



Trade Science Inc.

Environmental Science

An Indian Journal

Current Research Paper

ESAIJ, 3(3), 2008 [261-267]

A novel potentiometric technique to determine the dissolved oxygen (DO) and biological oxygen demand (BOD) of river, Lake and industrial waste water

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Received: 30th March, 2008 ; Accepted: 4th April, 2008

ABSTRACT

Generally, dissolved oxygen (DO) and biological oxygen demand (BOD) of waste water sample are determined at a particular temperature by the well known Winkler's volumetric method. The DO of water can also be determined by membrane electrodes (Clarke method), polarographic, galvanic type and luminescent optode methods; and each technique measurement has its own limitations. In the present investigation, we have used new potentiometric technique to determine the DO and BOD of lakes, ponds, rivers and industrial waste waters. The technique is simple and inexpensive and the results obtained are comparable to any other methods and are highly reproducible; and is need of the day for environmental monitoring of waters. © 2008 Trade Science Inc. - INDIA

KEYWORDS

Dissolved oxygen;
Biological oxygen demand;
Winkler's Method;
Mn²⁺ state;
Analyte;
Indicator platinum electrode.

INTRODUCTION

Winkler's iodometric method^[1] has undergone various modifications for DO analysis to eliminate or minimize effects of interferences; nevertheless, the method still is inapplicable to a variety of industrial and domestic wastewaters^[2]. Moreover, the iodometric method is not suited for field testing and cannot be adapted easily for continuous monitoring or for DO determinations in situ.

Polarographic methods using the dropping mercury electrode or the rotating platinum electrode have not been reliable always for the DO analysis in domestic and industrial wastewaters because impurities in the test solution can cause electrode poisoning or other interferences^[3,4]. With membrane covered electrode systems these problems are minimized, because the sens-

ing electrode is protected by an oxygen-permeable plastic membrane that serves as a diffusion barrier against impurities^[6-8]. Under steady-state conditions the current is directly proportional to the DO concentration^[7].

Polarographic^[5,6] as well as the galvanic^[7] type membrane electrodes are being used for DO measurements in lakes and reservoirs^[9,10] for stream survey and control of industrial effluents^[11,12], for continuous monitoring of DO in activated sludge units^[13] and for estuarine and oceanographic studies^[14]. Being completely submersible, membrane electrodes are suited for analysis in situ. Their portability and ease of operation and maintenance make them particularly convenient for field applications. In laboratory investigations, membrane electrodes have been used for continuous DO analysis in bacterial cultures, including the BOD test^[7,15].

Membrane electrodes provide a good method for

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DO analysis in polluted waters, highly colored waters, and strong waste effluents. They are recommended for use especially under conditions that are unfavorable for use of the iodometric method, or when that test and its modifications are subject to serious errors caused by interferences.

Oxygen-sensitive membrane electrodes of the polarographic^[5,6] or galvanic type^[7] are composed of two solid metal electrodes in contact with supporting electrolyte separated from the test solution by a selective membrane. The basic difference between the galvanic and the polarographic systems is that in the former the electrode reaction is spontaneous (similar to that in a fuel cell), while in the latter an external source of applied voltage is needed to polarize the indicator electrode. Polyethylene and fluorocarbon membranes are used commonly because they are permeable to molecular oxygen and are relatively rugged. In all these instruments the "diffusion current" is linearly proportional to the concentration of molecular oxygen. The current can be converted easily to concentration units (e.g., milligrams per liter) by a number of calibration procedures.

Over the years a number of methods for dissolved oxygen determination have been developed. These methods have been found to vary widely in their sensitivity, susceptibility to electrode poisoning by the presence of undesirable compounds, and, in some instances, sensitivity to a slow flowing or static aqueous media. Some methods require a very clean sample, devoid of extraneous chemical compounds, but only a few are adaptable to continuous on-line measurement.

