

*Training module # WQ - 11*

***The chemistry of dissolved oxygen measurement***

New Delhi, May 1999

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CSMRS Building, 4th Floor, Olof Palme Marg, Hauz Khas,  
New Delhi – 11 00 16 India  
Tel: 68 61 681 / 84 Fax: (+ 91 11) 68 61 685  
E-Mail: dhvdelft@del2.vsnl.net.in

DHV Consultants BV & DELFT HYDRAULICS

with  
HALCROW, TAHAL, CES, ORG & JPS

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# 1 Module context

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This module deals with significance and chemistry of dissolved oxygen measurement. Modules in which prior training is required to complete this module successfully and other available, related modules in this category are listed in the table below.

While designing a training course, the relationship between this module and the others, would be maintained by keeping them close together in the syllabus and place them in a logical sequence. The actual selection of the topics and the depth of training would, of course, depend on the training needs of the participants, i.e. their knowledge level and skills performance upon the start of the course.

No.	Module title	Code	Objectives
1	<i>Basic water quality concepts</i>	WQ - 01	<ul style="list-style-type: none"><li>• Discuss the common water quality parameters</li><li>• List important water quality issues</li></ul>
2	<i>Basic chemistry concepts</i>	WQ - 02	<ul style="list-style-type: none"><li>• Convert units from one to another</li><li>• Discuss the basic concepts of quantitative chemistry</li><li>• Report analytical results with the correct number of significant digits.</li></ul>
3	<i>How to prepare standard solutions</i>	WQ - 04	<ul style="list-style-type: none"><li>• Select different types of glassware</li><li>• Use an analytical balance and maintain it.</li><li>• Prepare standard solutions.</li></ul>
4	<i>How to measure dissolved oxygen</i>	WQ - 12	<ul style="list-style-type: none"><li>• Collect water sample for measurement of dissolved oxygen</li><li>• Determine the quantity of dissolved oxygen</li></ul>

## 2 *Module profile*

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<b>Title</b>	:	The chemistry of dissolved oxygen (DO) measurement
<b>Target group</b>	:	HIS function(s): Q1, Q2, Q3, Q5
<b>Duration</b>	:	1 session of 90 min
<b>Objectives</b>	:	After the training the participants will be able to: <ul style="list-style-type: none"><li>• Appreciate significance of DO measurement</li><li>• Understand the chemistry of DO measurement by Winkler method</li></ul>
<b>Key concepts</b>	:	<ul style="list-style-type: none"><li>• Significance</li><li>• Solubility of oxygen</li><li>• Sampling</li><li>• Chemistry of Winkler method</li></ul>
<b>Training methods</b>	:	Lecture, demonstration, exercises and open discussion
<b>Training tools required</b>	:	OHS
<b>Handouts</b>	:	As provided in this module
<b>Further reading and references</b>	:	<ul style="list-style-type: none"><li>• Analytical Chemistry: An introduction, D.A. Skoog and D. M. West/1986. Saunders College Publishing</li><li>• Chemistry for Environmental Engineering, C.N. Sawyer, P.L. McCarty and C.F. Parkin. McGraw-Hill, 1994</li></ul>

## 3 Session plan

No	Activities	Time	Tools
1	<b>Preparations</b>		
2	<b>Introduction:</b> <ul style="list-style-type: none"> <li>• Introduce the subject of dissolved oxygen, explain its significance</li> <li>• Explain aerobic and anaerobic decomposition process in polluted water body.</li> <li>• Explain minimum standard requirements for normal aquatic life in natural water body</li> </ul>	5 min	OHS OHS OHS
3	<b>Solubility of oxygen</b> <ul style="list-style-type: none"> <li>• Explain solubility of oxygen in water as a function of temperature, salinity and partial pressure</li> <li>• Demonstrate how to calculate the saturated DO level at a given temperature and pressure using text Table 1, text section 8.1</li> <li>• Ask participants to practice calculating the saturated DO level.</li> </ul>	30 min.	OHS OHS Handout
4	<b>Collection and storage of samples</b> <ul style="list-style-type: none"> <li>• Explain the precautions in collection and storage of samples</li> <li>• Demonstrate the use of the DO sampler, text section 8.2</li> </ul>	10 min.	OHS DO sampler
5	<b>Winkler Method</b> <ul style="list-style-type: none"> <li>• Explain the chemistry of Winkler method</li> <li>• Explain how nitrite interference is eliminated with azide modification, text section 8.3</li> </ul>	20 min.	OHS OHS
6	<b>Standard solutions</b> <ul style="list-style-type: none"> <li>• Ask participants meaning of secondary standard solution (sodium thio-sulphate). Explain (in short) the meaning of primary &amp; secondary standards used in titrimetric methods.</li> <li>• Demonstrate how to calculate the exact normality of given sodium thio-sulphate solution.</li> </ul>	20 min.	OHS Handout
7	<b>Summary</b> <ul style="list-style-type: none"> <li>• Summarise the session</li> <li>• Clarify doubts</li> </ul>	5 min.	OHS

