

C H A P T E R - IIIANALYSIS OF WATERMINERAL ANALYSISa) TEMPERATURE :

Measurement of temperature is an important parameter required to get an idea of self purification of rivers, reservoirs and control of treatment plant. Water temperature is also important parameter for fish life. It is the important factor for calculating the solubility of oxygen and the carbon dioxide, bicarbonate and carbonate equilibrium. The temperature of drinking water has an influence on its taste.

APPARATUS :

A thermometer having a quick response, with  $0.1^{\circ}\text{C}$  division, checked against a precision thermometer.

PROCEDURE :

Immerse the thermometer directly in the water body for a period of time sufficient to permit constant reading. If it is not possible to take reading directly, then collect water in a sampling bottle, nearly one litre, and measure the temperature by dipping the thermometer in the sample. But while collecting the sample, it must not be exposed to heat or direct solar radiation. Tap water temperature should be measured in a bottle through which the water flows until a constant reading is reached.

Record temperature in celsius scale to the nearest given in Table I.

Table I.

| Water sample from<br>Shiroli | Water sample<br>from Panchaganga | Water sample from<br>Jayanti Nala |
|------------------------------|----------------------------------|-----------------------------------|
| Winter season                |                                  |                                   |
| 26°C                         | 26.5°C                           | 27°C                              |
| Summer season                |                                  |                                   |
| 27°C                         | 27.5°C                           | 28°C                              |
| Rainy season                 |                                  |                                   |
| 25°C                         | 25°C                             | 26°C                              |

b) pH :

For most practical purposes the pH of aqueous solutions can be taken as negative logarithm of hydrogen ion activity. pH values from 0 to 7 are diminishingly acidic, 7 to 14 increasingly alkaline and 7 is neutral.

The pH of natural water usually lies in the range of 4.4 to 8.5. Its value is governed largely by the carbon dioxide/bicarbonate/carbonate equilibrium. It may be affected by humic substances by changes in the carbonate equilibria due to the bioactivity of plants and in some cases by hydrolyzable salts. The effect of pH on the chemical and biological properties of liquids makes its determination very important. It is used in

several calculations in analytical work and its adjustment is necessary for some analytical procedures.

The determination of pH conventional chemical means is not practicable and the equilibria which are involved depend to some extent on temperature. The precise accepted scale of pH must therefore be based on an agreed primary standard. The colorimetric indicator methods can be used only if approximate pH values are required.

The pH determination is usually done by electrometric method which is the most accurate method and free of interference.

pH meter :

pH was measured in direct pH meter digital given in Table-II.

Table II

|                  | Water sample<br>from Shirol<br>pH | Water sample<br>from Panchaganga<br>pH | Water sample<br>from Jayanti nala<br>pH |
|------------------|-----------------------------------|----------------------------------------|-----------------------------------------|
| Winter<br>season | 7.96                              | 7.89                                   | 7.9                                     |
| Summer<br>season | 7.99                              | 7.98                                   | 7.92                                    |
| Rainy<br>season  | 7.95                              | 7.88                                   | 7.93                                    |

c) CONDUCTIVITY :

Conductivity is the capacity of water to carry an electrical current and varies both with number and types of ions the solution contains, which in turn is related to the concentration of ionized substances in the water. Most dissolved inorganic substances in water are in the ionised form and hence contribute to conductance.

Rough estimation of dissolved ionic contents of water sample can be done by multiplying specific conductance (in  $\mu$  siemens/cm) by an empirical factor which may vary from 0.55 to 0.9 depending on the soluble components of water and on the temperature of measurement. Conductivity measurement gives rapid and practical estimate of the variations in the dissolved mineral contents of a water supply.

Procedure :

Conductivity measurement is affected by :

1. The nature of the various ions, their relative concentration and the ionic strength of water,
2. Dissolved  $\text{CO}_2$ .
3. Turbidity.
4. Temperature (For precise work, the conductivity must be determined at  $25^\circ\text{C}$ ).

Conductivity was measured by conductivity instrument.

1. Adherent coating formation of the sample substances on the electrodes should be avoided which requires through washing of cell with distilled water at the end of each measurement.
2. Keep the electrode immersed in distilled water.
3. Organic material coating can be removed with alcohol or acetone followed by washing with distilled water.