Compared to the photometric and amperometric end point detection, little attention has been paid to the potentiometric detection for use in titration probably because the electrochemical equilibrium at the platinum indicator electrode is considered to be established slowly and it is difficult to detect iodine at low concentration of 10^{-6} N. However, since potentiometry is simple, convenient and generally precise, it seems worthwhile exploiting potentiality of the potentiometric analysis.

In the present paper, we are indicating that the basic principle of Winkler's redox reactions can be successfully considered for an electro-chemical cell in potentiometric analysis to determine DO and BOD of water samples. The DO and BOD measurement through the electrode potentials and the Winkler's volumetric

titre values are determined in this two-in-one cell set up which has a magnetic bead stirrer provision for continuous mixing after the addition of titrant.

EXPERIMENTAL

One of the most useful titrations involving iodine is that originally developed by Winkler¹ to determine the amount of oxygen in samples of water. The dissolved oxygen content is not only important with respect to the species of aquatic life which can survive in the water, but is also a measure of its ability to oxidise organic impurities in the water.

Basic principle of determination of DO in water by potentiometric technique:

Electrochemical set up

In the present investigation of DO analysis of water by potentiometric technique, an electro-chemical cell is constructed with a redox potential indicator electrode, as given

Hg/Hg₂Cl₂/KCl (Satd) // Redox analyte/Pt
(reference electrode) (Indicator electrode)

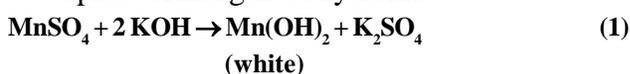
The emf of the cell, $E_{\text{cell}} = [E_{\text{Indi}} - E_{\text{ref}}]$
 $= E_{\text{Indi}} - 0.2422$.

Therefore, $E_{\text{Indi}} = E_{\text{cell}} + 0.2422$

Where, E_{ref} is a saturated calomel electrode of constant potential, 0.2422 Volts.

In the present potentiometric technique of investigation, the redox chemistry of reactions of only two stages of Winkler's¹ method are given prime importance to estimate the DO and BOD of water. The Winkler¹ reactions are as follows sequentially:

(i) Manganous sulfate reacts with the potassium hydroxide at p^H 12.0 to produce a white flocculent precipitate of manganous hydroxide:

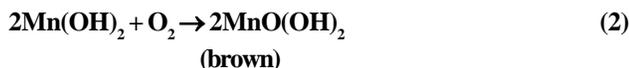


(ii) If there is any DO in the water, a second reaction



Figure 1: An electrochemical cell for DO measurement in water bodies

between the $\text{Mn}(\text{OH})_2$ and DO occurs immediately to form a brownish manganic oxide precipitate.



(iii) After the quantitative conversion of Mn^{2+} to Mn^{4+} state, a requisite amount of H_2SO_4 (1:1 sulphuric acid) is added at $\text{p}^{\text{H}} = 1.0 - 2.0$ to dissolve completely the brownish precipitate with continuous swirling with the help of magnetic stirrer. Manganic sulphate, $\text{Mn}(\text{SO}_4)_2$, is the product of this reaction.

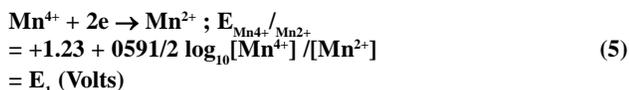


From step (iii) of reaction, it can be realized that Mn^{2+} reacts with an equivalent amount of dissolved oxygen and gets oxidized to Mn^{4+} state quantitatively. This gives rise to a steady potential at the platinum indicator electrode which can be recorded using a digital potentiometer.