# 4 Overhead/flipchart master

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## OHS format guidelines

Type of text	Style	Setting
Headings:	OHS-Title	Arial 30-36, Bold with bottom border line (not: underline)
Text:	OHS-lev1 OHS-lev2	Arial 26, Arial 24, with indent maximum two levels only
Case:		Sentence case. Avoid full text in UPPERCASE.
Italics:		Use occasionally and in a consistent way
Listings:	OHS-lev1 OHS-lev1-Numbered	Big bullets. Numbers for definite series of steps. Avoid roman numbers and letters.
Colours:		None, as these get lost in photocopying and some colours do not reproduce at all.
Formulas/ Equations	OHS-Equation	Use of a table will ease alignment over more lines (rows and columns) Use equation editor for advanced formatting only

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# Dissolved oxygen:

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1. Dissolved oxygen: significance
2. Why measure DO?
3. Standards: minimum oxygen in surface water
4. Solubility of oxygen
5. Dissolved oxygen sampler
6. Determining DO: Winkler method
7. Winkler method: chemistry
8. Standard solutions

# **Dissolved oxygen: significance**

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- Well-being of fish & normal aquatic life in natural surface water
- Aerobic decomposition of organic matter in polluted waters



# Why measure DO

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- To indicate health of a water body
- To monitor & operate aerobic waste water treatment plants
- To prevent corrosion in water treatment & distribution systems

# Surface Water Standards

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- Drinking water source without conventional treatment, after disinfection **6.0 mg/L**
- Drinking water source with conventional treatment, followed by disinfection **4.0 mg/L**
- Out-door bathing **5.0 mg/L**
- Fish culture and wild life propagation **4.0 mg/L**

# Solubility of oxygen

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See Table of saturation levels in handout

# Solubility of oxygen

---

- For saturation at other pressures

$$C'_s = C_s \times \frac{P - p}{760 - p}$$

Where:

$C'_s$  = Solubility at barometric pressure  $P$  & given temp, in mg/L

$C_s$  = Saturation at given temp from table, mg/L

$P$  = Barometric pressure, mm

$p$  = Pressure of saturated water vapour at temperature of the water selected from Table 1, mm

# Solubility of oxygen: example

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$T = 28^{\circ}\text{C}$ ,  $P = 710 \text{ mm}$ ,  $\text{Cl}^{-} = 600 \text{ mg/L}$ ,  $\text{DO} = 5.8 \text{ mg/L}$

1. *Calculate the saturation DO*
2. *Calculate percent saturation level.*

• From the table:

$C_s$  at  $0 \text{ mg/L Cl}^{-} = 7.9 \text{ mg/L}$

$C_s$  decreases  $0.008 \text{ mg/100 mg Cl}^{-}$

$p = 28 \text{ mm Hg}$

# Solubility of oxygen: example

---

- Correction for  $Cl^-$

$$\begin{aligned}C_s &= 7.9 - (0.008 \times 6) \\ &= 7.85 \text{ mg/L}\end{aligned}$$

- Correction for pressure

$$\begin{aligned}C'_s &= C_s \times \frac{P - p}{760 - p} \\ C'_s &= 7.85 \times \frac{710 - 28}{760 - 28} = 7.31 \text{ mg/L}\end{aligned}$$

