

(vi) Iron and Manganese

Iron and manganese are metallic elements present in many types of rock. Fe and Mn, both are commonly found in water and are essential elements required in small amounts by all living organisms. Concentrations of iron and manganese in groundwater are often higher than those measured in surface waters.

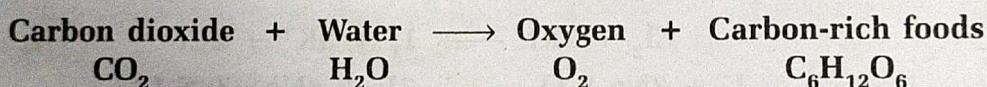
The Aesthetic Objective (AO) for iron in drinking water is less than or equal to 0.3 milligrams per litre (mg/L) while the Aesthetic Objective for manganese in drinking water is less than or equal to 0.05 mg/L. The taste and smell of manganese or iron at concentrations above the drinking water guidelines may be noted by some water users.

Standards for iron and manganese are based on levels that cause taste and staining problems and are set under EPA Secondary Drinking Water Standards. For most individuals 0.3 parts per million ppm of iron and 0.05 ppm of manganese is objectionable. Usually iron and manganese do not exceed 10 ppm and 2 ppm, respectively, in natural waters. Iron and manganese are found at higher concentrations however, that condition is rare.

The most common sources of iron and manganese in groundwater are naturally occurring, for example from weathering of iron and manganese bearing minerals and rocks. Industrial effluent, acid-mine drainage, sewage and landfill leachate may also contribute iron and manganese to local groundwater.

(vii) Dissolved Oxygen (DO)

~~✓~~ The dissolved oxygen (DO) is oxygen that is dissolved in water. The oxygen dissolves by diffusion from the surrounding air, aeration of water that has tumbled over falls and rapids and as a waste product of photosynthesis.



Fish and aquatic animals cannot split oxygen from water (H_2O) or other oxygen-containing compounds. Only green plants and some bacteria can do that through photosynthesis and similar processes. Virtually all the oxygen we breath is manufactured by green plants. A total of three-fourths of the earth's oxygen supply is produced by phytoplankton in the oceans.

Fish and other aquatic animals depend on D.O. to live. The amount of DO in water depends upon the:

1. Temperature of the water.
2. Quality of sediments.
3. The amount of oxygen taken out of the system respiration and decaying organism.

The DO is one of the most important parameter for the quality of water. The lower the DO of water it indicates the lower is the quality of water. Determination of DO is also essential for maintaining aerobic condition in the water as well as in the aerobic treatment of sewage or industrial waste water.

Effect of temperature

If water is too warm, there may not be enough oxygen in it. When there are so many bacteria or aquatic animal in the area, they may overpopulate, using DO in great amounts.

Oxygen levels also can be reduced through over fertilization of water plants by run-off from farm fields containing phosphates and nitrates (the ingredients in fertilizers). Under these conditions, the numbers and size of water plants increases. Then, if the weather becomes cloudy for several days, respiring plants will use much of the available DO. When these plants die, they become food for bacteria, which in turn multiply and use large amounts of oxygen, and this depleting all the oxygen.

How much DO an aquatic organism needs depends upon its species, its physical state, water temperature, pollutants present and more. Consequently, it's impossible to accurately predict minimum DO levels for specific fish and aquatic animals. For example, at 5°C (41°F), trout use about 50–60 milligrams (mg) of oxygen per hour; at 25°C (77°F), they may need five or six times that amount. Fish are cold-blooded animals. They use more oxygen at higher temperatures because their metabolic rates increase.

Numerous scientific studies suggest that 4–5 parts per million (ppm) of DO is the minimum amount that will support a large, diverse fish population. The DO level in good fishing waters generally averages about 9.0 parts per million (ppm).

Effect of the temperature in the DO can be represented by graph below.