The standard oxidation potential of the indicator electrode, Pt/ $\text{Mn}^{2+}; \text{Mn}^{4+}$, for 1M MnSO_4 solution is

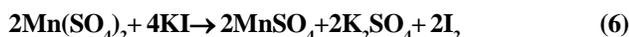


However, for particular $\text{Mn}^{2+}/\text{Mn}^{4+}$ concentration, we have the Nernst expression for reduction electrode potential (by Convention) at the Pt indicator electrode as

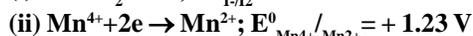
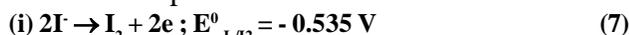


After the addition of requisite amount of KI solution, the measured equilibrium reduction potential (E_2) for overall redox reaction (5) at the indicator electrode can be explained as follows: Potassium iodide reduces Mn^{4+} to Mn^{2+} ions and I ions gets oxidized to iodine and the number of moles of iodine liberated is exactly equivalent to the number of moles of dissolved oxygen present in the water sample.

The release of iodine (I_2) imparts a brown coloration to water.



The redox reaction (6) takes place spontaneously at the platinum indicator electrode of the cell and a resultant potential is developed at the indicator electrode for these competitive reactions as mentioned below



The net redox electrode reaction can be thus represented as



Where 2I^- is oxidized to I_2 , and Mn^{4+} gets reduced to Mn^{2+} in solution.

The resultant potential (E_2) established at the Pt electrode is

$$E_{\text{redox}} = [E_{\text{Mn}^{4+}/\text{Mn}^{2+}} - E_{\text{I}^-/\text{I}_2}] = E_{\text{Resultant}} = E_2 \text{ (volts)} \quad (9)$$

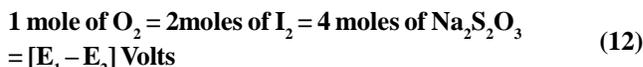
where

$$E_{\text{redox}} = \left| 1.23 + \frac{0.591}{2} \log_{10} \left[\frac{[\text{Mn}^{4+}]}{[\text{Mn}^{2+}]} \right] - \left[0.535 + \frac{0.591}{2} \log_{10} \left[\frac{[\text{I}_2]}{[\text{I}^-]^2} \right] \right| \quad (10)$$

$$\begin{aligned} E_{\text{redox}} &= [1.23 - 0.535] - \frac{0.591}{2} \log_{10} \frac{[\text{Mn}^{4+}][\text{I}^-]^2}{[\text{Mn}^{2+}][\text{I}_2]} \\ &= E_2 \text{ (volts)} \end{aligned} \quad (11)$$

The quantitative conversion of Mn^{4+} to Mn^{2+} is stoichiometrically equivalent to the amount of I_2 liberated; which is exactly equivalent to the number of moles of dissolved oxygen present in the water sample.

Therefore, based on the above stoichiometric relationship of reaction, one can arrive at the following quantitative relationship:



The present potentiometric technique of investigation of DO and BOD is based on this stoichiometric relationship.

Procedure

1. Preparation of standard MnSO_4 solution for DO calibration plot:

Theoretically, it is possible to calculate the stoichiometric amount of MnSO_4 needed to react with an equivalent amount of dissolved oxygen (DO mg/L) from step (ii) of winkler's method; and accordingly, different stan-

TABLE 1: Weight of MnSO_4 * equivalent to DO in water

| O_2/mgL | Weight equivalent to DO: (mg/250ml) MnSO_4 |
|-------------------------|---|
| 1 | 2.6410 |
| 2 | 5.2813 |
| 3 | 7.9313 |
| 4 | 10.5625 |
| 5 | 13.2033 |
| 6 | 15.8438 |
| 7 | 18.4850 |
| 8 | 21.1250 |
| 9 | 23.7656 |
| 10 | 26.4063 |

*M.W = 169.00

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standard manganous sulphate solutions are prepared for calibration DO plot as given in TABLE 1.

(Note: all the solutions are to be prepared in water sample containing DO to obtain a linear calibration plot; and are to be preserved in a closed bottles at constant temperature.