# Solubility of oxygen: example

---

***Saturation DO concentration is 7.31 mg/L***

- If sample DO concentration is 5.8 mg/L percent saturation =

$$\% \text{ saturation} = \frac{5.8}{7.31} = 79 \%$$

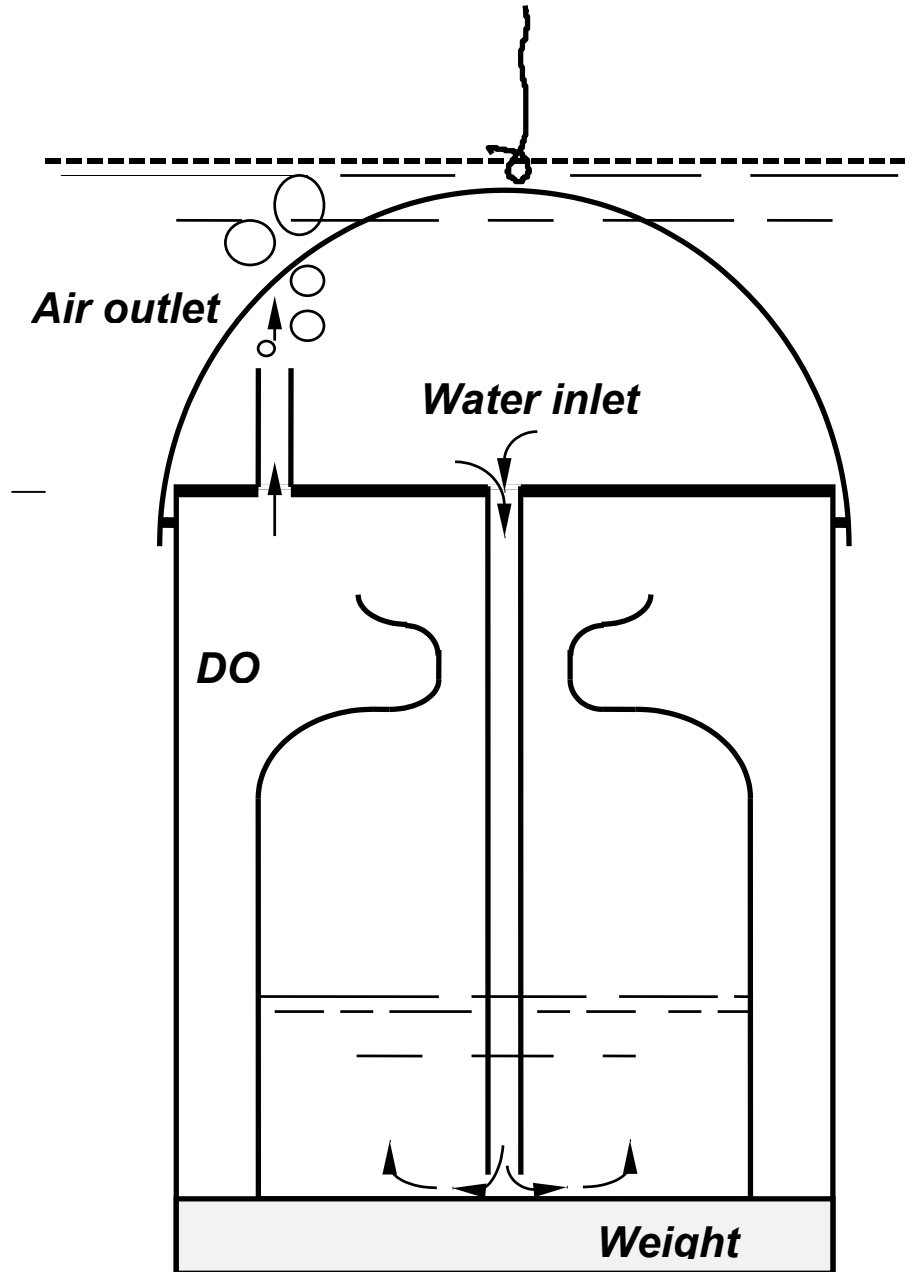
# Solubility of oxygen: exercise

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*Calculate the saturation DO level in water containing 2000 mg/L chloride at 26 °C at 720 mm barometric pressure. What is the percent saturation level if the DO content is 5.9 mg/L.*



# Dissolved oxygen sampler



# Winkler method

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Based on:

1. Reactions: releasing iodine = oxygen present in sample
2. Titration of liberated iodine

# Winkler method

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- Step 1 Determine presence of oxygen
- Step 2 Oxidise iodide to form iodine
- Step 3 Titrate iodine till pale straw colour
- Step 4 Change colour to blue
- Step 5 Titrate till solution is colourless
- Step 6 Note the final reading

# Winkler method

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## Step 1

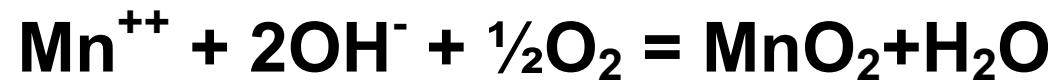
Add manganese sulphate & alkali iodide reagents

- *If no oxygen is present:*



white manganese hydroxide

- *If oxygen is present:*

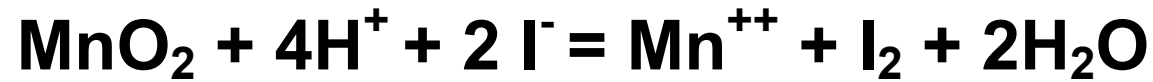


brown manganese dioxide

# Winkler method

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Add sulphuric acid.



*Iodine is formed by oxidation of iodide*

# Winkler method

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## Step 3

Titrate liberated iodine with sodium thio-sulphate standard solution



*Observe colour change to pale straw*

# Winkler method

---

## Step 4

Add starch indicator

*colour changes to blue*

## Step 5

Continue titration

*till solution becomes colourless*

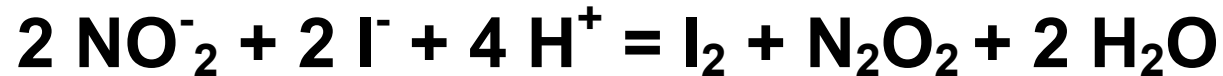
## Step 6

Note the final reading

# Nitrite interference & azide modification

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Nitrite in water samples causes interference by oxidising iodide as:



$\text{N}_2\text{O}_2$  then oxidised by oxygen entering sample during titration:



Results in erroneous high value.