Table III

Conductivity :

| Water from<br>Shiroli | Water from<br>Panchaganga | Water from<br>Jayantinala |
|-----------------------|---------------------------|---------------------------|
| $0.29 \times 10^{-2}$ | $0.28 \times 10^{-2}$     | $0.295 \times 10^{-2}$    |

TURBIDITY :

Suspension of particles in water interfering with passage of light is called turbidity.. Turbidity is caused by wide variety of suspended matter which range in size from colloidal to coarse dispersions depending upon the degree of turbulence and also ranges from pure inorganic substances to those that are highly organic in nature. Turbid waters are undesirable from

aesthetic point of view in drinking water supplies and may also affect products in industries. Turbid water also poses a number of problems in water treatment plants. Turbidity is measured to evaluate the performance of water treatment plants.

Principle : Turbidity can be measured either by its effect on the transmission of light which is termed as Turbidimetry or by its effect on the scattering of light which is termed as Nephelometry. Turbidimetry can be used for sample with moderate turbidity and nephelometer for samples with low turbidity. Higher the intensity of scattered light higher the turbidity.

Interferences : Colour is the main source of interference in the measurement of turbidity.

Apparatus : Turbidimeter or Klett Summerson.

Reagents :

1. Solution I : Dissolve 1.0 g Hydrazine sulfate and dilute to 100 ml.
2. Solution II : Dissolve 10.0 g hexamethylenetetramine and dilute to 100 ml.
3. Stock Turbidity Suspension : Mix 5 ml of solution I with 5 ml of solution II. Allow to stand for 24 hrs at  $25 \pm 2^\circ\text{C}$  and dilute to 100 ml. This solution III will have turbidity of 400 NTU.

4. Standard Turbidity Suspension : Dilute 10 ml of solution III as prepared above to 100 ml to have solution with turbidity of 40 NTU.

Procedure :

1. Prepare calibration curves in the range 0.400 unit by carrying out appropriate dilutions of solutions III and IV above and taking readings on turbidimeter.
2. Take sample or a suitably diluted aliquot and determine its turbidity either by visual comparison with the diluted standards or by reading on turbidimeter.
3. Read turbidity from the standard curves and apply correction due to dilution, if necessary.
4. Report the readings in turbidity unit to the nearest whole number.

Calculations : disk light penel  $\frac{A + B}{2}$

A = depth at s disk disappears

B = depth at s disk appears.

$$= 1) \frac{31 + 26}{2} = 28.5 \text{ s secchy disk light penetration.}$$

$$2) \frac{309 + 282}{2} = 295.5$$

## 3) Vertical attainual coefficient

$$\text{where } 1.9/s = \text{disk depth} = \frac{1.9}{28.5} = 0.06$$

Results - (1) Secchy disk transperancy 28.5, 295.5

(2) Vertical attainual coefficient 20.06

COLOUR :

When viewed by transmitted light through a depth of several feet, pure water exhibits a light blue colour which may be altered by the presence of organic matter to greenish blue, green, greenish yellow, yellow or brown. Colour is removed to make a water suitable for general and industrial applications. Coloured industrial wastewater may require colour removal before discharge in to water courses.

Colour used here is 'true colour', that is the colour of water from which turbidity has been removed. The term 'apparent colour' includes not only colour due to substances in solution but also that due to suspended matter. In some highly coloured industrial wastewaters, colour is contributed principally by colloidal or suspended material. In such cases both true colour and apparent colour should be determined.

The optimal method for removing turbidity without

removing colour has not been found yet. Filtration yields results that are reproducible from day to day and among laboratories. However some filtration methods may also remove some true colour. Results after centrifugation may vary with the sample nature and size and speed of the centrifuge when sample dilution is necessary, it can alter the measured colour, if large colour-bodies are present. While reporting results, the pretreatment adopted need to be mentioned.

The visual comparison method is applicable to nearly all samples of potable water. Pollution by certain industrial wastes may produce unusual colours that can not be matched. In such case an instrumental method is useful.

Table

|        | Water from<br>Shiroli | Water from<br>Panchaganga | Water from<br>Jayantinala |
|--------|-----------------------|---------------------------|---------------------------|
| Colour | Turbid<br>yellow      | Yellowish<br>white        | Yellow                    |

MINERAL ANALYSIS-IIACIDITY

Acidity of a liquid is its capacity to donate  $H^+$  ions. Since most of the natural waters and sewages are buffered by carbon dioxide - bicarbonate system, the acidity present due to free  $CO_2$  has no significance from public health view point. Waters containing mineral acidity (due to  $H_2SO_4$  and  $HCl$ ,  $HNO_3$ ) are unacceptable. Further, acid waters pose problem of corrosion and interfere in water softening.

