ENVIRONMENTAL ENGINEERING LABORATORY CV708

Hours / week: 3 **I.A. Marks: 25**
Exam Hours: 3 **Exam. Marks: 50**

1) Determination of Solids in Sewage: Total Solids, Suspended Solids, Dissolved Solids, Volatile Solids, Fixed Solids, Settable Solids.
2) Determination of Chlorides and Sulphates
3) Determination of Alkalinity, Acidity and pH.
4) Determination of Calcium, Magnesium and Total Hardness.
5) Determination of Dissolved Oxygen.
6) Determination of BOD.
7) Determination of COD.
8) Determination of percentage of available chlorine in bleaching powder.
9) Residual Chlorine and Chlorine Demand.
10) Jar Test for Optimum Dosage of Alum
11) Turbidity determination
12) Determination of Iron.
13) Determination of Fluorides
14) Total Count Test & MPN Determination.

References:

1. Manual of Water & Wastewater Analysis — NEERI Publication.
2. Standard Methods for Examination of Water and Wastewater (1995), American Publication —Association, Water Pollution Control Federation, American Water Works Association, Washington DC.
3. IS Standards: 2490-1974, 3360-1974, 3307-1974.
4. Sawyer and McCarty, Chemistry for Environment Engineering.

Scheme of Examination: Any one of the above exercise is to be conducted in the examination by the student,

CONTENTS

ACIDITY

Aim: To estimate the amount of acidity present in a given sample of water

Theory: Acidity of a liquid is its capacity to donate H^+ ions. Since natural water and sewage are buffered by carbon dioxide - bicarbonate system, the acidity present due to free CO_2 has no significance from public health view point. Water containing mineral acidity (due to H_2SO_4 and HCl) is unacceptable. Further, acidic water poses problems of corrosion and interferes in water softening.

Procedure:

A] Mineral acidity

1. Measure 100 ml of water sample into a conical flask.
2. Add two drops of methyl orange indicator; if it gives an orange reddish colour, it indicates the presence of mineral acidity.
3. Titrate with 0.02N NaOH to get yellow end point. Note down the ml of titrant used.

B] Carbon dioxide acidity

1. Measure 100 ml of water sample into a conical flask.
2. Add three drops of phenolphthalein indicator
3. Titrate with 0.02N NaOH to get faint pink colour end point. Note down the ml of titrant used.

Tabulation:

Sl. No	Methyl orange indicator			Phenolphthalein indicator		
	Initial reading	Final reading	ml of NaOH used	Initial reading	Final reading	ml of NaOH used

Calculations:

$$\text{Mineral acidity (mg/I) as } CaCO_3 = \frac{\text{ml of 0.02N NaOH used (methyl orange indicator) x 1000}}{\text{ml of sample taken (100)}}$$

$$CO_2 \text{ acidity (mg/l) as } CaCO_3 = \frac{\text{ml of 0.02N NaOH used (Phenolphthalein indicator) x 1000}}{\text{ml of sample taken (100)}}$$

Note: If phenolphthalein gives pink colour on addition to the sample, acidity is not present.

Reagents used:

1. Methyl orange indicator: Dissolve 5.0 gm of methyl orange in 1.0 litre of distilled water.
2. Phenolphthalein indicator: Dissolve 5.0 gm of phenolphthalein in 1.0 litre of 50% ethyl alcohol.
3. 0.02N Sodium Hydroxide (NaOH): Dissolve 0.8 gm of NaOH and dilute to 1000ml using distilled water. Store in air tight, rubber stoppered corning glass bottle.

ALKALINITY

Aim: To estimate the amount of alkalinity present in a given sample of water.

Theory: Alkalinity of a water is a measure of its capacity to neutralize acids. The alkalinity is due to the salts of carbonates, bicarbonates, borate, silicates and phosphates along with hydroxyl ions in the free state. Alkalinity plays a major role in water and wastewater treatment processes, particularly in coagulation, softening and operational control of anaerobic digestion.