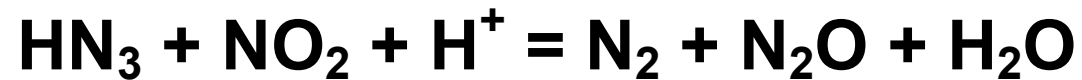
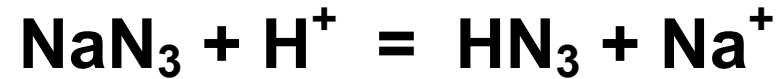
Final end point value not possible



# Nitrite interference & azide modification

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In azide modification, sodium azide  $\text{NaN}_3$  added with alkali reagent. Destroys nitrite, if present:



# Standard solutions

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- Primary standard solution:

- *Potassium dichromate*  $K_2 Cr_2 O_7$
- *Potassium Iodate*  $K I O_3$
- *Potassium hydrogen bi-iodate*  $KH (IO_3)_2$

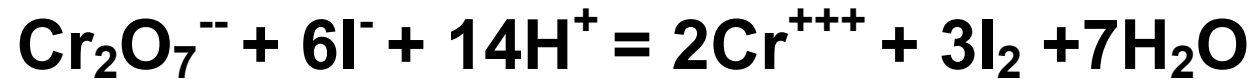
- Secondary standard solution:

- *Sodium thio-sulphate*  $Na_2S_2O_3 \cdot 5H_2O$

# Standardising secondary standard

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- Primary standards react with iodide ion



- The released iodine is titrated with secondary standard



# Standard solutions: example calculations

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Refer to handout

# Dissolved oxygen: summary

---

- Significance: monitor normal aquatic life
- Indian standard specify min of 4.0 mg/L
- Solubility of oxygen depends on partial pressure, temperature & salinity of water
- Avoid aeration of water during collection, use the DO sampler.
- Eliminate nitrite interference, use azide modification
- Liberated iodine equal to DO
- Primary standard: use potassium dichromate or bi-iodate
- Secondary standard: use sodium thio-sulphate

# **5 *Evaluation***

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## Questions

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- Q** 20 mL of 0.01 N potassium bi-iodate was reacted with excess iodide and sulphuric acid. The released iodine was titrated with a sodium thio-sulphate solution.
- (a) Calculate the normality of thio-sulphate solution if 7.5 mL solution was used in the titration.
- (b) What volumes of the solution and distilled water should be mixed to prepare 250 mL of 0.025 N standard solution.
- Q** Calculate the normality of KH (IO<sub>3</sub>)<sub>2</sub> solution containing 812.4 mg/l used to liberate iodine from iodide.
- 

**Q** Discuss the significance of DO measurement.

**Q** Calculate the DO in a sample of water if 6.8 mL of 0.025N sodium thiosulphate solution was used while titrating 200 mL of sample treated according to Winkler's method

### **True or false:**

- Organic pollution of surface waters results in decrease of DO
- Absence of oxygen in surface waters results in production of odorous compounds
- Good quality groundwater is always saturated with DO
- Presence of nitrite in water will result in over estimation of DO if azide modification is used.

# 6 *Handouts*

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## Dissolved oxygen:

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1. Dissolved oxygen: significance
2. Why measure DO?
3. Standards: minimum oxygen in surface water
4. Solubility of oxygen
5. Dissolved oxygen sampler
6. Determining DO: Winkler method
7. Winkler method: chemistry
8. Standard solutions

## Dissolved oxygen: significance

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- Well-being of fish & normal aquatic life in natural surface water
- Aerobic decomposition of organic matter in polluted waters

## Why measure DO

---

- To indicate health of a water body
- To monitor & operate aerobic waste water treatment plants
- To prevent corrosion in water treatment & distribution systems

## Standards: minimum oxygen in SW

---

- Drinking water source without conventional treatment, after disinfection 6.0 mg/L
- Drinking water source with conventional treatment, followed by disinfection 4.0 mg/L
- Out-door bathing 5.0 mg/L
- Fish culture and wild life propagation 4.0 mg/L

## Solubility of oxygen

---

For saturation at other pressures

$$C'_s = C_s \times \frac{P - p}{760 - p}$$

Where:

- $C'_s$  = Solubility at barometric pressure P & given temp, in mg/L
- $C_s$  = Saturation at given temp from table, mg/L
- P = Barometric pressure, mm
- p = Pressure of saturated water vapour at temperature of the water selected from Table 1, mm

## Example

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1. Calculate the saturation DO
2. Calculate percent saturation level

T = 28°C, P = 710 mm, Cl<sup>-</sup> = 600 mg/L

- From the table:  
C<sub>s</sub> at 0 mg/L Cl<sup>-</sup> = 7.9 mg/L  
C<sub>s</sub> decreases 0.008 mg/100 mg Cl<sup>-</sup>  
p = 28 mm Hg

- Correction for Cl<sup>-</sup>  
$$C_s = 7.9 - (0.008 \times 6)$$
$$= 7.85 \text{ mg/L}$$

- Correction for pressure

$$C'_s = C_s \times \frac{P - p}{760 - p}$$
$$C'_s = 7.85 \times \frac{710 - 28}{760 - 28} = 7.31 \text{ mg/L}$$

