**Aim: - Determination of Dissolved Oxygen.**

**Theory**

**Introduction:-**

Atmospheric oxygen is not readily soluble in water. Its solubility is directly proportional to its partial pressure. ( for example, at a specific temperature such as 200C, with Henry’s law constant being 43.8 mg/l x atmosphere and partial pressure of oxygen being 0.2094 atmosphere at 1 atmosphere of air, DO saturation value = 43.8 ( mg/l x atm ) x 0.2094 (atm) = 9.17 mg/l )

DO saturation decreases with rise in temperature, decreases with rise in salt concentration, decreases with rise in altitude and decreases with rise in organic concentration.

**Table- Variation of DO with temperature (clean water at Zero altitude or 1 atmospheric pressure**

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Temperature, C** | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 |
| **DO**  **Saturation mg/l** | 14.62 | 12.80 | 11.33 | 10.15 | 9.17 | 8.38 | 7.63 | 7.0 | 6.6 | 6.1 | 5.6 |

**Table- Variation of DO with salt concentration**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Temp** | **Chloride Concentration in Water at 1 Atm.** | | | | |
| **0 mg/l** | **1000 mg/l** | **5000 mg/l** | **10000 mg/l** | **20000 mg/l** |
| 0C | **DO Saturation Value mg/l** | | | | |
| 0 | 14.62 | 14.46 | 13.80 | 12.97 | 11.32 |
| 10 | 11.33 | 11.21 | 10.74 | 10.73 | 8.98 |
| 20 | 9.17 | 9.08 | 8.73 | 8.30 | 7.86 |
| 30 | 7.63 | 7.56 | 7.26 | 6.86 | 6.49 |

Higher altitudes with lowered atmospheric pressures have a profound effect on the solubility of oxygen in water. The altitude h (m) of any place is being known the corresponding atmospheric pressure (p mm of mercury) can be obtained from the equation

h = (0.0109803) p2 – (26.88852) p + (14119.57)

DO saturation value, at particular atmospheric pressure p mm of mercury = DO saturation at 760 mm of mercury x (P – P0) / (760- P0)

Where P0 = vapour pressure at a specific temperature.

**Table- Variation of DO with altitude (clean water)**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Temp.  0C | P0  mm | Alt = 0 m | Alt = 500 m | Alt = 1000 m | Alt = 2000 m | Alt = 3000 m |
| p = 760 mm | p = 716 mm | p = 763 mm | p = 596 mm | p = 527 mm |
| DO saturation value mg/l | | | | |
| 0 | 5 | 14.62 | 13.77 | 12.94 | 11.44 | 10.11 |
| 5 | 7 | 12.80 | 12.05 | 11.32 | 10.01 | 8.72 |
| 10 | 9 | 11.33 | 10.67 | 10.02 | 8.86 | 7.82 |
| 15 | 13 | 10.15 | 9.55 | 8.97 | 7.92 | 6.98 |
| 20 | 18 | 9.17 | 8.63 | 8.10 | 7.14 | 6.29 |
| 25 | 24 | 8.38 | 7.88 | 7.48 | 6.46 | 5.73 |
| 30 | 32 | 7.63 | 7.17 | 6.72 | 5.91 | 5.19 |

**Note: DO determined at a particular place (known altitude) and at a specific temperature should not exceed its corresponding saturation value (unless condition super saturation exist)**

Decrease of DO with increase in organic concentration indicates pollutional load of receiving water bodies. This is of great significance to sanitary engineers.

Higher temperature, higher salt concentration, higher altitude and higher organic content have a compounding effect in drastically decreasing the solubility of oxygen in water. However these parameters rarely combine to produce the worst effect in nature.

