10.0 EXPERIMENT ON DETERMINATION OF DISSOLVED OXYGEN

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PREAMBLE:

"**How to determine dissolved oxygen in Water and Wastewater**".

Test procedure is in accordance to IS: 3025 (Part 38) - Reaffirmed 2003.

In addition to our Indian Standard, we also discuss in brief regarding the procedure stated in

(1) APHA Standard Methods for the Examination of Water and Wastewater - 20th Edition. Method 4500-O G.
(2) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Method 360.1.

10.1 AIM

To determine dissolved oxygen (DO) in the given water sample with the stipulations as per **IS: 3025 (Part 38) - Reaffirmed 2003.**

10.2 INTRODUCTION

Before performing this experiment, few questions may arise to the learners:

1. What is meant by Dissolved Oxygen (DO)? Is it oxygen in dissolved form?
2. Why we need to determine DO?
3. What are the methods available to determine DO?
4. Is it measured in natural water or wastewater?
5. Whether is it mandatory as per our codal provision to determine DO?

The term Dissolved Oxygen is used to describe the amount of oxygen dissolved in a unit volume of water. Dissolved oxygen (DO) is essential for the maintenance of healthy lakes and rivers. It is a measure of the ability of water to sustain aquatic life.

The dissolved oxygen content of water is influenced by the source, raw water temperature, treatment and chemical or biological processes taking place in the distribution system.

The presence of oxygen in water is a good sign. Depletion of dissolved oxygen in water supplies can encourage the microbial reduction of nitrate to nitrite and sulfate to sulfide. It can also cause an increase in the concentration of ferrous iron in solution, with subsequent discoloration at the tap when the water is aerated.

Hence, analysis of dissolved oxygen is an important step in water pollution control and wastewater treatment process control. There are various methods available to measure Dissolved Oxygen, which we will discuss in detail.

In a healthy body of water such as a lake, river, or stream, the dissolved oxygen is about 8 parts per million. The minimum DO level of 4 to 5 mg/L or ppm is desirable for survival of aquatic life.

Now imagine that a source of oxygen demanding wastes, such as feed lot, a paper mill or a food processing plant, is built besides the river. The facility begins operating and discharging wastes into the river.

This increases the BOD and affects the concentration of DO in the waters downstream.

The wastes serve as the food for certain aerobic bacteria. as it moves downstream, the conc. of bacteria increases. Because these bacteria remove oxygen from water, their population increase causes a decline in the amount of DO.

Beyond certain point, most of the wastes break down. The conc. of DO rises as the river recovers oxygen from the atmosphere and aquatic plants.
Thus DO test is the basis for BOD test which is an important parameter to evaluate organic pollution potential of a waste.

It is necessary for all aerobic biological wastewater treatment processes to control the rate of aeration.

10.2.1 ENVIRONMENTAL SIGNIFICANCE

Drinking water should be rich in dissolved oxygen for good taste.

DO test is used to evaluate the pollution strength of domestic and industrial waste.

Higher values of DO may cause corrosion of Iron and Steel.

Algae growth in water may release oxygen during its photosynthesis and DO may even shoot upto 30 mg/L.

Oxygen is poorly soluble in water. Its solubility is about 14.6 for pure water at 0°C under normal atmospheric pressure and it drops to 7 mg/l at 35°C.

Higher temperature, biological impurities, Ammonia, Nitrates, ferrous iron, chemicals such as hydrogen sulphide and organic matter reduce DO values.

Aerobic bacteria thrive when oxygen is available in plenty. Aerobic conditions do prevail when sufficient DO is available within water. End products of aerobiosis are stable and are not foul smelling.

It is necessary to know DO levels to assess quality of raw water and to keep a check on stream pollution.

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DO test is necessary for all aerobic biological wastewater treatment processes to control the rate of aeration.