Principle :

The mineral acids present and contributing mineral acidity can be calculated by titrating or neutralizing samples to pH 4.3. The  $CO_2$  and bicarbonates (carbonic acid) present in the sample can be neutralized completely by continuing the titration to pH 8.3.

Interferences :

Colour, turbidity, iron, aluminium and residual chlorine are prime sources of interference. Colour and turbidity can be avoided using potentiometric titrations. Residual chlorine can be removed by adding thiosulfate.

Reagents :

1. Standard sodium hydroxide 0.02 N : Dissolve 2.2 g NaOH

and dilute to 1000 ml using  $\text{CO}_2$  free distilled water. Store in air-tight, rubber stoppered pyrex/corning glass bottle to protect from atmospheric  $\text{CO}_2$ . Standardize against 0.02 N potassium biphthalate.

2. Phenolphthalein indicator : Dissolve 0.5 g in 500 ml 95% ethyl alcohol. Add 500 ml distilled water. Add dropwise 0.02 N NaOH till faint pink colour appears.

3. Methyl orange indicator : Dissolve 0.5 g and dilute to 1000 ml with  $\text{CO}_2$  free distilled water.

Procedure :

1. Measure suitable volume of sample (50 ml) in 250 ml conical flask or beaker depending upon the method to be followed.

2. Add 2 drops of methyl orange and titrate with standard 0.05 N NaOH till colour changes to faint orange characteristic of pH 4.4 - 4.3.

3. Note down the volume of NaOH required. 1.20 cc A

4. Add 2-3 drops phenolphthalein indicator and continue titration with NaOH till faint colour appears indicating pH 8.3.

5. Note down the volume of additional NaOH required 0. cc B

6. Calculate as follows :

1. Each ml of 0.05 N NaOH is = 1 mg  $\text{CaCO}_3$

Therefore, acidity mineral or due to  $\text{CO}_2$  as mg/l  $\text{CaCO}_3$  =

$$= \frac{1.2 \text{ ml } 0.05 \text{ N NaOH required} \times 1000 \times 50}{50 \text{ ml sample}}$$

$$= 60 \text{ mg/liter}$$

2. In case if normality of NaOH is other than 0.05 N calculate as follows :

3. Acidity mineral or due to  $\text{CO}_2$  as mg/l,  $\text{CaCO}_3$  =

$$= \frac{A/B \times N \times 50000}{\text{ml sample}}$$

$$= \frac{1.2 \times .05 \times 50,000}{50}$$

$$= 60 \text{ mg/litre.}$$

where :

A = 1.2 ml NaOH required for sample to raise pH upto 4.4 - 4.3.

B = 0. cc ml NaOH required for sample to raise pH from 4.4 to 8.3.

N = normality of NaOH used - 0.05 N.

## Burette Reading of Water sample

Table

| Water from Shirol<br>pool | Water from<br>Panchaganga | Water from<br>Nayantinala |
|---------------------------|---------------------------|---------------------------|
| Not acidic                | Not acidic                | Acidic<br>30 mg/litres.   |

ALKALINITY :

The alkalinity of a water is a measure of its capacity to neutralize acids. The alkalinity of natural waters is due to the salts of carbonates, bicarbonates, borates, silicates and phosphates along with the hydroxyl ions in the free state. However the major portion of the alkalinity in natural waters is caused by hydroxide, carbonate and bicarbonates which may be ranked in order of their association with high pH values. Alkalinity values provide guidance in applying proper doses of chemicals in water and waste water treatment processes, particularly in coagulation, softening and operational control of anaerobic digestion.

Principle

Alkalinity of sample can be estimated by titrating with

standard sulfuric acid. Titration to pH 8.3 or decolourization of phenolphthalein indicator will indicate complete neutralization of OH and 1/2 of  $\text{CO}_3$  while to pH 4.5 or sharp change from yellow to orange of methyl orange indicator will indicate total Alkalinity, (complete neutralization of OH,  $\text{CO}_3$ ,  $\text{HCO}_3$ ).