**Saturation DO concentration is 7.31 mg/L**

If sample DO concentration is 5.8 mg/L percent saturation =

$$\% \text{ saturation} = \frac{5.8}{7.31} = 79 \%$$

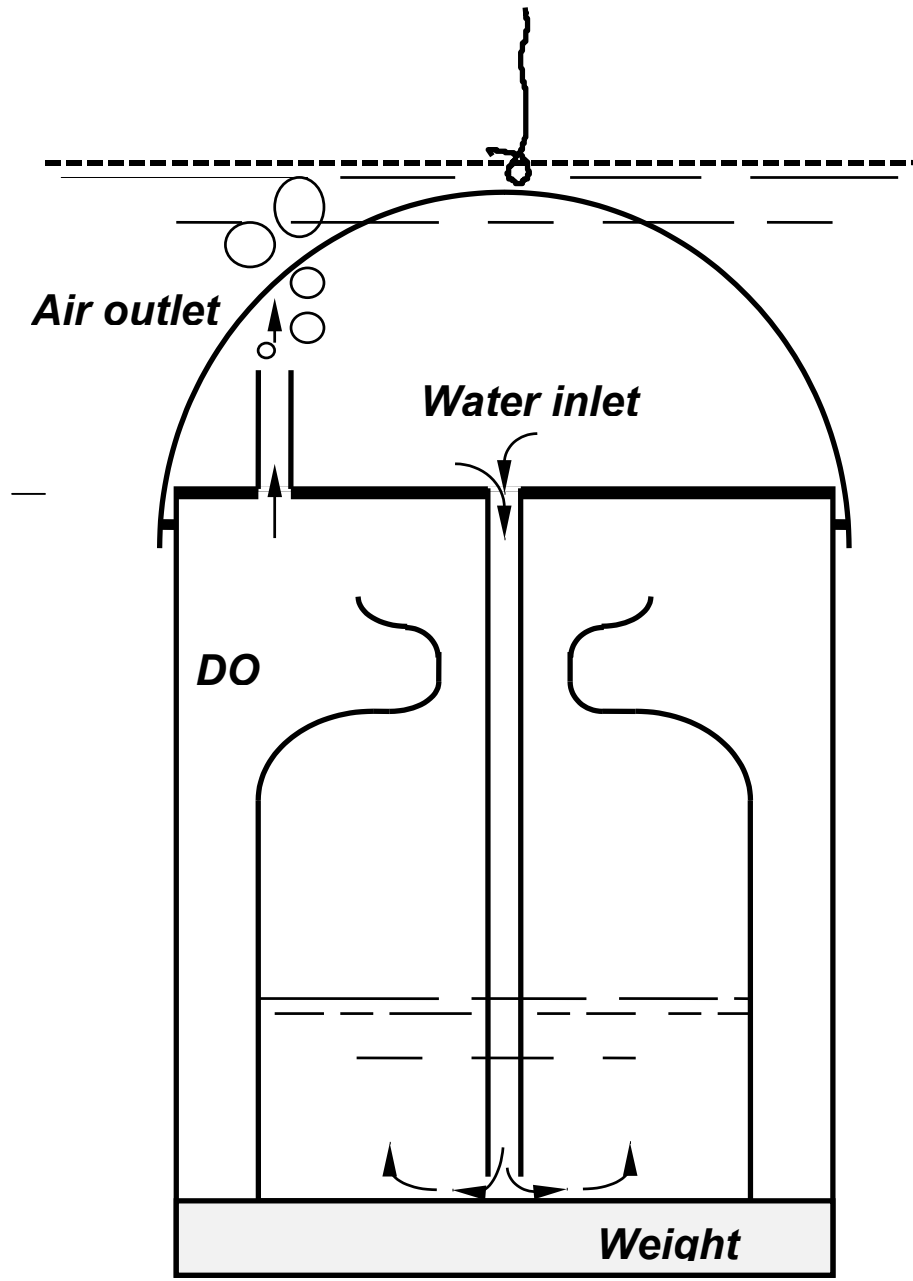
## 4. Solubility of oxygen: exercise

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Calculate the saturation DO level in water containing 2000 mg/L chloride at 26°C at 720 mm barometric pressure. What is the percent saturation level if the DO content is 5.9 mg/L.

# Dissolved oxygen sampler

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## Winkler method

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Based on:

- Reactions: releasing iodine = oxygen present in sample
  - Titration of liberated iodine
- 

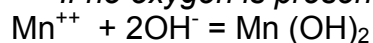
Step 1	Determine presence of oxygen
Step 2	Oxidise iodide to form iodine
Step 3	Titrate iodine till pale straw colour
Step 4	Change colour to blue
Step 5	Titrate till solution is colourless
Step 6	Note the final reading

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### Step 1

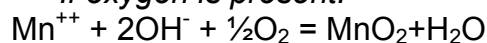
Add manganese sulphate & alkali iodide reagents

- *If no oxygen is present:*



white manganese hydroxide

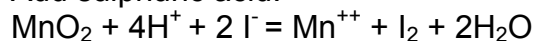
- *If oxygen is present:*



brown manganese dioxide

### Step 2

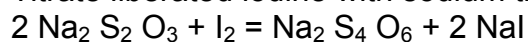
Add sulphuric acid.