10.3 PRINCIPLE

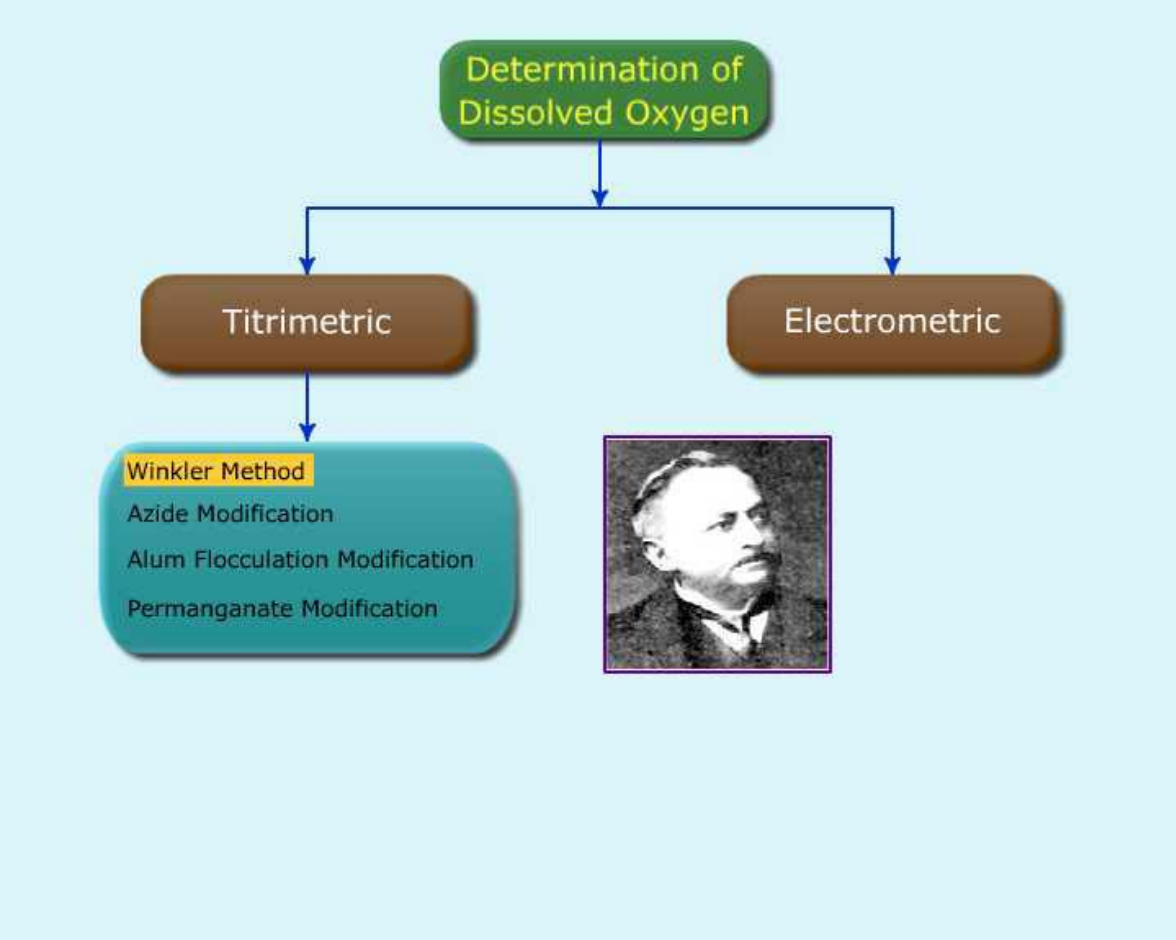
Dissolved Oxygen can be measured either by titrimetric or electrometric method.

(1) Titrimetric Method

Titrimetric method is based on the oxidizing property of DO while the electrometric method (using membrane electrodes) is based on the rate of diffusion of molecular oxygen across a membrane. It is most accurate method to determine DO.

There are different titrimetric methods based on the nature of sample to be tested.

(a) Winkler Method
(b) Azide Modification
(c) Alum Flocculation Modification
(d) Permanganate Modification



However, in all the above the basic principle remains same.

Choice of the method depends upon the type of sample to be tested

Azide Modification:

In this method, interference caused by nitrate is removed effectively. Presence of nitrate is most interference in biologically treated effluent and incubated BOD samples.

Alum Flocculation Modification:

If the sample contains suspended solids (especially effluent samples), then this method will be suitable.