Inferences : As indicated in acidity estimation.

Reagents :

1. Standard  $\text{H}_2\text{SO}_4$  0.05 N : Prepare 0.1N  $\text{H}_2\text{SO}_4$  by diluting 7.5 ml conc.  $\text{H}_2\text{SO}_4$  to 1000 ml. standardize it against standard  $\text{Na}_2\text{CO}_3$  0.1 N. Dilute appropriate vol. of  $\text{H}_2\text{SO}_4$  (approx. 0.1) to 1000 ml to obtain standard 0.05 N  $\text{H}_2\text{SO}_4$ .
2. Phenolphthalein indicator : Dissolve 0.5 g in 500 ml 95% ethyl alcohol. Add 500 ml distilled water. Add dropwise 0.02 N NaOH till faint pink colour appears.
3. Methyl orange indicator : Dissolve 0.5 g and dilute to 1000 ml with  $\text{CO}_2$  free distilled water.

Procedure :

1. Take 50 ml sample in a conical flask and add 2-3 drops of phenolphthalein indicators.
2. If pink colour develops titrate with 0.02 N  $\text{H}_2\text{SO}_4$  till it appears or pH is 8.3 Note the vol. of  $\text{H}_2\text{SO}_4$  required. 0.4 cc.

3. Add 2-3 drops methyl orange to the same flask, and continue titration till pH comes down to 4.5 or yellow colour changes to orange.

Note the vol. of  $H_2SO_4$  added = 3.6 cc

4. In case pink colour does not appear after addition of phenolphthalein continue as in 3 above.
5. Calculate Total (T), phenolphthalein (P) and methyl orange alkalinity as follows and express in mg/l as  $CaCO_3$  :

P - Alkalinity, mg/l as  $CaCO_3$  = A X 1000/ml sample =

$$= P = \frac{0.4 \times 1000}{50} = 8.0$$

T - Alkalinity, mg/l as  $CaCO_3$  = B X 1000/ml sample =

$$= T = \frac{3.6 \times 1000}{50}$$

In case  $H_2SO_4$  is not 0.05 N apply the following formula:

$$\text{Alkalinity, mg/l as } CaCO_3 = \frac{A/B \times N \times 50000}{\text{ml of sample}} =$$

$$= \frac{.4/3.6 \times .05 \times 50,000}{50}$$

$$= 0.55 \text{ mg/ml}$$

where A = ml of  $H_2SO_4$  required to bring the pH to 8.3 = 0.4 ml

B = ml of  $H_2SO_4$  required to bring the pH to 4.5 = 3.6 ml

N = Normality of  $H_2SO_4$  used = 0.05

CHLORIDE :

Chloride anion is generally present in natural waters. The presence of chloride in natural waters can be attributed to dissolution of salt deposits, discharges of effluents from chemical industries, oil well operations, sewage discharges, irrigation drainage, contamination from refuse leachates, and seawater intrusion in coastal areas. Each of these sources may result in local contamination of both surface water and ground-water.

The salty taste produced by chloride depends on the chemical composition of the water. A concentration of 250 mg/L may be detectable in some waters containing sodium ions. On the other hand, the typical salty taste may be absent in water containing 1000 mg/L chloride when calcium and magnesium ions are predominant. A high chloride content also has a deleterious effect on metallic pipes and structures as well as on agricultural plants.

Three methods are suggested for the estimation of chloride (i) Involving titration against standard mercuric nitrate solution, (ii) An argentometric method, and (iii) A potentiometric method. The mercurimetric method is recommended when an accurate determination of chloride is required, particularly at low concentrations. The potentiometric method is suitable only

when the sample is coloured or turbid, argentometric method is the simplest one and can easily be carried out.

Principle : Chloride is determined in a natural or slightly alkaline solution by titration with standard silver nitrate, using potassium chromate as an indicator. Silver chloride is quantitatively precipitated before red silver chromate is formed.

Interferences : Bromide, iodide and cyanide are measured as equivalent of chloride ions.

If the sample contains sufficient thiosulfate, thiocyanate cyanide, sulfite and sulfide to interfere seriously with the determination, they may be oxidised to non-interfering substance as follows.

Measure a suitable quantity of sample into a conical flask and dilute to 150 ml with water. Add 25 ml  $\text{H}_2\text{O}_2$  (3%) and boil for 15 minutes, then add further 10 ml  $\text{H}_2\text{O}_2$  and boil for 5 minutes. Repeat the same until the solution is thiocyanate free.