2. A calomel reference and an indicator Pt -electrodes are inserted into a closed glass container/cell. A thermometer is also inserted to record the temperature of the DO water sample. A combined glass electrode is inserted to control the desired p^H of the solution. 25ml of the prepared stock solution (TABLE 1) carefully pipetted out into the cell containing the electrodes set up.
3. The electrodes are connected to a digital potentiometer.
4. Magnetic stirrer is used to obtain homogeneous mixing of reagents
5. 0.5ml of 4N NaOH is added ($p^H = 12.0$) and solu-

tion is kept for 10-15 minutes.

6. 6.0 ml of 1:1 H_2SO_4 is introduced to the cell and kept for 15-20 minutes with continuous swirling of solution with the help of magnetic stirrer.(Note : $p^H = 1.0 - 2.0$).
7. The equilibrium potential (E_1 mv) of the indicator electrode recorded using a potentiometer.
8. Then, 4.0ml of 10% KI solution is added into the cell having the electrodes kept for another 10 -15 minutes with solution swirling and record the steady electrode potential (E_2 mv) using potentiometer.
9. The difference between E_1 and E_2 is noted and is given in TABLE 2 for a particular standard $MnSO_4$ solution from among the prepared series of solutions. It can be observed that stoichiometry as given in equation (11) holds good for the determination of DO of water sample by potentiometric analysis (TABLE 2).

10. Potentiometric analysis data

TABLE 2: Calibration data for [$E_1 - E_2$] mv and the dissolved oxygen

| Weight of $MnSO_4$ / 250ml 'g' | Emf (mv) $MnSO_4$ solution | Emf (mv) after the addition of NaOH | Emf (mv) after the addition of 1:1 H_2SO_4 E_1 | Emf (mv) after the addition of KI E_2 | $E_1 - E_2$ (mv) | Dissolved oxygen (DO) mg/L |
|--------------------------------|----------------------------|-------------------------------------|--|---|------------------|----------------------------|
| 0.0212 | 203 | -80 | 890 | 260 | 710 | 8 |
| 0.0189 | 181 | -68 | 889 | 261 | 690 | 7 |
| 0.0159 | 148 | -20 | 892 | 240 | 670 | 6 |
| 0.0132 | 114 | 0 | 890 | 242 | 648 | 5 |
| 0.0106 | 128 | -4 | 872 | 246 | 630 | 4 |
| 0.0079 | - | 15 | 865 | 241 | 610 | 3 |

TABLE 3: Potentiometric analysis data for dissolved oxygen (DO) at lab temperature

| Weight of $MnSO_4$ /250ml 'g' | Indicator electrode potential $Mn^{2+} \rightarrow Mn^{4+} + 2e$ E_1 (mv) | Indicator electrode potential $2Mn^{2+} + 4I^- \rightarrow Mn^{2+} + 2I_2$ E_2 (mv) | Emf equivalent to $DO = E_1 - E_2$ (mv) | Dissolved oxygen (DO)mg/L |
|-------------------------------|---|---|---|---------------------------|
| 0.0212 | 970 | 260 | 710 | 8 |
| 0.0189 | 951 | 261 | 690 | 7 |
| 0.0159 | 910 | 240 | 670 | 6 |
| 0.0132 | 892 | 242 | 650 | 5 |
| 0.0106 | 876 | 246 | 630 | 4 |
| 0.0079 | 851 | 241 | 610 | 3 |

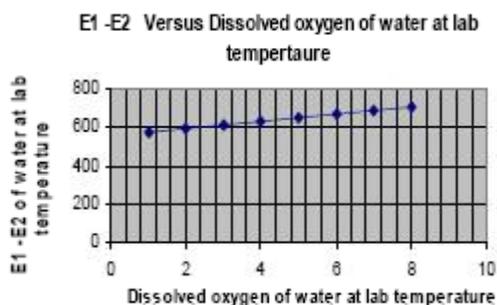


Figure 2: A calibration plot for DO measurement for BOD

11. 1st day DO determination from graph :

[$E_1 - E_2$] of 1st day water is noted from the results as D_1 from graph (figure 3).