Permanganate Modification:

If the sample contains iron (Fe^{2+}) ions. Addition of 1mL of potassium fluoride and azide solution can be adopted to suppress the interference due to (Fe^{3+}).

This method is not useful when the sample contains sulphites, thiosulphates and high BOD.

The Titrimetric principle:

Divalent Manganese salt in solution is precipitated by strong alkali to divalent manganese hydroxide.

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

Addition of Potassium iodide or Potassium hydroxide is added to create a pinkish brown precipitate.

In the alkaline solution, dissolved oxygen present in the sample rapidly oxidized to form trivalent or higher valency hydroxide.

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

$MnO(OH)_2$ appears as a brown precipitate. There is some confusion about whether the oxidised manganese is tetravalent or trivalent. Some sources claim that $Mn(OH)_3$ is the brown precipitate, but hydrated MnO_2 may also give the brown colour.

Iodide ions are added and acidified (acid facilitates the conversion by the brown), which reduces tetravalent hydroxides back to their stable divalent state thereby liberating equivalent amount of iodine.

$$Mn(OH)_2 + 2\,KI + H_2O \rightarrow Mn(OH)_2 + I_2 + 2KOH$$

Thiosulphate solution is used, with a starch indicator, to titrate the iodine.

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

This iodine is equivalent to dissolved oxygen present in the sample.

(2) Electrometric Method

The electrode method offers several advantages over the titrimetric method including speed, elimination or minimization of interferences, field compatibility, continuous monitoring and insitu measurement.

Dissolved oxygen can be measured by a special sensor kept in an electrochemical cell by the amperometric method.

The cell comprises a sensing electrode, a reference electrode and a supporting electrolyte, a semi-permeable membrane, which served dual function.

It separates the water sample from the electrolyte, and at the same time, permits only the dissolved oxygen to diffuse from the water sample through the membrane into the supporting electrolyte.

The diffusion current created by migration of oxygen through a permeable membrane is linearly proportional to the concentration of molecular oxygen in the sample.

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The sample is treated with manganous sulphate, alkaline-iodide-azide reagent and finally sulfuric acid. The first two chemicals combine with dissolved oxygen to form a compound which, when acid is added, releases free iodine (from the potassium iodide).