If the sample is too coloured or turbid to allow the end point to be readily detected, this interference may be reduced by the following treatment with a suspension of aluminium hydroxide.

Add 3 ml Aluminium hydroxide suspension to the measured quantity of sample. Stir thoroughly, set aside for a few minutes and filter. Wash the precipitate with distilled

water. collect the washings with the filtrate and continue as described under procedure.

Reagents :

1. Potassium chromate indicator : Dissolve 50 g  $K_2CrO_4$  in distilled water. Add  $AgNO_3$  till definite red precipitate is formed. Allow to stand for 12 hrs. Filter and dilute to 1000 ml.

2. Silver nitrate 0.0141N : Dissolve 2.395 g  $AgNO_3$  and dilute to 1000 ml. Standardize against NaCl, 0.0141N.

1 ml of 0.0141N AgNo = 0.5 mg, cl

3. Sodium chloride 0.0141 N : Dissolve 824.1 mg NaCl (dried at  $140^\circ C$ ) and dilute to 1000 ml.

1 ml = 0.5 mg, cl.

4. Special reagent to remove colour and turbidity : Dissolve 125 g.  $AlK(SO_4)_2 \cdot 12H_2O$  or  $AlNH_4(SO_4)_2 \cdot 12H_2O$  and dilute to 1000 ml. Warm to  $60^\circ C$  and add 55 ml conc.  $NH_4OH$  slowly. Let stand for 1 hr. Transfer to a large bottle and wash PPT by successive addition with thorough mixing and decanting with distilled water until free from chloride when freshly prepared, a suspension occupies a Volume of approximately 1 L.

Procedure :

1. Take 100 ml sample and adjust the pH between 7.0 and 8.0.

2. Take 50 ml well mixed sample adjusted to pH 7.0-8.0 and add 1.0 ml  $K_2CrO_4$ .
3. Titrate with standard  $AgNO_3$  solution till  $AgCrO_4$  starts precipitating.
4. Standardize  $AgNO$  against std.  $NaCl$ .
5. For better accuracy titrate distilled water (50 ml) in the same way to establish reagent blank.
6. Calculate as follows :

$$I \quad \text{Chloride mg/L} = \frac{(A-B) \times N \times 35.45 \times 1000}{\text{ml sample}}$$

where A = ml  $AgNO$  required for sample

B = ,, ,, ,, , blank

N = Normality of  $AgNO_3$  used.

$$II \quad \text{Chloride mg/L} = \frac{1.8 \times 0.02 \times 35.45 \times 1000}{50}$$

$$= 25.5 \text{ mg/L}$$

| Results                 | Chloride content |
|-------------------------|------------------|
| Water from Shirol       | 25.5 mg/L        |
| Water from Panchaganga  | 25.00 mg/L       |
| Water from Jayanti nala | 26.00 mg/L       |

CALCIUM AND MAGNESIUM :

Calcium and Magnesium are common constituents of natural waters and important contributors to the hardness of water. The calcium and magnesium content may range from zero to several hundreds milligrams per litre, depending on source and treatment of water. These salts break down on heating to form harmful scale in boilers, pipes and cooking utensils. Small concentration of calcium carbonate combat corrosion of metallic pipes by laying down protective coating. Chemical softening treatment, reverse osmosis, electrodialysis or ion exchange is used to reduce and to maintain the levels of calcium and/or magnesium in water required for potable and industrial purposes.

In number of studies death rates from cardiovascular disease are inversely correlated with the hardness of water, but there is insufficient proof that either the calcium or magnesium in water is directly involved. In addition there is no firm evidence in man that drinking hard-water causes any ill effect, conversely there have been a number of studies where the results suggest that water hardness protects against disease.

These determinations are usually required for raw and potable water but not for grossly polluted rivers or sewages. However the determination is required sometimes for industrial wastes, where it is essential to destroy organic matter. This

can be done by evaporation and ignition or by treating the sample as described in preliminary treatment under metal analysis.