Procedure:

1. Measure 100 ml of water sample into a conical flask.
2. Add three drops of phenolphthalein indicator, if pink colour develops, it indicates the presence of Hydroxide alkalinity.
3. Titrate with 0.02N Sulphuric acid till pink colour disappears. Note down the ml of titrant used (P).
4. Add two to three drops of methyl orange indicator to the same flask and continue titration to get a colour change from orange to faint pink. Note down the ml of titrant used (M).

Tabulation

Sl. No	Phenolphthalein indicator			Methyl orange indicator		
	Initial burette reading	Final burette reading	ml of H_2SO_4 used (P)	Initial burette reading	Final burette reading	ml of H_2SO_4 used (M)

Calculations:

Hydrode alkalinity (mg/I) as $CaCO_3$ = $\frac{\text{ml of 0.02N } H_2SO_4 \text{ used (P) x 1000}}{\text{ml of sample taken (100)}}$

Carbonate alkalinity (mg/I) as $CaCO_3$ = $\frac{\text{ml of 0.02N } H_2SO_4 \text{ used (M) x 1000}}{\text{ml of sample taken (100)}}$

Total alkalinity (mg/l) as $CaCO_3$ = $\frac{\text{ml of 0.02N } H_2SO_4 \text{ used (P + M) x 1000}}{\text{ml of sample taken (100)}}$

Note: If phenolphthalein does not gives pink colour on addition to the sample, the hydroxide alkalinity is zero and continue as in step 4 above.

(a) If P=0, Total alkalinity is due to bicarbonates
(b) If P < 1/2 T, Alkalinity due to carbonates = 2P
Alkalinity due to bicarbonates = T - 2P
(c) If P > 1/2 T, Alkalinity due to carbonates = 2 (T - P)
Alkalinity due to hydroxides = 2P - T
(d) If P=1/2 T, Total alkalinity is due to bicarbonates
(e) If P=T, Alkalinity is due to hydroxides only.

Reagents used:

1. Methyl orange indicator: Dissolve 5.0 gm of methyl orange in 1.0 litre of distilled water.
2. Phenolphthalein indicator: Dissolve 5.0 gm of phenolphthalein in 1.0 litre of 50% ethyl alcohol.
3. 0.02N Sulfuric acid: Prepare 0.1 N H_2SO_4, by diluting 3.0 ml of sulfuric acid in one litre of distilled water. Standardise against 0.1N sodium carbonate solution. Dilute appropriate volume of 0.1 N H_2SO_4 to 1000 m1 to obtain 0.02N sulfuric acid

CHLORIDES

Aim: To estimate the amount of chlorides present in a given sample of water.

Theory: Chloride ion is generally present in natural water due to dissolution of salt deposits, sewage discharges, refuse leachates, sea water intrusions etc. The salty taste produced by chloride depends on the chemical composition of water. High chloride content has a deleterious effect on metallic pipes and structures as well as on agricultural activities.

Procedure:

1. Measure 100 ml of water sample into a conical flask.
2. Add two drops of potassium chromate indicator.
3. Titrate with N/35.5 Silver Nitrate solution to get yellow to brick red end point. Note down the ml of titrant used.

Tabulation:

Sl. No	Initial burette reading	Final burette reading	ml of $AgNO_3$ used	Chlorides in mg/l

Calculations:

$$\text{Chloride (mg/l)} = \frac{\text{ml of N/35.5 } AgNO_3 \times 1000}{\text{ml of sample taken}}$$

Reagents used:

1. **Potassium chromate indicator**: Dissolve 50 gm of potassium chromate in a small quantity of distilled water. Add $AgNO_3$ solution to produce a light red precipitate. Allow to stand for 12 hours and make up to one litre.

2. **N/35.5 Silver Nitrate solution**: Dissolve 4.78 gm of Silver Nitrate in one litre of distilled water. Standardise with standard sodium chloride solution.

Note: If the sample is too turbid or coloured, add 3m1 of Aluminum hydroxide suspension to the measured quantity of sample. Stir thoroughly, set aside for a few minutes and filter. Wash the precipitate with distilled water and collect the washings with the filtrate and continue the titration.