12. 5th Day DO measurement

25 ml of unknown DO sample + add 0.0265g of $MnSO_4 \cdot H_2O$ [Molecular Weight=169] + 0.5 ml of NaOH- keep for 10-15 minutes + Add 6.0 ml of 1:1 H_2SO_4 + dissolve the precipitate - keep for 15 minutes and record its E_1 value. Add 4.0 ml of KI

and take E_2 value after 10 minutes. Find the difference, $[E_1 - E_2]$ for the sample.

- 5th day DO value of the water sample is obtained from the calibration graph (figure 3).

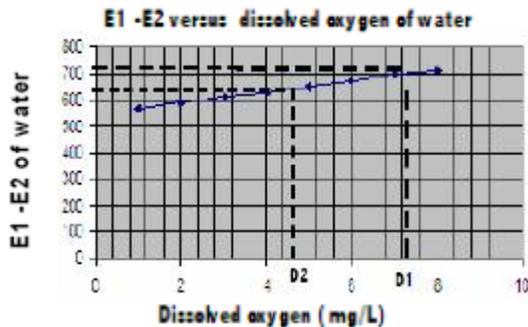


Figure 3: A plot of DO (mg/L) vs E_1, E_2 (mv) for BOD

Winkler’s Titration

14. The estimated DO and BOD of water samples from potentiometric analysis are further corroborated by results of Winkler’s titration values obtained in the same two-in-one cell for all the prepared $MnSO_4$ solutions. All the $MnSO_4$ solutions (TABLE 1) are then titrated in the same cell set up itself as given:

25 ml of water containing DO is pipetted out into the cell. The procedure as mentioned for potentiometric analysis is followed for Winkler’s titration in the cell, too. A burette filled with standard $Na_2S_2O_3$ solution is inserted into the cell as shown in the figure 4. The swirling sample is then titrated to a pale, straw colour, After recording E_2 (mv) value using a potentiometer, 1ml of freshly prepared starch is added and titrated against standard (0.005N) $Na_2S_2O_3$ solution.



Figure 4: An electrochemical set up for Winkler’s iodometric titration in the same cell set up

When blue colour of the solution of the cell disappears with addition of last drop of $Na_2S_2O_3$ solution, the end point of the titration is recorded as V ml.(TABLE 4).

TABLE 4 : Dissolved oxygen by Winkler’s method

| S.no | Weight of $MnSO_4$ g | Volume of thiosulphate consumed,ml | DO of water samples Mg/L |
|------|----------------------|------------------------------------|--------------------------|
| 1 | 0.0212 | 4.6 | 7.68 |
| 2 | 0.0189 | 3.9 | 6.4 |
| 3 | 0.0159 | 3.7 | 6.0 |
| 4 | 0.0132 | 3.3 | 5.4 |
| 5 | 0.0106 | 2.1 | 3.4 |
| 6 | 0.0079 | 1.5 | 2.4 |

TABLE 5: BOD of Madivala lake water by potentiometric analysis at lab temperature

| Weight of $MnSO_4/250ml$ ‘g’ | E_1-E_2 mv 1 st day | $E_1 -E_2$, 5 th day | Dissolved oxygen Fro graph D_1 mg/L | Dissolved oxygen From graph D_2 mg/L | BOD= $D_1 - D_2/P$ mg/L |
|------------------------------|----------------------------------|----------------------------------|---------------------------------------|--|-------------------------|
| 0.0212 | 703 | 656 | 7.60 | 4.50 | 31.6 |

1 mole of $O_2 = 2$ moles of $I_2 = 4$ moles of $Na_2S_2O_3$
 1mol of $Na_2S_2O_3 = 1/4^{th}$ mole of $O_2 = 8g$ of O_2
 1ml of 1N $Na_2S_2O_3 = 8$ mg O_2/L
 ‘V’ ml of 0.005N $Na_2S_2O_3 = 8 \times V \times 0.0051N$
 \therefore D.O of water sample =

$$\frac{8 \times \text{Titre Vol} \times 0.005N \times 1000}{25} \text{ } 22^\circ C$$

Therefore.