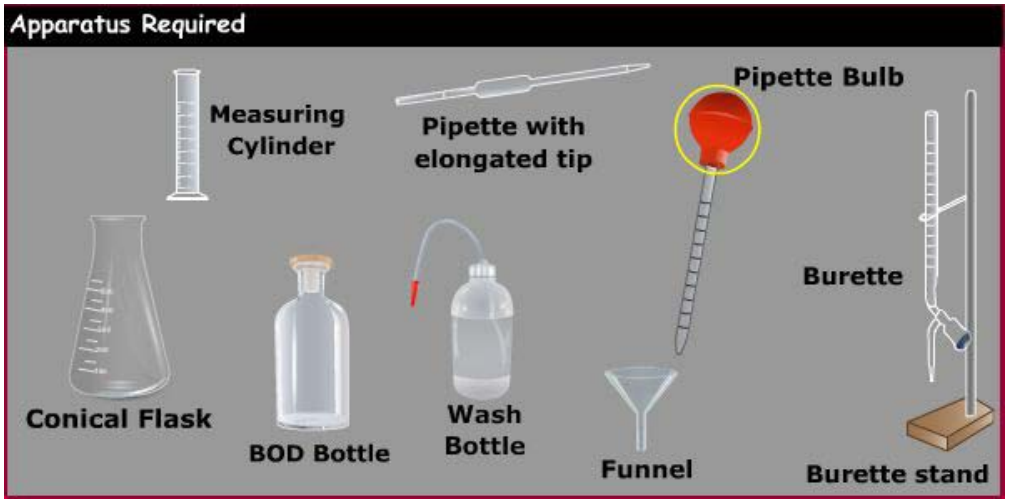
10.4 MATERIALS REQUIRED

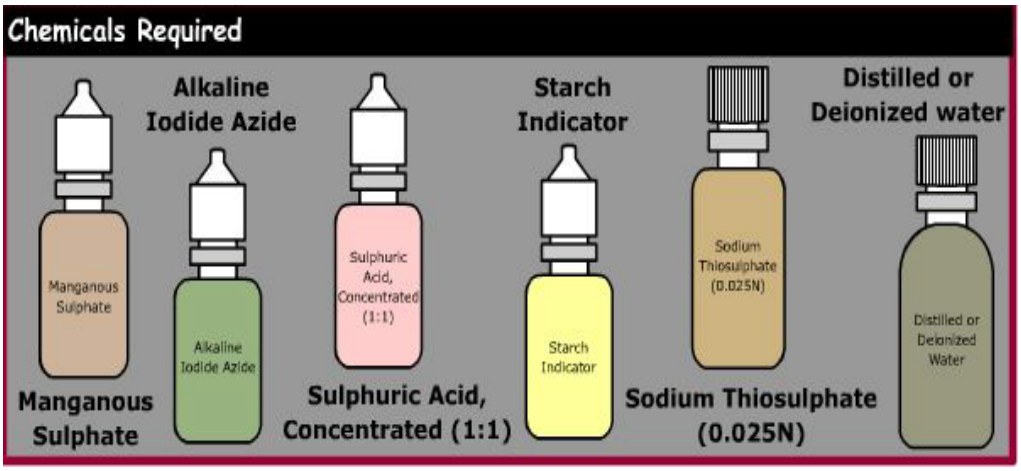
10.4.1 APPARATUS REQUIRED

1. Burette
2. Burette stand
3. 300 mL glass stoppered BOD bottles
4. 500 mL conical flask
5. Pipettes with elongated tips
6. Pipette bulb
7. 250 mL graduated cylinders
8. Wash bottle