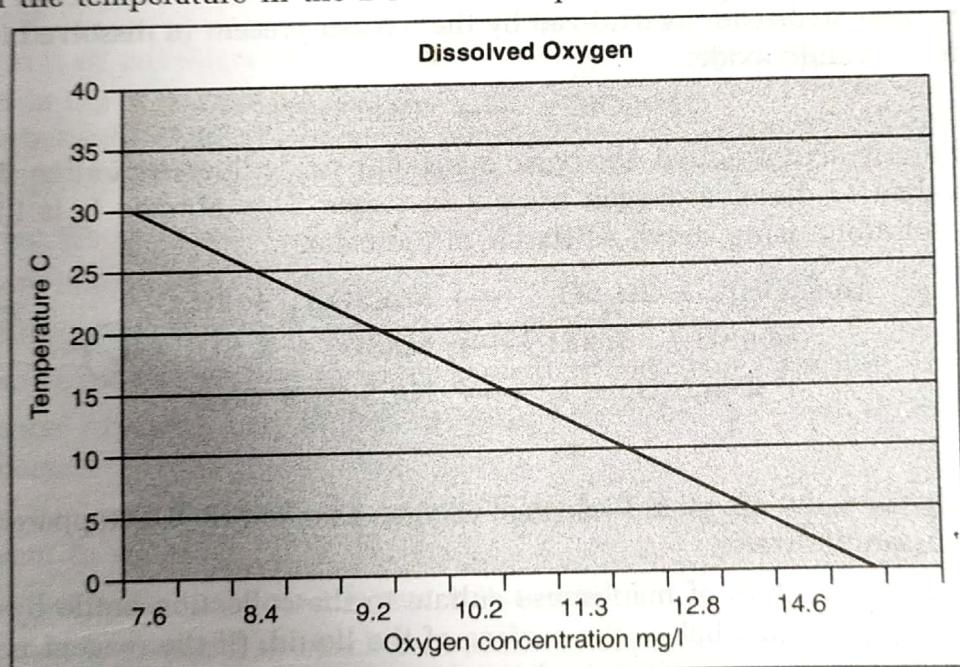


Fig. 4.3 Effect of temperture on solubility of oxygen in water

Determination of Dissolve Oxygen

Determination of dissolve oxygen in water is usually depends upon the Biological Oxygen Demand (B.O.D.) test.

Oxygen is one of the most important as well as common dissolved gases in water.

Dissolve oxygen is vital for the support of aquatic life in water bodies.

Oxygen can dissolve in water in following three ways:

(1) It enters the water directly from the atmosphere.

(2) It can introduce into the water by algae.

(3) It is introduced by mechanical equipment during treatment process.

Water usually contains 8 mg of dissolved oxygen per liter at room temperature. The solubility of oxygen in water ranges from 14.6 ppm at 0°C to about 7 ppm at 35°C under 1 atmospheric pressure.

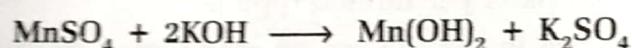
Solubility of oxygen in water is inversely proportional to pressure. So most of the critical conditions related to dissolved oxygen deficiency in water occur during the hot days of summer, when temperatures are high.

The solubility of dissolved oxygen is less in salt water than it is in clear water.

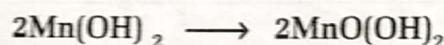
Principle involved in determination of dissolved oxygen

The dissolved oxygen content in water is usually determined by the Winkler's method.

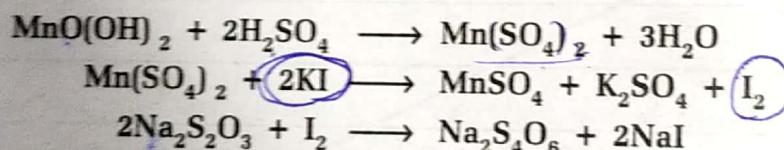
The principle involved in this method is that when MnSO_4 is added to the sample of water containing alkaline potassium iodide, manganese hydroxide is formed.



This manganese hydroxide is oxidized by the oxygen present in dissolved form in water sample to basic manganic oxide.



When sulphuric acid is added, the basic mangamic oxide liberates iodine. This liberated iodine is equivalent to dissolved oxygen present in water. This liberated I_2 is titrated with a standard hypo solution, using starch as starch as indicator.