**Importance of DO determination:-**

1. DO determination at various points along the river course are carried out to define pollution status of the river. DO level more than 3 mg/lit (or 40% saturation value) is desirable for the existence and growth of fish and such other forms of aquatic life (it is usual to fine DO in the range of 6 to 8 mg/lit normal flowing river water).
2. Do measurements are important for maintaining aerobic conditions in aerobic biological treatment units.
3. Determination of DO is the basis of the BOD test
4. DO values are used to control the corrosion of iron and steel distribution system and steam boilers.

**DO Fixation:-**

Many times, particularly while determining DO of the river water sample, it is no convenient to carry out the entire determination in the fields. As DO values change with time during transit (from the sampling site to the laboratory) because of variation in temperature and biological reactions, it is necessary to fix DO in the samples at the site at the time and temperature of collection.

DO fixation is done by adding 2 ml of Manganous Sulphate and 2 ml alkali iodide azide. For best results the Sample may be stored below 10 C during transit and titrated within 6 hours of fixation.

**DO determination:-**

**Principle:-**

For estimating of DO content in a sample, an iodide added to the sample is oxidized under acidic conditions to free iodine. The amount of free iodine liberated is equivalent to the amount of DO originally present in the sample. (The liberated iodine is estimated by titrating against standardized sodium thiosulphate using starch as an indicator).

The amount of free iodine estimated is a measure of DO in the sample.

**Standardization of Na2S2O3:-**

1. **Necessity:-**

For preparing a standard solution of sodium thiosuplhate, equivalent weight (equal to mol. wt) is obtained from the formulae Na2S2O35H2O. As water of hydration is lost under varying condition of temperature and humidity, the normality of sodium thiosulphate will not be exactly as calculated from its formulae.

Further, dilute Na2S2O3 on standing undergoes aerobic oxidation and also degradation by absorption of atmospheric CO2. Therefore for best results it is necessary to standardize a dilute titrant against a primary standard (such as K2Cr2O7) on the day of titration.

1. **Method of standardization using standard K2Cr2O7**
2. Place about 2 gm of KI in a conical flask.
3. Add 100 ml of distilled water (to suppress sublimation of iodine)
4. Add 10 ml of dilute sulphuric acid (prepared by taking 9 ml distilled water and 1 ml of concentrated H2SO4 to it)
5. Add 10ml of 0.025N K2Cr2O7
6. Add 100 ml of distilled water (to prevent masking of starch end point by greenish trivalent chromium ions)

6KI + 7H2SO4 + K2Cr2O7 Cr2(SO4)3 + 3I20 + 4K2SO4 + 7H2O

This is slow reaction. Wait for 5 minutes to allow all the dichromate added to react completely to release an equivalent amount of free iodine.

1. Titrate against the given (approx. 0.025 N) Na2S2O3 using starch as indicator (1 to 2 ml)
2. Record the volume of titrant used (V ml) upto the point when blue colour in the flsk just disappears.

Then – Na2S2O3  K2Cr2O7

N x V N1 x V1

Normality of titrant = N = =

This value of N should be used for determination of DO.

**Importance of azide in alkali - Iodide-Azide (Winkler’s azide modification)**

Azide is used to suppress nitrite ion interference samples of biologically treates sewage effluents, stagnant river water samples and incubated BOD samples generally contain nitrites. During DO determination when H2SO4 is added, nitrites convert iodide, to free iodine

2NaNO2 + 2Nal + 2H2SO4 N2O2 + I20 + 2H2O + 2Na2SO4

The reduced N2O2 is oxidized by atmospheric oxygen to nitrate again, with some of the first – reaction products entering the second reaction maintain equilibrium.

N2O2 + ½ O2 + H2O + Na2SO4 2NaNO2 + H2SO4

Thus the interfering nitrite is recycled, which liberates more free I20 and blue colour with starch. This is erroneously interpreted as due to the presence of high DO in the sample (even when there is none sometimes).

NaN3 + NaNO2 + H2SO4  N2 + N2O + H2O + Na2SO4

Interference due to Fe2+ aldehydes, ketones (and even NO2) can be removed by oxidizing the reducing agents by using excess of acidified KMnO4. Excess KMnO4 is reduced by potassium oxalate before DO determination.