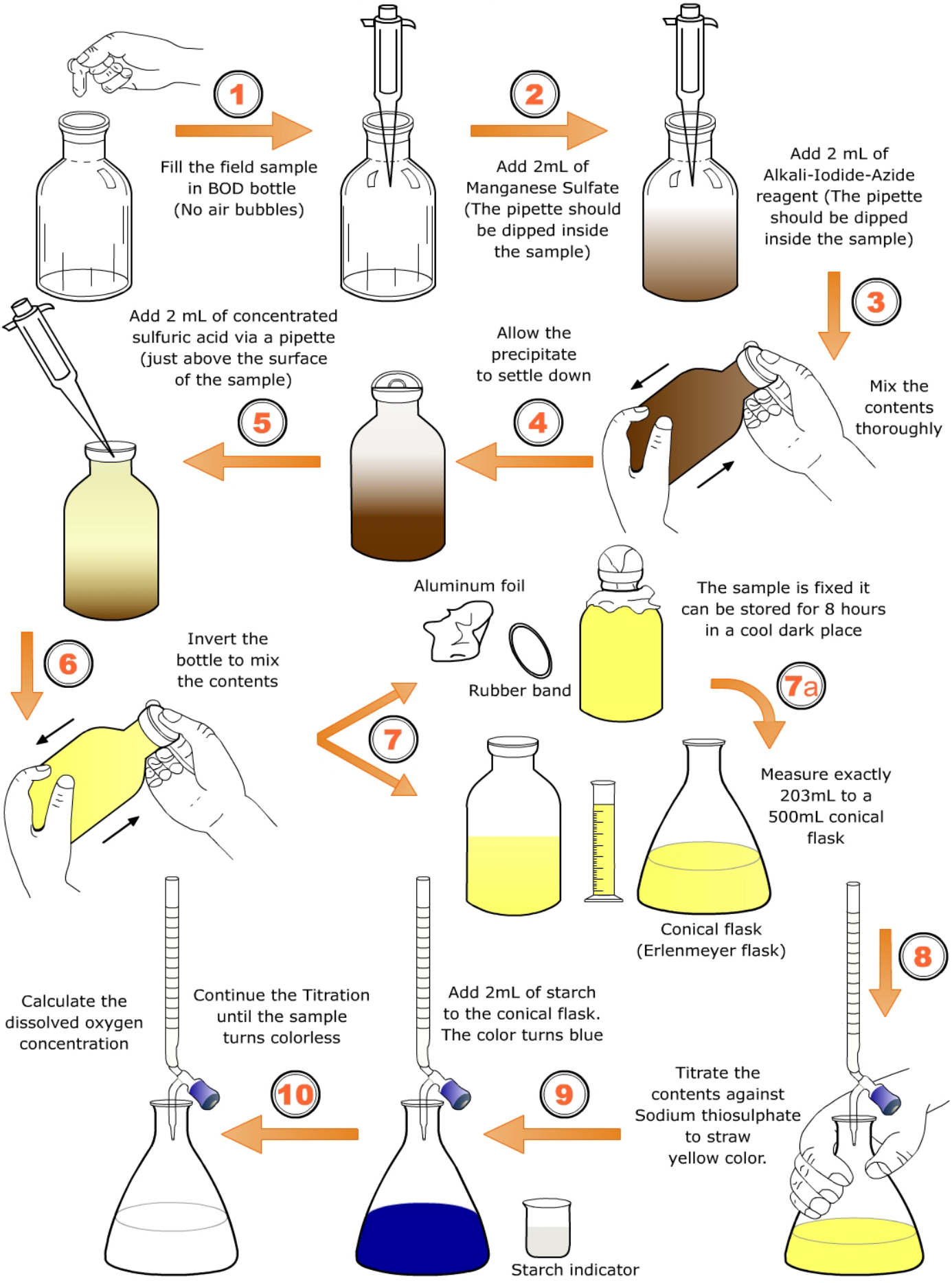
10.4.2 CHEMICALS REQUIRED

1. Manganous sulphate solution
2. Alkaline iodide-azide solution
3. Sulfuric acid, Concentrated
4. Starch indicator solution
5. Sodium thiosulphate
6. Distilled or deionized water
7. Potassium Hydroxide
8. Potassium Iodide
9. Sodium Azide


Apparatus Required
Measuring Cylinder
Pipette with elongated tip
Pipette Bulb
Conical Flask
BOD Bottle
Wash Bottle
Funnel
Burette
Burette stand


Chemicals Required
Manganous Sulphate
Alkaline Iodide Azide
Sulphuric Acid, Concentrated (1:1)
Starch Indicator
Sodium Thiosulphate (0.025N)
Distilled or Deionized water
Manganous Sulphate
Alkaline Iodide Azide
Sulphuric Acid, Concentrated (1:1)
Starch Indicator
Sodium Thiosulphate (0.025N)
Distilled or Deionized Water

PROCEDURE CHART



10.5 SAMPLE HANDLING AND PRESERVATION

Preservation of sample is not practical. Because biological activity will continue after a sample has been taken, changes may occur during handling and storage.

If analysis is to be carried out with in two hours of collection, cool storage is not necessary. If analysis can not be started with in the two hours of sample collection to reduce the change in sample, keep all sample at 4° C.

Do not allow samples to freeze. Analysis should begin as shown as possible. Do not open sample bottle before analysis.

Begin analysis within six hours of sample collection.

10.5.1 PRECAUTIONS

The experiment involves lot of solutions and additions of strong acid and alkali and hence care should be taken.

- Dissolved oxygen concentrations may change drastically depending upon depth, distance, temperature and period of sampling.
- If the sample was obtained by a sampling device of some kind, the water cannot be simply poured into a BOD bottle, since this would cause aeration of the sample. Instead, the sample must be drawn off from a tube located near the bottom of the sampling device. Place the rubber tube into the bottom of the BOD bottle and fill the bottle, again allowing the bottle to overflow.
- For shallow depth use normal water samplers. However for depth greater than 150 cm (5 ft), use Kemmerer Sample Bottles.

In the case of electrode method:

- Membrane-covered electrode systems minimize the interferences often encountered with dropping mercury or rotating platinum electrodes.
- The sensing element is protected by an oxygen permeable membrane, which serves as a diffusion barrier against matrix interference problems.

10.6 PROCEDURE:

For testing the given sample, first the reagents are required to be prepared.