HARDNESS

Aim: To estimate the amount of Hardness (Total, Temporary and Permanent) present in a given sample of water.

Theory: Hardness of water is not a specific constituent but is a variable and complex mixture of anions and cations. In fresh water, the principal hardness causing ions are Calcium and Magnesium in addition to Strontium, Iron, Barium etc. The Carbonates and bicarbonates of Magnesium and Calcium cause temporary hardness or carbonate hardness and can be easily removed by boiling. Permanent hardness or the non- carbonate hardness is mainly due to Sulphates, Nitrates and Chlorides of calcium and Magnesium and cannot be removed by boiling. Hardness is commonly expressed as mg $CaCO3$ equivalent per litre.

Hard waters are undesirable because they lead to greater soap consumption, scaling of boilers, causing corrosion and incrustation of pipes, making food tasteless etc.

Procedure:

(a) Total Hardness:

1. Measure 100 ml of sample into a conical flask.
2. Add 1.0m1 of Ammonia buffer solution and three drops of Erichrome black-T indicator
3. Titrate with standard EDTA solution to get an end point of wine red to blue. Note down the ml of titrant used.

(b) Permanent Hardness:

Take a known quantity of water and boil it for long period, cool and filter. Repeat the above procedure and note down the ml of EDTA used.

Tabulation

SI. No	Raw water sample				Boiled water sample			
	Initial burette reading	Final burette reading	ml of EDTA used	Hardness in mg/l	Initial burette reading	Final burette reading	ml of EDTA used	Hardness in mg/I

Calculations:

Total Hardness (mg/l) as $CaCO_3$ = $\frac{\text{ml of EDTA used (unboiled) x 1000}}{\text{ml of sample taken (100)}}$

Permanent Hardness (mg/I) as $CaCO_3$ = $\frac{\text{ml of EDTA used (boiled) x 1000}}{\text{ml of sample taken (100)}}$

Temporary Hardness (mg/l) as $CaCO_3$ = Total hardness — Permanent Hardness

(a) If Total Hardness > Total alkalinity
Then,
1. Alkaline hardness = Total alkalinity
2. Non-alkaline hardness = Total hardness - Total alkalinity

(b) If Total Hardness < < Total Alkalinity
Then,
1. Alkaline hardness = Total hardness
2. Non alkaline hardness = Nil

Reagents used:

1) **Erichrome black-T indicator:** Dissolve 0.10 gm Erichrome black- T in 20 ml of ethyl alcohol
2) **Ammonia buffer**: Dissolve 6.75 gm of ammonium chloride in 75 ml of liquid ammonia and dilute to 100 ml with distilled water
3) **Standard EDTA solution**: Dissolve 4.0 gm of sodium salt of EDTA and 0.1 gm of magnesium chloride in 800 ml of distilled water and standardise with calcium chloride solution.

DETERMINATION OF SOLIDS IN WATER

Aim: To estimate the amount of Total solids, Volatile solids, dissolved solids and suspended solids present in a given sample of water/wastewater.

Theory: The term solids refer to the matter either filterable or infilterable that remains as residue upon evaporation and subsequent drying at a defined temperature. The residue after evaporation and subsequent drying in hot air oven at a temperature range of 103-105 °C of a known volume of sample is the total solids. Whereas, loss in weight on ignition of the same sample at 550 °C in which the organic matter is converted to CO_2 and H_2O while temperature is controlled to prevent decomposition and volatilization of inorganic matter as much as consistent with complete oxidation of organic matter are volatile solids.

