

# COMENIUS BILATERAL PARTENARIATE 2012/2014

WATER POLLUTION IN URBAN AREAS:

ANALYSIS AND TREATMENT

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## DETERMINATION OF DISSOLVED OXYGEN DO



<b>PREAMBLE:</b> .....	<b>3</b>
<b>1 AIM</b> .....	<b>3</b>
<b>2 INTRODUCTION</b> .....	<b>3</b>
<b>2.1 ENVIRONMENTAL SIGNIFICANCE</b> .....	<b>4</b>
<b>3 PRINCIPLE</b> .....	<b>4</b>
<b>4 MATERIALS REQUIRED</b> .....	<b>6</b>
<b>4.1 APPARATUS REQUIRED</b> .....	<b>6</b>
<b>4.2 CHEMICALS REQUIRED</b> .....	<b>6</b>
<b>5 SAMPLE HANDLING AND PRESERVATION</b> .....	<b>7</b>
<b>5.1 PRECAUTIONS</b> .....	<b>7</b>
<b>6 PROCEDURE</b> .....	<b>8</b>
<b>6.1 PREPARATION OF REAGENTS</b> .....	<b>8</b>
<b>6.2 TESTING OF SAMPLE</b> .....	<b>10</b>
<b>7 CALCULATION</b> .....	<b>11</b>
<b>7.1 TABLE</b> .....	<b>11</b>
<b>7.2 DATA SHEET</b> .....	<b>12</b>
<b>9 INFERENCE</b> .....	<b>13</b>
<b>10 EVALUATION</b> .....	<b>13</b>
<b>KEY TO ITEMS:</b> .....	<b>15</b>



## EXPERIMENT ON DETERMINATION OF CHEMICAL OXYGEN DEMAND

### PREAMBLE:

“How to determine chemical oxygen demand in Water and Wastewater”. Test procedure is in accordance to IRSA-CNR (Method 4120 A1) – 1994 Edition.

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

- (1) Metodi Analitici per le acque IRSA-CNR - 1994 Edition. Method 4120 A1.
- (2) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Method 360.1.

### 1 AIM

To determine chemical oxygen demand in the given water sample with the stipulations as per IRSA-CNR (Method 4120 A1) – 1994 Edition.

### 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).

## **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.

DO test is the basis for BOD test which is an important parameter to evaluate organic pollution potential of a waste.

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

## **3 PRINCIPLE**

Dissolved Oxygen can be measured by titrimetric or electrometric 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.

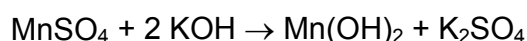
#### **Permanganate Modification:**

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

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

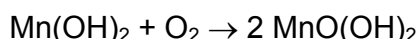
#### **The Titrimetric principle:**

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



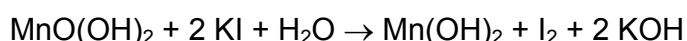
Addition of Potassium iodide or Potassium hydroxide is added to create a pinkish brown precipitate.

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

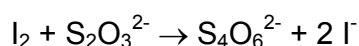


$\text{MnO(OH)}_2$  appears as a brown precipitate. There is some confusion about whether the oxidised manganese is tetravalent or trivalent. Some sources claim that  $\text{Mn(OH)}_3$  is the brown precipitate, but hydrated  $\text{MnO}_2$  may also give the brown colour.

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.



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



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



## **4 MATERIALS REQUIRED**

### **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

### **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



## **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 within two hours of collection, cool storage is not necessary. If analysis can not be started within 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 soon as possible. Do not open sample bottle before analysis.

Begin analysis within six hours of sample collection.

### **5.1 PRECAUTIONS**

The experiment involves a 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.



## 6 PROCEDURE

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

### 6.1 PREPARATION OF REAGENTS

#### a) Manganous Sulphate Solution

Dissolve Manganese Sulphate

→ 436g of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  (or)

→ 382g of  $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$  (or)

→ 364 g of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$

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 364g of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  and transfer it to the beaker. To dissolve the content, place it in the magnetic stirrer

Note: 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

→ 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  $\text{NaN}_3$  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  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  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