10.6.1 PREPARATION OF REAGENTS

a) Manganous Sulphate Solution

Dissolve Manganese Sulphate

→ 480g of $MnSO_4.4H_2O$ (or)

→ 400g of $MnSO_4.2H_2O$ (or)

→ 364 g of $MnSO_4.H_2O$

in freshly boiled and cooled distilled water, filter the solution and make up to 1000 mL (One litre). In this experiment, we are using Manganese sulphate Mono hydrate,

Take 364 g Manganese sulphate Mono hydrate ($MnSO_4.H_2O$) and transfer it to the beaker. To dissolve the content, place it in the magnetic stirrer.

The solution should not give blue color by addition of acidified potassium iodide solution and starch.

b) Alkaline Iodide Sodium Azide Solution

To prepare this reagent we are going to mix three different chemicals

Dissolve either

→ 500 g of Sodium Hydroxide (or)

→ 700 g of Potassium Hydroxide and

→ 135 g of Sodium Iodide (or)

→ 150 g of Potassium Iodide

To prepare this reagent, take 700 g of Potassium hydroxide and add 150 g of potassium iodide and dissolve it in freshly boiled and cooled water, and make up to 1000 mL (One litre).

Dissolve 10 g of Sodium Azide (NaN_3) in 40 mL of distilled water and add this with constant stirring to the cool alkaline iodide solution prepared.

c) Sodium Thiosulphate Stock Solution

Weigh approximately 25 g of sodium thiosulphate $(Na_2S_2O_35H_2O)$ and dissolve it in boiled distilled water and make up to 1000 mL. Add 1 g of Sodium Hydroxide to preserve it.

d) Starch Indicator

Weigh 2 g of starch and dissolve in 100 mL of hot distilled water. In case if you are going to preserve the starch indicator add 0.2 g of salicylic acid as preservative.

e) Sulphuric Acid

10.6.2 TESTING OF SAMPLE

- Take two 300-mL glass stoppered BOD bottle and fill it with sample to be tested. Avoid any kind of bubbling and trapping of air bubbles. Remember – no bubbles!

(Or)

- Take the sample collected from the field. It should be collected in BOD bottle filled upto the rim.
- Add 2mL of manganese sulfate to the BOD bottle by inserting the calibrated pipette just below the surface of the liquid.
- Add 2 mL of alkali-iodide-azide reagent in the same manner.
- Squeeze the pipette slowly so no bubbles are introduced via the pipette (The pipette should be dipped inside the sample while adding the above two reagents. If the reagent is added above the sample surface, you will introduce oxygen into the sample).
- If oxygen is present, a brownish-orange cloud of precipitate or floc will appear.
- Allow it to settle for sufficient time in order to react completely with oxygen.
- Add 2 mL of concentrated sulfuric acid via a pipette held just above the surface of the sample.
- Carefully stopper and invert several times to dissolve the floc.
- At this point, the sample is "fixed" and can be stored for up to 8 hours if kept in a cool, dark place.
- Rinse the burette with sodium thiosulphate and then fill it with sodium thiosulphate. Fix the burette to the stand.
- Measure out 203 mL of the solution from the bottle and transfer to an conical flask.
- Titration needs to be started immediately after the transfer of the contents to conical flask.
- Titrate it against sodium thiosulphate using starch as indicator. (Add 3 - 4 drops of starch indicator solution)
- End point of the titration is first disappearance of the blue color to colorless.
- Note down the volume of sodium thiosulphate solution added which gives the dissolved oxygen in 7.9 mL
- Repeat the titration for concordant values.

10.7 CALCULATION

For determining the Dissolved Oxygen (DO) in the given water sample, the readings are required to be tabulated.

10.7.1 TABLE

Trial No.	Temperature (ºC)	Volume of Sample (mL)	Burette Reading (mL)		Volume of Titrant (mL)	Dissolved Oxygen (mg/L)
			Initial	Final		
1.						
2.						
3.						