Calcium can be estimated by atomic absorption spectrophotometer, flame photometer, permanganate or EDTA titrimetric method and can also be calculated from calcium hardness data. The multiplying factor is 0.4 when hardness is expressed as  $\text{CaCO}_3$ . Magnesium can be estimated by atomic absorption spectrophotometric method and gravimetric method after removing calcium salts. However it is permissible in almost all cases to calculate the magnesium content from the difference between the total hardness in the same units. The appropriate factor to be used to convert the difference to magnesium is 0.244 if both total and Ca hardness are expressed as  $\text{CaCO}_3$ .

Most common method applicable for routine analysis, because of its simplicity and rapidity is E.D.T.A. titrimetric method, which is discussed in hardness.

#### Principle :

In alkaline condition, EDTA reacts with Ca and Mg to form a soluble chelated complex. Ca and Mg ions develop wine red colour with eriochrome black 'T' under alkaline condition. When EDTA is added as a titrant, Ca and Mg divalent ions get complexed resulting in a sharp change from wine red to blue

which indicates end-point of the titration. The pH for this titration has to be maintained at  $10.0 \pm 0.1$ . At a higher pH i.e. at about 12.0  $\text{Mg}^{++}$  ion precipitates and only  $\text{Ca}^{++}$  ion remains in solution. At this pH Murexide indicator forms a pink colour with  $\text{Ca}^{++}$ . When EDTA is added  $\text{Ca}^{++}$  gets complexed resulting in a change from pink to purple which indicates end point of the reaction.

Interferences : Metal ions do interfere but can be overcome by addition of inhibitors.

#### Reagents

1. Buffer solution : Dissolve 16.9 g  $\text{NH}_4\text{Cl}$  in 143 ml  $\text{NH}_4\text{OH}$ . Add 1.25 g magnesium salt of EDTA to obtain sharp change in colour of indicator and dilute to 250 ml. If magnesium salt of EDTA is unavailable, dissolve 1.179 g disodium salt of EDTA (AR grade) and 780 mg  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  or 644 mg  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in 50 ml distilled water. Add to above solution of  $\text{NH}_4\text{Cl}$  in  $\text{NH}_4\text{OH}$  and dilute to 250 ml.
2. Inhibitor : Dissolve 4.5 g hydroxyl amine hydrochloride in 100 ml 95% ethyl alcohol or isopropyl alcohol.
3. Eriochrome black T indicator : Mix 0.5 g dye with 100g NaCl to prepare dry powder.
4. Murexide Indicator : Prepare a ground mixture of 200 mg of murexide with 100 g of solid NaCl.

5. Sodium hydroxide 2N : Dissolve 80 g NaOH and dilute to 1000 ml.
6. Standard EDTA solution 0.01 M : Dissolve 3.723 g EDTA sodium salt and dilute to 1000 ml. Standardize against standard Ca solution, 1 ml = 1 mg  $\text{CaCO}_3$ .
7. Standard calcium solution : Weigh accurately 1.0 g AR grade  $\text{CaCO}_3$  and transfer to 250 ml conical flask. Place a funnel in the neck of a flask and add 1 + 1 HCl till  $\text{CaCO}_3$  dissolves completely. Add 200 ml distilled water and boil for 20-30 min. to expel  $\text{CO}_2$ . Cool and add few drops of methyl red indicator. Add  $\text{NH}_4\text{OH}$  3N dropwise till intermediate orange colour develops. Dilute to 1000 ml to obtain 1 ml = 1 mg  $\text{CaCO}_3$ .

Procedure :

A) Total Hardness

1. Take 25 or 50 ml well mixed sample in porcelain dish or conical flask.
2. Add 1-2 ml buffer solution followed by 1 ml inhibitor.
3. Add a pinch of Eriochrome black T and titrate with standard EDTA (0.01 M) till wine red colour changes to blue. Note down the Vol. of EDTA required. (A).
4. Run a reagent blank. Note the vol. of EDTA (B).

5. Calculate vol. of EDTA required by sample,

$C = (A - B)$  from vol, of EDTA required in steps 3 & 4.