*Iodine is formed by oxidation of iodide*

### Step 3

Titrate liberated iodine with sodium thio-sulphate standard solution



*Observe colour change to pale straw*

### Step 4

Add starch indicator

*colour changes to blue*

### Step 5

Continue titration

*till solution becomes colourless*

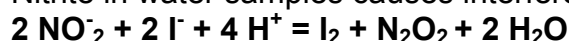
### Step 6

Note the final reading

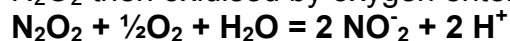
## Nitrite interference & azide modification

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Nitrite in water samples causes interference by oxidising iodide as:



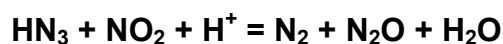
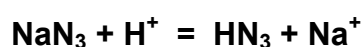
$\text{N}_2\text{O}_2$  then oxidised by oxygen entering sample during titration:



- Results in erroneous high value.
- Final end point value not possible

In azide modification, sodium azide  $\text{NaN}_3$  added with alkali reagent.

Destroys nitrite, if present:



## Standard solutions

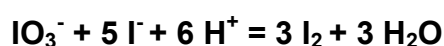
---

- Primary standard solution:  
Potassium dichromate  $\text{K}_2 \text{Cr}_2 \text{O}_7$   
Potassium Iodate  $\text{KIO}_3$   
Potassium hydrogen bi-iodate  $\text{KH}(\text{IO}_3)_2$
- Secondary standard solution:  
Sodium thio-sulphate  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

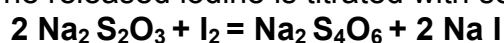
## Standardising secondary standard

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- Primary standards react with iodide ion  
 $\text{Cr}_2\text{O}_7^{2-} + 6\text{I}^- + 14\text{H}^+ = 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O}$



The released iodine is titrated with secondary standard



## Dissolved oxygen: summary

---

- Significance: monitor normal aquatic life
- Indian standard specify min of 4.0 mg/L
- Solubility of oxygen depends on partial pressure, temperature & salinity of water
- Avoid aeration of water during collection, use the DO sampler.
- Eliminate nitrite interference, use azide modification
- Liberated iodine equal to DO
- Primary standard: use potassium dichromate or bi-iodate
- Secondary standard: use sodium thio-sulphate

## Standard solutions: example calculations

---

**Q.** *20 mL of 0.01 N potassium bi-iodate was reacted with excess iodide and sulphuric acid. The released iodine was titrated with a sodium thio-sulphate solution.*

**(a)** *Calculate the normality of thio-sulphate solution if 7.5 mL solution was used in the titration.*

**A.** Equivalents of bi-iodate reacted and equivalents of iodine realised  
=  $0.01 \text{ meq/mL} \times 20 \text{ mL} = 0.2 \text{ meq}$ .  
This is also equal to the equivalents of thio-sulphate reacted.  
Therefore strength of thio-sulphate  
=  $0.2 \text{ meq} / 7.5 \text{ mL} = 0.0266 \text{ N}$ .

**(b)** *What volumes of the solution and distilled water should be mixed to prepare 250 mL of 0.025 N standard solution.*

**A.** Equivalent of thio-sulphate required for 250 mL, 0.025 N solution  
=  $0.025 \text{ meq/mL} \times 250 \text{ mL} = 6.25 \text{ meq}$ .  
Assuming that V mL of 0.0266 N solution is needed,  
 $V \times 0.0266 \text{ meq/mL} = 6.25 \text{ meq}$   
or  $V = 235 \text{ mL}$   
Therefore distilled water required  
=  $250 - 235 = 15 \text{ mL}$ .

**Q.** *Calculate the normality of  $\text{KH}(\text{IO}_3)_2$  solution containing 812.4 mg/l used to liberate iodine from iodide.*

**A.** Molecular weight of potassium bi-iodate = 390 g

Therefore strength of the solution  
=  $0.8123 \text{ g/L} \times 1 \text{ mole} / 390 \text{ g} = 0.0021 \text{ M}$

or normality =  $6 \text{ equivalents/mole} \times 0.0021 \text{ mole/L}$   
=  $0.0126 \text{ N}$

# ***7 Additional handouts***

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These handouts are distributed during delivery and contain test questions, answers to questions, special worksheets, optional information, and other matters you would not like to be seen in the regular handouts.

It is a good practice to pre-punch these additional handouts, so the participants can easily insert them in the main handout folder.

# 8 *Main text*

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## Contents

1.	General	1
2.	Collection and storage of samples	3
3.	Winkler method with azide modification	4



# The chemistry of dissolved oxygen (DO) measurement

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## 1. General

Surface water in contact with air, dissolves oxygen through molecular diffusion. Dissolved oxygen (DO) levels in natural and wastewater depends on the physical, chemical and biological activities in water body. If the dissolved oxygen (DO) is not consumed by reactions in the water, it ultimately reaches saturation value. Table 1 gives saturation levels as a function of temperature and chloride concentration. The solubility of oxygen decreases as the concentration of dissolved solids increases. Chloride concentration is used as a measure of the seawater-freshwater mix in a sample. The chloride content of seawater is about 19,000 mg/L.