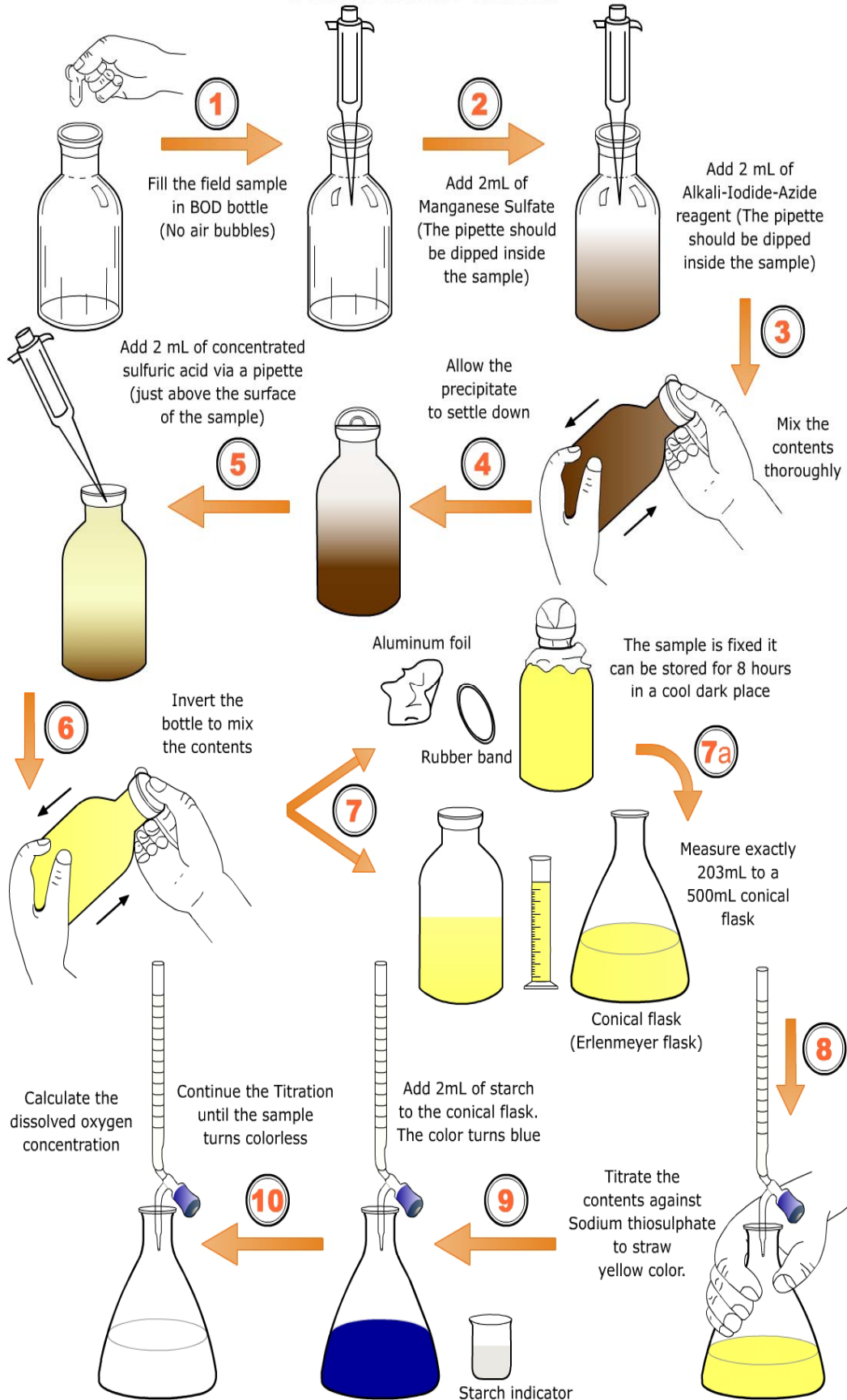
Weigh approximately 2 g of starch and dissolve in 100 mL of hot distilled water.

In case if you are going to preserve the starch indicator add 0.2 g of salicylic acid as preservative.

#### e) Sulphuric Acid



## PROCEDURE CHART





## 6.2 TESTING OF SAMPLE

- Take two 200-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.



## 7 CALCULATION

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

### 7.1 TABLE

ID	Temperature (°C)	Volume of Sample (mL)	Burette Reading (mL)		Volume of Titrant (mL) Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> solution used)	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 20° 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.



## 7.2 DATA SHEET

### DETERMINATION OF DISSOLVED OXYGEN DATA SHEET

Date Tested : \_\_\_\_\_

Tested By : 5AC Class, Group A

Project Name : \_\_\_\_\_

Sample Number : \_\_\_\_\_

Sample Location : \_\_\_\_\_ (Lat \_\_\_\_\_ & Long \_\_\_\_\_)

Sample Description : Surface water

ID	Temperature (°C)	Volume of Sample (mL)	Burette Reading (mL)		Volume of Titrant (mL)  Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> solution used)	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

#### Specimen Calculation:

Volume of Sodium thiosulphate  $V_1 = 7.9$  mL

Normality of Sodium thiosulphate  $N_1 = 0.025$  N

Volume of Sample  $V_2 = 200$  mL

#### Dissolved Oxygen (mg/L):

$$DO = \frac{\text{Volume of Sodium Thiosulfate} \times 0.2 \times 1000}{\text{Volume of sample taken}} =$$
$$= \frac{7.9 \times 0.2 \times 1000}{200} = 7.9 \text{ mg/L}$$

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)



## 8 INTERPRETATION OF RESULTS

The Dissolved Oxygen in the given sample of water at 20.0 °C = **7.9 mg/L**.

## 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 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)  $\text{NaN}_4$
  - b)  $\text{NaN}_3$
  - c)  $\text{NaN}_2$
  - d)  $\text{NaN}$
4. The precipitate formed after the addition of  $\text{MnSO}_4$  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