6. Calculate as follows :

Total hardness

$$\text{as CaCO}_3 \quad \text{mg/L} = \frac{\text{B.R.} \times 1000}{\text{ml sample}} = \frac{\text{B.R.} \times 1000}{50} =$$

$$= 3.2 \text{ ml} = \frac{3.2 \times 1000}{50}$$

$$= 64 \text{ mg/L}$$

where  $C = \text{Vol, of EDTA required by sample.}$

$D = \text{mg CaCO}_3 \text{ equivalent to 1.0 ml EDTA titrant.}$

#### B. Calcium Hardness

1. Take 25 or 50 ml sample in a porcelain dish.
2. Add 1 ml NaOH to raise pH to 12.0 and a pinch of murexide indicator.
3. Titrate immediately with EDTA till pink colour changes to purple. Note the vol, of EDTA required ( $A'$ ).
4. Run a reagent blank. Note the ml of EDTA required and keep it aside to compare end points of sample titrations.
5. Standardize the EDTA (0.1 m) solution following the procedure of calcium hardness from 1 to 4. using standard calcium solution.

6. Calculate as follows :

$$\begin{aligned}
 \text{Calcium hardness} & \quad \text{mg/L} = \frac{A' \times D \times 1000}{\text{ml sample}} \\
 \text{as CaCO}_3 & \\
 & = \frac{B.R. \times 1000 \times 1.05}{50} \\
 & = \frac{2.8 \times 1000 \times 1.05}{50} \\
 & = 58.6 \text{ mg/L}
 \end{aligned}$$

where A' = Vol. of EDTA used by sample

D = mg CaCO<sub>3</sub> equivalent to 1.0 ml EDTA titrat

C. Magnesium Hardness :

$$\begin{array}{rcl}
 \text{Magnesium Hardness} & = & \text{Total hardness} - \text{Ca hardness} \\
 \text{as CaCO}_3 & & \text{as CaCO}_3 \quad \quad \text{as CaCO}_3
 \end{array}$$

D. Alkaline (Carbonate) Hardness and Non Alkaline (Non-Carbonate) Hardness.

These types of hardness can be calculated from total hardness and total alkalinity as follows.

If total hardness > Total alkalinity  
           as CaCO<sub>3</sub>                      as CaCO<sub>3</sub>

Then

1. Alkaline Hardness = Total alkalinity
2. Non alkaline Hardness = Total hardness -  
total alkalinity  
= (64-58.6) X 0.244  
= 1.3176

|    |                    |                    |
|----|--------------------|--------------------|
| II | If total hardness  | Total alkalinity   |
|    | as $\text{CaCO}_3$ | as $\text{CaCO}_3$ |

Then,

- I. Alkaline hardness = Total hardness
- II. Nonalkaline hardness = Nil.

#### Table

#### Results

|                            | Water from<br>Shiroli | Water from<br>Panchaganga | Water from<br>Jayantinala |
|----------------------------|-----------------------|---------------------------|---------------------------|
| Hardness due to<br>Calcium | 58.6 mg/L             | 56.5 mg/L                 | 65.5 mg/L                 |
| Total hardness             | 64.0 mg/L             | 65.0 mg/L                 | 70.0 mg/L                 |
| Non-alkaline hardness      | 1.317 mg/L            | 1.320 mg/L                | 1.350 mg/L                |

DEMAND ANALYSISDISSOLVED OXYGEN

All living organisms are dependent upon oxygen in one form or the other to maintain the metabolic processes that produce energy for growth and reproduction. Aerobic processes are the subject of great interest for their need for free oxygen. Dissolved Oxygen (DO) is also important in precipitation and dissolution of inorganic substances in water.

The solubility of atmospheric oxygen in fresh water ranges from 14.6 mg/L at 0°C to about 7.0 mg/L at 35°C under one atmospheric pressure. Since it is poorly soluble gas its solubility directly varies with the atmospheric pressure at any given temperature.

Analysis of DO is a key test in sanitary engineering practice. The following illustrations reveal importance of DO as a parameter :

1. It is necessary to know DO levels to assess quality of raw water and to keep a check on stream pollution.
2. In liquid waste dissolved oxygen is the factor that determines whether the biological changes are brought out by aerobic or anaerobic organisms.
3. DO test is the basis of BOD test which is an important parameter to evaluate pollution potential of wastes.

4. DO is necessary for all aerobic biological wastewater treatment processes.

5. Oxygen is an important factor in corrosion. DO test is used to control amount of oxygen in boiler feed waters either by chemical or physical methods.

6. DO is necessary for all aerobic biological wastewater treatment processes.

#### 1. THE WINKLER METHOD WITH AZIDE MODIFICATION

##### Principle :

Oxygen present in sample rapidly oxidizes the dispersed divalent managanous hydroxide to its higher valency which precipitates as a brown hydrated oxide after addition of NaOH and KI. Upon acidification, manganese reverts to divalent state and liberates iodine from KI equivalent to the original DO content. The liberated iodine is titrated against  $\text{Na}_2\text{S}_2\text{O}_3$  (N/80) using starch and an indicator.