Procedure:

A] Total solids and Volatile solids

1) Weigh the crusible/dish under dry condition **(W_1)**
2) Take a known volume of a well mixed sample
3) Evaporate the sample to dryness at 103-105 °C
4) Cool in a desicator, weigh and record the reading **(W_2)**
5) Ignite the dish at 550 °C for 30 minutes in a muffle furnace
6) Cool in a desicator and record the final weight **(W_3).**

Calculations:

Total solids $= \dfrac{(W_2 - W_1) \times 1000}{\text{ml of sample taken}}$

Volatile solids $= \dfrac{(W_2 - W_1) \times 1000}{\text{ml of sample taken}}$

Fixed solids = Total solids — Volatile solids

B] Suspended solids and Dissolved solids

1) Filter the sample through Whatmann filter paper (No.44)
2) Take a suitable quantity in a weighed dry crucible.
3) Evaporate to dryness at 103-105 °C in an oven
4) Cool in a desicator and record the weight

$$\text{Dissolved solids in mg/l} = \frac{(\text{weight of crusible with residue} - \text{weight of empty crusible}) \times 1000}{\text{ml of sample}}$$

Suspended solids = Total solids — Dissolved solids.

DISSOLVED OXYGEN

Aim: To estimate the amount of dissolved oxygen present in a given sample of water/wastewater.

Theory: Oxygen gas absorbed by water from the atmosphere is called dissolved oxygen. Dissolved oxygen is important in precipitation and dissolution of organic substances in water. The DO concentration varies in nature and wastewater to a large extent, from the state of no oxygen to saturation level. The saturation values changes with temperature, pressure, altitude and chloride concentration.
To assess the quality of raw water and to check the stream pollution, DO analysis is important. The performance evaluation of wastewater treatment plants, aerobic treatment processes etc are done by evaluating the DO values.

Procedure:

1. Collect the sample in a BOD bottle.
2. Add 1.0m1 of Manganous sulfate, followed by 1.0m1 of Alkaline Potassium Iodide (Azide) solution by dipping the pipette below the liquid level.
3. Inserting the stopper, mix well and allow the precipitate to settle down.
4. Add 2.0 ml of concentrated Sulfuric acid and mix well till precipitate goes into solution.
5. Take Calibrated volume** of this solution to a conical flask and titrate against 0.025N Sodium thiosulfate solution with starch as indicator to get an end point of blue to colourless. Record the ml of titrant used.

Tabulation

SI. No	Initial burette reading	Final burette reading	ml of $Na_2S_2O_3$ used	DO in mg/l

Calculation

Since 1 ml of 0.025N $Na_2S_2O_3$ = 0.2 mg oxygen, the ml of this solution used is equivalent to mg/litre of dissolved oxygen.

Calibrated Volume: Fill the BOD bottle completely with water and measure the exact volume of water filled. Since 4 ml of reagent is added, equal volume of sample is lost. Hence calibrated volume is worked as below

$$\frac{200 \times \text{exact capacity of bottle}}{(\text{exact capacity} - 4)}$$

Reagents used :

1. **Manganous sulfate solution**: Dissolve 480 gm of manganous sulfate crystals (MnSO4,4H20) in sufficient distilled water to make 1.0 litre.
2. **Alkaline Potassium Iodide**: Dissolve about 500 gm of sodium hydroxide, 20gm of sodium azide and 150 gm of Potassium Iodide in sufficient distilled water to make 1.0 litre.
3. **Standard Sodium thiosulfate (0.025N) solution**: Dissolve 6.2 gm of $Na_2S_2O_3$, $5H_2O$ in a boiled, cooled distilled water and dilute to 1000 ml. Preserve by adding 5 ml of chloroform per litre.

BIOCHEMICAL OXYGEN DEMAND

Aim: To determine the BOD of a given sample of wastewater.

Theory: The Biochemical oxygen demand (BOD) is defined as the amount of oxygen required by microorganisms while stabilizing biologically decomposable organic matter in a wastewater under aerobic condition. The BOD test is widely used to determine

1) The pollution load of wastewater
2) The degree of pollution in lakes and streams at any time and their self purification capacity and
3) Efficiency of wastewater treatment methods.

Procedure:

1. Prepare dilution water by aerating distilled water with supply of air and add to it 1.0m1 each of phosphate buffer solution, Magnesium sulfate solution, Calcium chloride and Ferric chloride to one litre of distilled water as the micro nutrients for bacteria.
2. Make several dilutions of sample to obtain required dilution factor. The following dilutions are normally suggested.
   0.1 to 1.0% for strong wastes
   1.0to 5.0% for raw and settled sewage
   5 to 25% for oxidized effluents and
   25 to 100% for polluted river water.
3. Fill up one BOD bottle with the mixture and the other one with dilution water (blank) in two sets.
4. Keep one set in BOD incubator for 5 days incubation at 20° C and find out immediate DO of blank and the sample bottle.
5. Find the DO of both the bottles kept in incubator after 5 days.