The solubility also depends on the partial pressure of oxygen. The solubility of atmospheric oxygen in fresh waters ranges from 14.6 mg/L at 0°C to about 7 mg/L at 35°C, under 1 atm. pressure.

For saturation at barometric pressures other than 760 mm,

$$C'_s = C_s \times \frac{P - p}{760 - p}$$

$C'$  = Solubility at barometric pressure P mm and given temperature, mg/L

$C_s$  = Saturation at given temperature from Table 1, mg/L

$p$  = Pressure of saturated water vapour at temperature of the water selected from table, mm.

In polluted waters the presence or absence of oxygen determines whether the decomposition of organic matter is brought about by aerobic or anaerobic organisms. Aerobic decomposition produces innocuous end products. In the absence of oxygen anaerobic organisms take over the decomposition process producing reduced compounds such as ammonia, hydrogen sulphide, mercaptans, etc., which cause environmental nuisance. Though the solubility of oxygen in water is very limited under ambient conditions, its presence is very necessary for the well-being of fish and normal aquatic life. Indian standards specify a minimum of 4 mg/L for such a purpose.

Measurement of DO is also important in monitoring and operation of aerobic wastewater treatment plants and corrosion prevention in water treatment and distribution systems.

**Table 1**

Saturation values of dissolved oxygen in water exposed to water saturated air containing 20.90 % oxygen under a pressure of 760 mm of mercury.

Temp. °C	Dissolved Oxygen mg/L			Vapour pressure mm Hg	
	Chloride concentration in water mg/L		Difference per 100 mg chloride		
	0	5000			10000
0	14.6	13.8	13.0	0.017	5
1	14.2	13.4	12.6	0.016	5
2	13.8	13.1	12.3	0.015	5
3	13.5	12.7	12.0	0.015	6
4	13.1	12.4	11.7	0.014	6
5	12.8	12.1	11.4	0.014	7
6	12.5	11.8	11.1	0.014	7
7	12.2	11.5	10.9	0.013	8
8	11.9	11.2	10.6	0.013	8
9	11.6	11.0	10.4	0.012	9
10	11.3	10.7	10.1	0.012	9
11	11.1	10.5	9.9	0.011	10
12	10.8	10.3	9.7	0.011	11
13	10.6	10.1	9.5	0.011	11
14	10.4	9.9	9.3	0.010	12
15	10.2	9.7	9.1	0.010	13
16	10.0	9.5	9.0	0.010	14
17	9.7	9.3	8.8	0.010	15
18	9.5	9.1	8.6	0.009	16
19	9.4	8.9	8.5	0.009	17
20	9.2	8.7	8.3	0.009	18
21	9.0	8.6	8.1	0.009	19
22	8.8	8.4	8.0	0.008	20
23	8.7	8.3	7.9	0.008	21
24	8.5	8.1	7.7	0.008	22
25	8.4	8.0	7.6	0.008	24
26	8.2	7.8	7.4	0.008	25
27	8.1	7.7	7.3	0.008	27
28	7.9	7.5	7.1	0.008	28
29	7.8	7.4	7.0	0.008	30
30	7.6	7.3	6.9	0.008	32

### Example 1

Calculate the saturation DO level in water containing 600 mg/L chloride at 28°C and 710 mmHg barometric pressure. What is the percent saturation level if the DO content is 5.8 mg/L.

From Table 1, at 28°C for 0 mg/L Cl<sup>-</sup> concentration  
C<sub>s</sub> = 7.9 mg/L, the concentration decreases at the rate of 0.008 mg/L per 100 mg/L Cl<sup>-</sup>  
Therefore for 600 mg/L Cl<sup>-</sup>, C<sub>s</sub> = 7.9 – (0.008 x 6) = 7.85 mg/L

The table also gives saturated water vapour pressure as 28 mmHg

Therefore saturation value at 710 mmHg pressure

$$C_s' = 7.85 \times \frac{710 - 28}{760 - 28}$$
$$= 7.31 \text{ mg/L}$$

$$\text{Therefore saturation level} = \frac{5.8}{7.31} \times 100 = 79 \%$$

## 2. Collection and storage of samples

Aeration of water sample during collection should be avoided. This can be done with the use of DO samplers which allow ingress of water near the bottom of the sample bottle without causing bubbling of the air in the bottle as it is replaced by the sample. The bottle should have a tapered and pointed stopper to avoid entrapment of air bubbles while stoppering. A 300 mL capacity BOD bottle is quite suitable for this purpose. Figure 1 shows the construction of a DO sampler. The sampler with the bottles inside is quickly lowered to the desired depth and held there. As the water enters the sampler, air bubbles are formed at the air exit tube. After the bubble formation stops, the sampler is pulled up and the bottles are carefully stoppered and removed from the sampler. It may be noted that even if the sampler is lowered rapidly to the desired depth, a certain amount of water from the overlying layers will be included in the sample. However, since the bottle is allowed to overflow within the sampler space, the error would be negligible.