Burette Solution: Sodium Thiosulphate

Pipette Solution: Sample

Indicator: Starch

End point : Disappearance of blue color

- For the calculation of DO the temperature at the time of measurement is 20º C and the volume of sample taken is 200 mL.
- sodium thiosulphate is taken in the burette
- For the first titration the Initial reading is 0 mL and the final reading is 7.8. The volume of sodium thiosulphate consumed to get the end point is 7.8 mL.
- For the second titration the Initial reading is 0 mL and the final reading is 7.9. The volume of sodium thiosulphate consumed to get the end point is 7.9 mL.
- For the third titration the Initial reading is 0 mL and the final reading is 7.9. The volume of sodium thiosulphate consumed to get the end point is 7.9 mL.
- For the second and third titration, we have achieved concordant value. So we can go for the calculations.

10.7.2 DATA SHEET

DETERMINATION OF DISSOLVED OXYGEN
DATA SHEET

Date Tested : August 30, 2010

Tested By : CEM OTC Class, Group A

Project Name : CEM, NITTTR Lab

Sample Number : BH1

Sample Location : Perungudi (Lat 12' 57'' 31.74 & Long 80'14'' 8.82)

Sample Description : Surface water

Trial No.	Temperature (°C)	Volume of Sample (mL)	Burette Reading (mL)		Volume of Titrant (mL)	Dissolved Oxygen (mg/L)
			Initial	Final		
1.	20.0	200	0	7.8	7.8	7.8
2.	20.0	200	0	7.9	7.9	7.9
3.	20.0	200	0	7.9	7.9	7.9

Model Calculation:

Volume of Sodium thiosulphate V_1 = 7.9 mL
Normality of Sodium thiosulphate N_1 = 0.025 N
Volume of Sample V_2 = 203.0 mL

$$Dissolved\ Oxygen = \frac{Volume\ of\ Sodium\ Thiosulphate * 0.2 * 1000}{Volume\ of\ Sample\ taken}$$

$$solved\ Oxygen = \frac{7.9*0.2*1000}{200} \quad = 7.9\ mg/L$$

When a 200 mL sample is used, 1 mL of sodium thiosulphate solution (0.025 M) is equivalent to 1 mg/L Dissolved Oxygen in the sample.

(If 7.9 mL of sodium thiosulphate was used, then the DO of the sample is 7.9 mg/L).

10.8 INTERPRETATION OF RESULTS

The Dissolved Oxygen in the given sample of water at 27ºC = **7.9 mg/L.**

10.9 INFERENCE

Dissolved oxygen of the tested sample is 7.9 mg/L. Test results shows the water is in healthy condition and fit for aquatic life. IS code does not mentioned minimum standards for DO. However, for healthy water body, the dissolved oxygen is about 8 parts per million.

10.10 EVALUATION

1. Winkler titration method is based on _____ property of Dissolved Oxygen.

    a) Reduction
    b) Oxidation
    c) Redox
    d) Decomposition

2. Dissolved oxygen in the water mainly depends upon Organic content of the water.

    a) True
    b) False

3. The ingredients of Alkali are NaOH, NaI

    a) NaN_4
    b) NaN_3
    c) NaN_2
    d) NaN

4. The precipitate formed after the addition of MnSO4 and Alkali azide is _____.

    a) Manganese Hydroxide
    b) Sodium sulphate
    c) Potassium sulphate
    d) Manganese oxide

5. Dissolved Oxygen depends only on Physical Properties of the water.

    a) True
    b) False

6. Along the stream the increase in dissolved oxygen in water will be at the

a) riffles
b) warm pool
c) bank erosion
d) top

7. The dissolved Oxygen in potable water_____.

a) imparts freshness
b) improves taste
c) improves smell
d) imparts colour

8. Sulphide and Sulphur dioxide interfere in the determination of dissolved oxygen.

a) True
b) False

9. The sample obtained for testing Dissolved Oxygen can be preserved by

a) adding the reagents and stored at 10 to 20 for up to 8 hours
b) storing at room temperature for up to 24 hours
c) storing at 0 for up to 24 hours
d) adding the reagents and stored at room temperature for up to 24 hours

10. Minimum DO in the fresh water for the survival of aquatic life is

a) 0 mg/l
b) 2 mg/l
c) 8 mg/l
d) 4 mg/l

KEY TO ITEMS:

1) b
2) True
3) b
4) a
5) False
6) a
7) a
8) a
9) a
10) d