Calculations:

BOD in mg/l = $(D_1 - D_2) - (B_1 - B_2)$ x Dilution factor

Where,

B_1 = DO of blank before incubation (1st day),

B_2= DO of blank after incubation (5 day)

D_1 = DO of diluted sample before incubation (1st day)

D_2 = DO diluted sample after incubation (5 day)

Reagents used:

1. **Manganous sulfate solution**: Dissolve 480 gm of manganous sulfate crystals ($MnSO_4$, $4H_2O$) in sufficient distilled water to make 1.0 litre.
2. **Alkaline potassium Iodide**: Dissolve about 500 gm of sodium hydroxide, 20gm of sodium azide and 150 gm of potassium Iodide in sufficient distilled water to make 21.0 litre.
3. **Standard sodium thiosulfate (0.025N) solution**: Dissolve 6.2 gm of $Na_2S_2O_3$, $5H_2O$ in boiled, cooled distilled water and dilute to 1000 ml. preserve by adding 5 ml of chloroform per litre.
4. **Phosphate buffer solution**: Dissolve 8.5 gms KH_2PO_4, 21.75 gms of K_2HPO_4, 33.4gms of $Na_2HPO_4.7H_2O$ and 1.7 gms of NH_4CI in distilled water and dilute to 1000ml.
5. **Magnesium sulfate**: Dissolve 82.5gms of $MgSO_47H_2O$ in 1 litre of distilled water.
6. **Calcium chloride**: Dissolve 27.5gms of anhydrous $CaCl_2$ and dilute to 1000ml.
7. **Ferric Chloride**: Dissolve 0.25 gms of $FeCl_3$ $6H_2O$ in 1 litre of distilled water

Note: In case of the wastes which are not expected to have sufficient bacterial population, add seed to the dilution water. Generally 2ml settled sewage is considered sufficient for 1000ml dilution water.

CHEMICAL OXYGEN DEMAND

Aim: To determine the COD of a given Sample of wastewater

Theory: The chemical oxygen demand (COD) test determines the oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant. The test can be employed for the same purpose as the BOD test taking in to account its limitations. The limitation of the test lies in its inability to differentiate between biologically oxidizable and biologically inert material. COD determination has an advantage over BOD determination in that the results can be obtained in about 5 hours as compared to 5 days required for BOD test.

Procedure:

1. Place the diluted 20ml sample with distilled water in flat bottom flask and add to it 10ml of potassium dichromate solution. Then carefully add 30ml of conc. H_2SO_4, mix after each addition thoroughly. Add about 10mg each of $HgSO_4$ and $AgSO_4$ crystals.
2. Attach the flask to condenser and reflux the mixture for two hours. Then wash down the condenser with little distilled water, remove the flask and cool.
3. Dilute the mixture to about 140ml with distilled water and titrate excess of dichromate with standard ferrous ammonium sulfate using ferroin indicator. The colour change is sharp, changing from bluish green to wine red.

Calculations:

$$\text{COD in mg/l} = \frac{(A - B) \times N \times 800}{\text{ml of sample}}$$

Where A = ml of $Fe(NH_4)_2 (SO_4)_2$ for blank
B = ml of $Fe(NH_4)_2 (SO_4)_2$ for sample
N = Normality of $Fe(NH_4)_2 (SO_4)_2$

Reagents used:

1) **Stadard Potassium dichromate 0.2N**: Dissolve 12.259gm of $K_2Cr_2O_7$ dried at 103^0 C for 24 hours in distilled water and dilute to 1000ml.
2) **Standard ferrous ammonium sulfate 0.1N**: dissolve 39gms of $Fe(NH_4)_2$ $(SO_4)_2$, $6H_2O$ in about 400ml distilled water. Add 20ml of concentrated sulfuric acid and dilute to 1000ml
3) F**erroin indicator**: Dissolve 1.485gms of 1 – 10 Phenanthroline monohydrate and 695 mg $FeSO_4$ $7H_2O$ and dilute to 100ml with distilled water