Procedure

1. Carefully fill a 300-mL glass Biological Oxygen Demand (BOD) stoppered bottle brim-full with sample water.
2. Immediately add 2 mL of manganese sulfate to the collection bottle by inserting the calibrated pipette just below the surface of the liquid. (If the reagent is added above the sample surface, you will introduce oxygen into the sample.) Squeeze the pipette slowly so no bubbles are introduced via the pipette.
3. Add 2 mL of **alkali-iodide-azide** reagent in the same manner.
4. Stopper the bottle with care to be sure no air is introduced. Mix the sample by inverting several times. Check for air bubbles; discard the sample and start over if any are seen. If oxygen is present, a brownish-orange cloud of precipitate or floc will appear. When this floc has settled to the bottom, mix the sample by turning it upside down several times and let it settle again.
5. 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. As an added precaution, squirt distilled water along the stopper, and cap the bottle with aluminum foil and a rubber band during the storage period.

6. In a glass flask, titrate 20 mL of the sample with sodium thiosulfate to a pale straw color. Titrate by slowly dropping titrant solution from a calibrated pipette into the flask and continually stirring or swirling the sample water.
7. Add 2 mL of starch solution so a blue color forms.
8. Continue slowly titrating until the sample turns clear. As this experiment reaches the endpoint, it will take only one drop of the titrant to eliminate the blue color. Be especially careful that each drop is fully mixed into the sample before adding the next. It is sometimes helpful to hold the flask up to a white sheet of paper to check for absence of the blue color.
9. The concentration of dissolved oxygen in the sample is equivalent to the number of milliliters of titrant used. Each mL of sodium thiosulfate added in steps 6 and 8 equals 1 mg/L dissolved oxygen.

Result Analysis

The total number of milliliters of titrant used in steps 6–8 equals the total dissolved oxygen in the sample in mg/L. Oxygen saturation is temperature dependent—gas is more soluble in cold waters, hence cold waters generally have higher dissolved oxygen concentrations. Dissolved oxygen also depends on salinity and elevation, or partial pressure.

Significance for the determination of dissolve oxygen

1. Determination of dissolve oxygen in water is very essential for boiler feed water.
2. It is also very important in sanitary engineering practices.
3. Dissolve oxygen present in water can cause corrosion in boiler.
4. Dissolve oxygen is very important for aquatic organisms to maintain their biological process.
5. It is also very important for precipitation and dissolution of inorganic substances present in water.
6. D.O. test helps to assess the raw water quality.
7. D.O test is essential to check on stream pollution.
8. The rate of biodegradable oxidation can be measured by determining residual dissolve oxygen in water bodies.
9. All the aerobic treatment processes depends upon the amount of dissolve oxygen present in water.
10. Determination of dissolve oxygen is highly desirable to maintain favorable condition for the growth of fish and other aquatic organism.
11. A minimum dissolve oxygen level which is 4ppm must be maintained for survival of aquatic life.

(viii) Biological Oxygen Demand (BOD)

The Biochemical Oxygen Demand (B.O.D.) of sewage or of polluted water is the amount of oxygen required for the biological decomposition of dissolved organic matter under aerobic condition and at the standardized time and temperature. Usually, the time is taken as 5 days and the temperature 20°C as per the global standard.

Determination of Biological Oxygen Demand (B.O.D.)

The B.O.D. test is one of the most important methods in sanitary analysis to determine the polluting power, or strength of sewage, industrial wastes or polluted water. It serves as a measure of the amount of clean diluting water required for the successful disposal of sewage by dilution. The test has its widest application in measuring waste loading to treatment plants and in evaluating the efficiency of such treatment systems.

The test consists in taking the given sample in suitable concentrations in dilute water in B.O.D. bottles. Two bottles are taken for each concentration and three concentrations are used for each sample. One set of bottles is incubated in a B.O.D. incubator for 5 days at 20°C; the dissolved oxygen (initial) content (D_1) in the other set of bottles will be determined immediately. At the end of 5 days, the dissolved oxygen content (D_2) in the incubated set of bottles is determined. Then the BOD is calculated in ppm as:

$$\text{B.O.D.} = (D_1 - D_2)/P$$

Where, P = decimal fraction of sample used.

D_1 = dissolved oxygen of diluted sample (mg/L), immediately after preparation.