##### Interferences :

Ferrous ion, ferric ion, nitrite, microbialmass and high suspended solids constitute the main sources of interference. Modifications in the estimation procedure to reduce these interferences are described in the procedure.

### Apparatus

1. BOD bottles capacity 300 ml.
2. Sampling device for collection of samples.

### Reagents

1. Manganese sulphate : Dissolve 480 g  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ , 400 g  $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$  or 364 g  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  and dilute to 1000 ml. Filter if necessary. This solution should not give colour with starch when added to an acidified solution of KI.
2. Alkali iodide-azide reagent : Dissolve 500 g NaOH (or 700 g KOH) and 150 g KI or 135 g. NI dilute to 1000 ml. Add 10 g  $\text{NaN}_3$  dissolved in 40 ml distilled water. This solution should not give colour with starch solution when diluted and acidified.
3. Sulphuric acid :  $\text{H}_2\text{SO}_4$ , Conc. 1 ml is equivalent to about 3 ml alkali-iodide - azide reagent.
4. Starch indicator : Prepare paste or solution of 2.0 g L.R. grade soluble starch powder and 0.2 salicylic acid as preservative in distilled water. Pour this solution in 100 ml boiling water. Allow to boil for few minutes, cool and then use.
5. Stock sodium thiosulphate 0.1 N : Dissolve 24.82 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in boiled distilled water, preserve by adding 0.4 g solid NaOH or 1.5 ml 6 n NaOH and dilute to 1000 ml.

6. Standard sodium thiosulphate 0.025 N : Dilute 250 ml stock  $\text{Na}_2\text{S}_2\text{O}_3$  solution to 1000 ml with freshly boiled and cooled distilled water. Add preservative before making up the volume. (This solution will have to be standardized against standard of dichromate solution for each set of titrations).

Procedure :

1. Collect sample in a BOD bottle using DO sampler.
2. Add 2 ml  $\text{MnSO}_4$  followed by 2 ml of alkali-iodide-azide reagent. The tip of the pipette should be below the liquid level adding these reagents. Stopper immediately.
3. Mix well by inverting the bottle 2-3 times and allow the precipitate to settle leaving 150 ml clear supernatant.
4. At this stage, add 2 ml conc.  $\text{H}_2\text{SO}_4$ . Mix well till precipitate goes into solution.
5. Take 203 ml in a conical flask and titrate against  $\text{Na}_2\text{S}_2\text{O}_3$  using starch as an indicator. When 2 ml  $\text{MnSO}_4$  followed by 2 ml alkali-iodideazide reagent is added to the samples as in (2) above 4.0 ml of original sample is lost. This 203 ml taken for titration will correspond to 200 ml of original sample.

Calculations

$$\text{DO (mg/liter)} = \frac{\text{ml of titrant} \times \text{Normality} \times 8 \times 1000}{V_2 \left( \frac{V_2 - V}{V_1} \right)}$$

where  $V_1$  = vol. of sample

$V_2$  = vol. of sample titrated

$V$  = vol of  $\text{MnSO}$  and  $\text{KI}$  added

Reading : (a) 2.4 cc

mean .. 2.4 cc

(b) = 1.2 cc with water

$$\begin{aligned} (1) \quad \text{DO} &= \frac{\text{ml. of titrant} \times N \times 8 \times 1000}{V_2 \left( \frac{V_2 - V}{V_2} \right)} \\ &= \frac{2.4 \times 0.025 \times 8 \times 1000}{50 \left( \frac{300 - 4}{300} \right)} \\ &= \frac{480}{49.3333} \\ &= 9.7297 \text{ mg/lit.} \end{aligned}$$

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$$(2) \quad DO = \frac{1.2 \times 0.025 \times 8 \times 1000}{\left( \frac{300 - 4}{300} \right)}$$

$$= \frac{240}{49.3333}$$

$$= 4.8648 \text{ mg/Liter.}$$

### Results

(1) Water from Shirolī = 9.7297 mg/L

(2) Water from Panchaganga = 4.8048 mg/L

(3) Water from Jayantinala = 5.755 mg/L.