**Significance of DO in Tap Water:-**

When residual chloride is present in tap water, chloride concentration being generally low, DO fluctuates with temperature and atmospheric pressures. However it has no sanitary significance.

When residual chlorine is absent in tap water, a low DO in the sample particularly below 4 mg/l suggest that water quality is suspect and aeration and disinfection are necessary.

**Procedure of Test**

**Step 1 – Sampling (Select any ONE)**

|  |  |
| --- | --- |
| **Flowing River GIF | Gfycat** | **ELEKTRA KB GIF - Find & Share on GIPHY** |
| **a) River** | **b) Ocean** |
|  |  |
| **c) Sewage** | **d) between the aeration tank and secondary clarifier** |

**Step 2 – Method of Sampling (Select any ONE)**

|  |  |  |
| --- | --- | --- |
| http://cr4.globalspec.com/PostImages/200902/swing_sampler_B8BAAC03-9A7D-4506-9815630D2FFCE05A.jpg | **http://water.me.vccs.edu/courses/env211/changes/composite.gif** | http://i.ytimg.com/vi/BF8c1hr2gmA/maxresdefault.jpg |
| **a) Grab sample** | **b) Compositing** | **c) Integrated** |

**Step 3 – Collecting Waste Water Sample (Select any ONE)**

|  |  |
| --- | --- |
| BÃ¼rkle Wide-Mouth Sampling Bottles with Tamper-Evident Safety Cap ... | Bod Bottle Stopper at Thomas Scientific |
| **a) Plastic bottle** | **b) DO bottle** |
| https://cdn.shopify.com/s/files/1/2407/1409/products/conical-flask-glass-1000-ml-pack-of-2-1000ml-100ml-250ml-500ml-50ml-laboratory-equipments-deal-laboratorydeal_999_1024x1024.jpg?v=1582066350 | Ambar Glass Transformer Oil Sampling Bottle, Size: 2500 ml, Rs 250 ... |
| **c) Conical Flask** | **d) Amber Glass** |

**Step 4 – DO Fixation at Site during Sample Collection (Select any ONE)**

**a) Alkali – iodide azide and Manganous Sulfate/Manganese (II) sulfate (MnSO₄)**

**b) Concentrated Sulphuric Acid**

**c) Potassium dichromate**

**Step 5 – To make acidic conditions which chemicals are been added**

|  |  |
| --- | --- |
|  |  |
| **a) Concentrated Sulphuric Acid** | **b) Concentrated Nitric Acid** |
| HYDROCHLORIC ACID | Guru Enterprises | Glacial Acetic Acid at Rs 45/kg | Acetic Acid | ID: 10666904888 |
| **c) Hydrocholric Acid** | **d) Acetic Acid** |

**Step 6 – Detection of DO presence**

|  |  |
| --- | --- |
|  |  |
| **a) white precipitation** | **b) brown precipitation** |

**Step 7 – Volume iodine solution in a conical flask**

**a) 200 ml b) 203 ml c) 204 ml d) 250 ml**

**Step 8 – Indicator used for titration**

|  |  |
| --- | --- |
|  | Eriochrome Black T - Wikipedia |
| **a) Starch Indicator** | **b) Eriochrome Black T** |

**Step 9 – When indicator is added, Initial Colour will be**

|  |  |
| --- | --- |
| Borosilicate Glass Erlenmeyer Flask, 250mL |  |
| **a) Orange** | **b) Blue** |

**Step 10 – Stop the titration at the end point, when the solution in the flask turns**

|  |  |
| --- | --- |
| Lab 7: Preparation of Oxygen | Erlenmeyer Flasks | Glass, Plastic | Fisher Scientific |
| **a) Colourless** | **b) Bluish Green** |

**Step 11 – Calculation of Dissolved Oxygen**

**The volume of titrant = 6 ml**

**Step 12- Write Conclusion**