D_2 = dissolved oxygen of diluted sample (mg/L), at the end of 5 days incubation.

Among the three values of B.O.D. obtained for a sample select that dilution showing the residual dissolved oxygen of at least 1 mg/L and a depletion of at least 2 mg/L. If two or more dilutions are showing the same condition then select the B.O.D. value obtained by that dilution in which the maximum dissolved oxygen depletion is obtained.

Apparatus Required

1. B.O.D. bottles of 300 ml capacity
2. B.O.D. incubator
3. Burette
4. Pipette
5. Air compressor
6. Measuring cylinder etc.

Reagents Required

1. Distilled water
2. Phosphate buffer solution
3. Magnesium sulphate solution
4. Calcium chloride solution
5. Ferric chloride solution

6. Acid and alkali solution
7. Seeding
8. Sodium sulphite solution
9. Reagents required for the determination of Dissolve Oxygen.

Procedure

1. Place the known volume of distilled water in a 5 litre flask (generally about 3 litres of distilled water will be needed for each sample).
2. Add 1mL each of phosphate buffer, magnesium sulphate solution, calcium chloride solution and ferric chloride solution for every litre of distilled water.
3. Seed the sample with 1–2 mL of settled domestic sewage.
4. Saturate the dilution water in the flask by aerating with a supply of clean compressed air for at least 30 minutes.
5. Highly alkaline or acidic samples should be neutralised to pH 7.
6. Destroy the chlorine residual in the sample by keeping the sample exposed to air for 1 to 2 hours or by adding a few mL of sodium sulphite solution.
7. Take the sample in the required concentrations. The following concentrations are suggested:
 - Strong industrial waste : 0.1, 0.5 and 1 per cent
 - Raw and settled sewage : 1.0, 2.5 and 5 per cent
 - Oxidised effluents : 5, 12.5 and 25 per cent
 - Polluted river water : 25, 50 and 100 per cent
8. Add the required quantity of sample (calculate for 650 mL dilution water the required quantity of sample for a particular concentration) into a 1000 mL measuring cylinder. Add the dilution water up to the 650mL mark.
9. Mix the contents in the measuring cylinder.
10. Add this solution into two B.O.D. bottles, one for incubation and the other for determination of initial dissolved oxygen in the mixture.
11. Prepare in the same manner for other concentrations and for all the other samples.
12. Lastly fill the dilution water alone into two B.O.D. bottles. Keep one for incubation and the other for determination of initial dissolved oxygen.
13. Place the set of bottles to be incubated in a B.O.D. incubator for 5 days at 20°C. Care should be taken to maintain the water seal over the bottles throughout the period of incubation.
14. Determine the initial dissolved oxygen contents in the other set of bottles and note down the results.
15. Determine the dissolved oxygen content in the incubated bottles at the end of 5 days and note down the results.
16. Calculate the B.O.D. of the given sample.

(a) Observation table. Determination of D_1 , D_2 and B.O.D.

Sample no. or description	Concentration	Dissolved oxygen content mg/L				B.O.D. mg/L (5 days 20°C)	
		Initial (D_1)		Final (D_2)			
		Bottle no.	D.O. value	Bottle no.	D.O. value		

Note: B.O.D. value in mg/L = $\left(\frac{D_1 - D_2}{P} \right)$

If concentration is 0.1 per cent, then $P = \left(\frac{0.1}{100} = 0.001 \right)$ and so on.

Sample Calculation

D_1 = Initial Dissolved Oxygen = mg/L

D_2 = Dissolved Oxygen at the end of 5 days = mg/L

P = Decimal fraction of sample used =

Therefore, mg/L of B.O.D. = $\frac{(D_1 - D_2)}{P} = \dots$

Result: Dissolve oxygen of sample is found to be x ppm.

(b) Observation table. Numbers of Samples and B.O.D. at 20°C

Sample no. of description	mg/L 5 days B.O.D. at 20°C

BOD test is usually influenced by the following factors:

1. pH value of wastewater.
2. Toxic material present in water.
3. Nitrification process.
4. Types of micro organism.

