acid solution

PROCEDURE:

1. Prepare a series of standard by diluting various volume of standard fluoride solution to 100ml . Prepare a range between 0 and 1.4 mg/l
2. To 50 ml of each standard add 10ml mixed acid Zirconyl SPADNS reagent
3. Set the spectrophotometer to a wavelength of 570nm. Adjust the spectrophotometer to zero absorbance with reference solution i.e. distilled water with reagent.
4. Plot the concentration along x-axis and absorbance along y-axis to obtain a calibration curve.
5. Repaet the process for the given water sample.
6. By referring the calibration curve, the concentration for the observed absorbance is read out.

OBSERVATIONS:

Table 1: Observations for Calibration

S.No.	Stock Fluoride solution in ml	Fluoride	Absorbance

Table 2:

S.No.	Sample	Absorbance	Fluoride in µg from graph	Fluoride in mg

CALCULATIONS:

$$\text{F in mg/l} = \frac{A \times B}{V \times C}$$

Where,

A = µg F determined

B= sample diluted to this volume

C = portion taken for colour development

V = Volume of the sample

RESULTS:

The fluoride content in the given water samples are;……