Note: For standardization of $Fe(NH_4)_2$ $(SO_4)_2$, use10ml of standard $K_2Cr_2O_7$, acidify by adding 10ml Conc. H_2SO_4 and titrate with Ferrous ammonium sulfate using ferroin indicator. **Calculate N by $N_1V_1 = N_2V_2$**

AVAILABLE CHLORINE IN BLEACHING POWDER

Aim: To estimate the amount of chlorine available in a given sample of bleaching powder.

Theory: Bleaching powder to be used in water treatment (disinfection) process is to be analyzed for percentage of Chlorine present, so that the dosage can be fixed and the grading can be done on the sample.

Procedure:

1. Weigh accurately 2.5gms of bleaching powder and grind with distilled water till a paste is formed and decant off the fine part into 250m1 flask. Again grind the material left behind and repeat the procedure of decanting. Make the solution to 250ml.
2. Take 25ml of the solution and add 2gm of Potassium Iodide crystals and 100ml of distilled water and then add 2ml glacial acetic acid.
3. Titrate it against standardized Sodium Thiosulafte solution with starch as indicator to get an end point of blue to colourless. Note down the ml of titrant used.

Tabulation:

Sl. No	Initial burette reading	Final burette reading	ml of $Na_2S_2O_3$ (0.1N) used	Available Chlorine in percent by weight

Calculations:

Available Chlorine, percentage by weight = $\frac{A \times N \times 35.46}{W}$

Where

A =Volume of Std. Sodium thiosulfate used

B= Normality of std. Sodium Thiosulfate solution

W= Weight in gms of sample taken for test

Reagents used:

1. **Standard Sodium Thiosulfate solution 0.1N**: Weigh 24.82 gms $Na_2S_2O_3.5H_2O$ in boiled and cooled distilled water and dilute to 1000m1.
2. **Starch Indicator**: Dissolve I gm starch in 10 ml cold water and pour with constant stirring into 200 ml of boiling water. Allow to settle and use clear supernatant liquid.

DETERMINATION OF TOTAL NITROGEN IN WATER & SEWAGE

The estimation of nitrogen in various forms is of great importance. In sewage and polluted waters most of the nitrogen is in the form of organic nitrogen and ammonia. As time progresses, the organic nitrogen is gradually converted to ammonia nitrogen and later on if aerobic conditions and nitrifying bacteria are present to nitrites and nitrates. Water with ammonia and organic nitrogen are considered to be polluted.

Reagents

i) Sodium hydroxide solution 12 (20)
ii) Standard Ammonium chloride solution (21)
iii) Nesslers reagent (22)
iv) Sulphuric acid
v) Phenolphthalein

Procedure

Take 500 ml sample of water or 50 ml sewage diluted to 100 ml in a distillation flask. Add 1.0 ml Copper sulphate solution and 100 ml cone. Sulphuric acid. Digest the mixture till solution becomes straw coloured. Cool and bring the volume to 250 ml. Add a few drops of Phenolphthalein and make it alkaline with sodium hydroxide solution. Distil the mixture and collect the distillate in a bottle. Measure the volume of distillate. Take a known volume of distillate in a Nessler's tubes, take known amount of ammonium chloride solution (0.1, 0.2, 0.3, 0.4, 0.5, 0.6 ml). Add 75 ml distilled water to each tube. Add 2.0 ml Nesslers reagent and water to make the volume to 100 ml. After 10 minutes, compare the colours of standard with sample and record the ml of NH_4Cl solution of the temporary standard matching with the sample.

$$\text{Total nitrogen mg/1 as N} = \frac{VD}{VD_n} \times \frac{\text{ml of } NH_4Cl \text{ in standard} \times 0.001 \times 1000}{S}$$

VD = Volume distilled
VD_n = Volume distilled nesslerised
S = Original sample distilled