Limitations of BOD test

1. The pre treatment of wastewater is required if water contains toxic waste before the BOD test.
2. BOD test is applicable only in the case of biodegradable organic waste.
3. High concentration of bacteria is required to be present in the sample of sewage.
4. Before applying the BOD test it is necessary to reduce the effects of nitrifying bacteria or organisms.
5. The time required for the test is long.

(ix) Chemical Oxygen Demand (COD)

The oxygen required for the degradation of the organic matter biologically is called the Biochemical Oxygen Demand (BOD). The industrial and municipal waste water effluents may contain very high amounts of organic matter and if discharged into natural water bodies, it can cause complete depletion of dissolved oxygen leading to the mortality of aquatic organisms.

"The amount of oxygen needed to consume the organic and inorganic materials is called the Chemical Oxygen Demand (COD)".

There exists a definite correlation between the COD and BOD under certain conditions and by determining the COD, the information about the BOD of the water/waste water can be derived.

Potassium dichromate is considered the best oxidant due to its strong oxidizing ability, its applicability to a wide variety of samples and ease of manipulation makes it very efficient.

Determination of C.O.D. of Waste Water

Reagents Required

1. Potassium dichromate (Standard solution): $K_2Cr_2O_7 - 0.004167\text{ M (0.0250 N)}$
2. Mohr's Salt: Ferrous ammonium sulphate (Standard solution): $FeSO_4 \cdot (NH_4)_2SO_4 (0.025\text{ M})$.
3. Mercuric Sulphate: Powdered $HgSO_4$.
4. Silver Sulphate: Powdered Ag_2SO_4 .
5. Phenanthroline ferrous sulphate indicator solution.
6. Concentrated Sulphuric acid: $H_2SO_4 18\text{ M}$.

Procedure

1. 50 ml of sample was taken into a refluxing flask and several boiling stones were added.
2. 0.1 g $HgSO_4$ was added to the solution.
3. 5 ml of concentrated H_2SO_4 was also added to the solution.
4. To ensure that $HgSO_4$ dissolved completely, the solution was swirled slowly while adding Sulphuric acid. 0.1 g of Ag_2SO_4 was added to this solution.
5. Finally Potassium dichromate was added. Thorough mixing of the solution was ensured by swirling the flask in a water bath to recover any volatile substances that may have escaped from the liquid state.

6. The flask was then attached to the condenser and further cooling was done.
7. 20 ml of Sulphuric acid was added to the solution in the flask continuing cooling and swirling to mix the solution.
8. The solution was refluxed for 1 hour.
9. A blank run (using 50 ml distilled water instead of sample) was simultaneously conducted with the same procedure after cooling; the solution was transferred to an Erlenmeyer flask.
10. The reflux flask was rinsed thrice, pouring the rinsing water to the Erlenmeyer flask. The solution was diluted to about 300 ml and about 8 drops of Phenophthaline ferrous sulphate was added to the solution as an indicator.
11. The solution was titrated against the Mohr's salt and the titer volume required for the color change from blue-green to reddish blue was noted.

The same procedure was repeated for the blank run.

Observations: Titer Value of Sample and blank

Solution	Initial reading	Final Readind	Titer Value
Sample	-	-	V _s
Blank	-	-	V _{bl}

Calculations

$$\text{COD} = 8000 \times (V_{bl} - V_s) \times M / \text{original volume of sample taken mg/l}$$

Where, V_{bl} = Titer volume for the blank

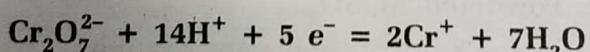
V_s = Titer volume for the sample

M = Molarity of Mohr's solution



Discussions and Results

Potassium dichromate acts as a strong oxidizing agent and oxidizes the organic and inorganic matter in the waste water. The reaction can be expressed as:



If chlorides are present in the sample it will interfere with the oxidation of the organic matter. To ensure non-interference of chlorides Mercury Sulphate is added which will form complex of mercuric chloride. An amount of 10 g of Mercury Sulphate is required for 1 g of Chlorides to form complex.

Sulphuric acid is added to the mixture so that the mercury is completely dissolved. Besides, it assists in oxidizing the nitrogen compounds in the sample and the increased heat will accelerate the reaction rate.

Silver Sulphate catalyses the reaction and also assists in the oxidation of the nitrogen compounds.