When samples are to be collected at large depths, samplers with mechanism to open the inlet port through a messenger weight sent from the surface are used.

The DO in the sample may be consumed by micro-organisms in the sample during storage and transport. The DO may also increase if algae are present in the water and the sample is stored in light. The DO, therefore, should be 'fixed' immediately after collection. This can be done by adding manganous sulphate, alkali-iodide-azide and sulphuric acid reagents in the manner described in the DO determination procedure.

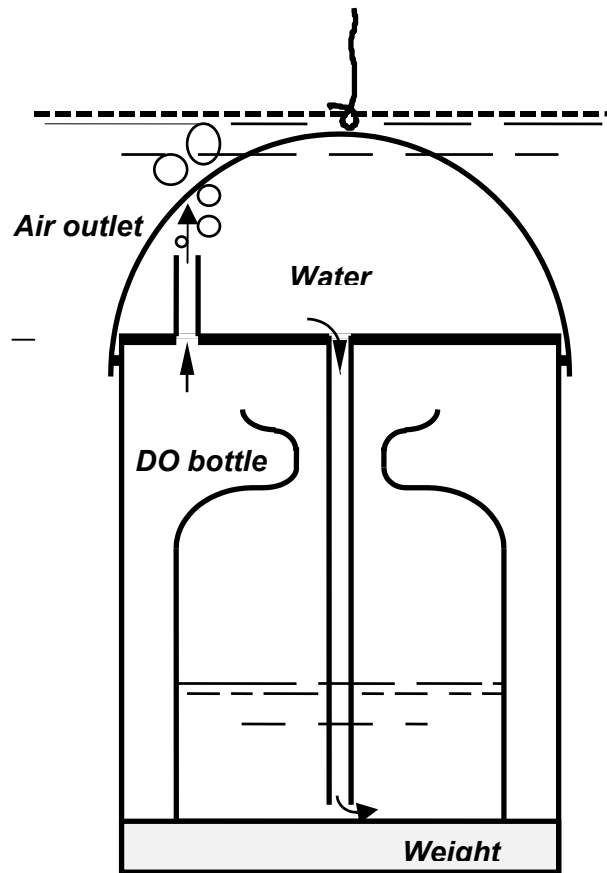


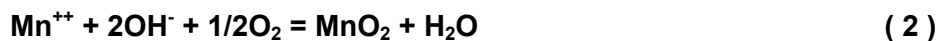
Figure 1 Dissolved oxygen sampler

### 3. Winkler method with azide modification

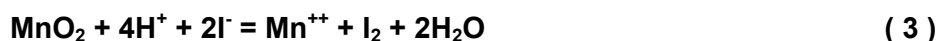
The method is based upon reactions that release iodine equivalent to the amount of oxygen originally present in the sample and titration of the liberated iodine. In the first step manganous sulphate and alkali iodide reagents are added. If no oxygen is present the manganous ion reacts only with the hydroxide ion to form a white precipitate of manganous hydroxide:



If oxygen is present the manganous ion is oxidised and brown precipitate of manganese dioxide is formed:



Upon addition of sulphuric acid iodine is formed by oxidation of iodide:



Sodium thiosulphate standard solution is used to titrate iodine



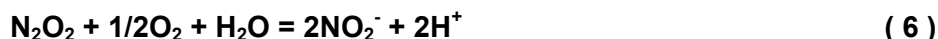
The end point of titration is obtained by first titrating iodine to a pale straw colour and then adding starch indicator which combines with iodine to give a blue colour. The titration is continued till the iodine complexed with starch is also reacted and the blue colour disappears.

Note that all the reagents except the standard solution are added in excess to ensure complete reactions.

Nitrites if present in the sample cause interference by oxidising iodide:



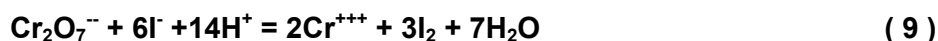
$\text{N}_2\text{O}_2$  in turn is oxidised by oxygen entering the sample during titration:



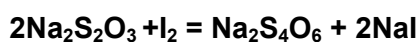
Thus it becomes impossible to reach a definite end point and high results are obtained. In the azide modification, sodium azide added with the alkali reagent destroys the nitrite, if present:



Sodium thiosulphate is a secondary standard. Because of its water of hydration it cannot be dried to a compound of definite composition. It also undergoes oxidation under storage. Therefore it is standardised against a primary standard, either dichromate or bi-iodate. Both react with iodide ion to release an equivalent amount of iodine:



The released iodine is titrated with sodium thiosulphate.



The reactions described above involve oxidation-reduction reactions. The valence number for the reactants in these reactions is equal to the number of electrons released or accepted by them. Since the equations are balanced, we can find the valence number from the number of electrons accepted by iodine or released by iodide in each reaction. One iodine atom is reduced to iodide upon acceptance of one electron. Thus the valence number for thiosulphate is 1, for dichromate and for bi-iodate it is 6, Equations (4), (9) and (10), respectively.