Mercury sulphate is added first in order to allow the chlorine atoms to combine with mercury. If Silver Sulphate is added first, the chlorine would bind with the silver. Mercury sulphate may be added after; however it will take some time for the chlorine to detach from

the silver and bind to mercury. Thus, it is best to add mercury sulphate first, it assists in oxidizing the nitrogen compounds in the sample and the increased heat will accelerate the reaction rate.

Silver Sulphate catalyses the reaction and also assists in the oxidation of the nitrogen compounds. Mercury sulphate is added first in order to allow the chlorine atoms to combine with mercury. If Silver Sulphate is added first, the chlorine would bind with the silver. Mercury sulphate may be added after; however it will take some time for the chlorine to detach from the silver and bind to mercury. Thus, it is best to add mercury sulphate first. The titer volume of the sample gives the volume of Ferrous Ammonium Sulphate required to react with the excess potassium dichromate in the solution. Similarly, the titer volume for the blank (distilled water) gives the volume of Ferrous Ammonium Sulphate required to react with the excess potassium dichromate in the blank. The equation for the titration can be expressed as:



From above equation it can be seen that one molecule of dichromate corresponds to one molecule of Mohr's salt.

Thus, the difference in volume of excess $\text{K}_2\text{Cr}_2\text{O}_7$ reacting with Mohr's solution can be calculated from the expression:

$$\text{Excess volume of Potassium Dichromate} = (\text{Original vol. } \text{K}_2\text{Cr}_2\text{O}_7 - \text{vol. of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ used for oxidation}) \text{ solution} - (\text{Original vol. } \text{K}_2\text{Cr}_2\text{O}_7 - \text{vol. of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ used for oxidation}) \text{ blank}$$

$$= (\text{Vol. of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ used for oxidation}) \text{ blank} - (\text{Vol. of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ used for oxidation}) \text{ solution}$$

Hence, the difference in the titer volume for the solution and the blank is used to find out the Chemical Oxygen Demand directly.

TABLE 4.6: Comparision of Biological Oxygen Demand and Chemical Oxygen Demand and its Analysis

S.No.	Biological Oxygen Demand	Chemical Oxygen Demand
1	The value of B.O.D. is less.	The value of C.O.D. is greater to B.O.D.
2	It is time taking process it requires minimum 3 days (at 30°C) or 5 days (at 20°C)	It requires 3 hours, so it requires comparatively less time.
3	BOD test is usually influenced by types of micro organism seed, nitrification process, mineral matter contend, toxic material present as well as pH value of water.	C.O.D. test is not much influenced by these factors.
4	It is the quantity of oxygen required by a definite volume of water for oxidizing the organic matter contained in it by micro organisms under specific conditions.	Chemical oxygen demand is the amount of oxygen required by organic as well as inorganic matter in a sample of water for its oxidation by a strong chemical oxidizing agent such as $\text{K}_2\text{Cr}_2\text{O}_7$.

5	For is determination the dissolved oxygen content of the sample with or without dilution is measured before and after incubation at 20°C for 5 days or at 27°C for 3 days and it is expressed in mg of oxygen required per liter of water.	It is expressed as ppm of oxygen taken from oxidizing agent in two hours.
6	BOD values can be calculated by $BOD = D_1 - D_2 \times F$ <p>D_1 = D.O. at diluted waste water sample before incubation, mg/l.</p> <p>D_2 = D.O. of diluted water sample after 5 days incubation at 20°C, mg/l</p> <p>F = dilution factor</p>	C.O.D. value can be calculated by $8000 \times (V_{BL} - V_S) \times M$ <p>V_{BL} = Titer value for the blank</p> <p>V_S = Titer value for the sample</p> <p>M = Molarity of the solution</p>
7	B.O.D. values are useful in process design, loading calculations, measurement of treatment efficiency, self purifying capacity of stream of water and stream pollution control.	C.O.D. test is used in calculation of the effluent of treatment plants, proposing standards for discharging various effluents.
8	Industrial waste water do not respond to BOD test.	COD test is applicable to industrial waste water.
9	It is the value of biologically oxidizable organic matter only.	It can not differentiate biologically oxidizable and biological inert organic matter.