1. D.O of water sample \equiv

$$\frac{8 \times \text{Vol} \times 0.005N \times 1000}{25} \text{ at } 22^\circ C$$

2. BOD of water sample at lab temperature

- Determine the DO of waste water on 1st day(D_1) at lab($20^\circ C$) temperature
- Determine the DO of the same waste water on the 5th day(D_2) at $20^\circ C$

Volume of dilution, $P = 25/250$
 $= 0.1$

Therefore

BOD of water sample = $\frac{D_1 - D_2}{P}$

TABLE 6 : BOD of Madivala lake water by Winkler’s method at lab temperature

| Weight of $MnSO_4/250ml$ ‘g’ | Volume of 0.0051N Thiosulphate consumed, ml. 1 st day | Volume of 0.0051N Thiosulphate consumed, ml. 5 th day | Dissolved oxygen D_1 mg/L | Dissolved oxygen D_2 mg/L | BOD= $D_1 - D_2/P$ mg/L |
|------------------------------|--|--|-----------------------------|-----------------------------|-------------------------|
| 0.0212 | 19.2 | 11.3 | 7.68 | 4.52 | 31.6 |

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RESULTS AND DISCUSSION

The determination of dissolved oxygen (DO) and Biological oxygen demand (BOD) of water/waste waters are always confined to conventional techniques like Winkler's^[1] titrimetry, Oxygen membrane^[5], Amperometric membrane^[5], polarographic^[5,6], Galvanic cell^[6-8] and luminescence optode methods. The results of analysis of these techniques have their own merits and demerits. The present investigation highlights a novel potentiometric technique successfully to determine the DO and BOD; and COD of waste water samples for the first time.

In the present methodology of determination of DO and BOD of water samples, the stoichiometry of Winkler's^[1] reactions (5) and (7) are given prime importance. Accordingly, stoichiometric amounts of MnSO_4 react with NaOH at alkaline condition ($\text{pH} > 12$) to produce a white flocculent precipitate of manganous hydroxide (equation 1).

If there is any DO in the water, a second reaction between the $\text{Mn}(\text{OH})_2$ and equivalent amount of dissolved oxygen (DO) occurs spontaneously to form a brownish manganic sulphate precipitate, $\text{Mn}(\text{SO}_4)_2$, (Equation 2).

The weight of MnSO_4 to DO relationship is given in TABLE 1. In the present investigation, an exact amount of MnSO_4 as given in TABLE 1 is dissolved in 250ml of water and different such solutions are prepared by taking different amounts of MnSO_4 for DO calibration plot (figure 1). The equilibrium electrode potential values (mv) of the indicator electrode against a standard calomel reference electrode are recorded at the beginning for MnSO_4 solutions; and as well, after the addition of requisite amounts of NaOH , 1:1 H_2SO_4 , KI solutions as precisely as stated elsewhere in the procedure.

It is evident from equation (3) that Mn^{2+} in solution is quantitatively transformed to Mn^{4+} state in alkaline condition by reacting with an equivalent amount of dissolved oxygen from water. The equilibrium potential value (E_1) of the indicator electrode is recorded, which is due to the presence of free quantitatively converted Mn^{4+} ions in solution after the addition of 1:1 H_2SO_4 acid. The observed equilibrium potential (E_2) value of the solution is due to the presence of quantitatively formed Mn^{2+} ions from Mn^{4+} state after the redox reactions with the addition of 10% KI solution.

Interestingly, Bharath N and Palanna O.G^[16] have shown a quantitative relationship (equation -11) between the difference of these two potential values [$E_1 - E_2$] (mv) is related to an equivalent amount of dissolved oxygen (DO) present in water samples for solutions prepared as given in TABLE 1. The below mentioned techniques of analysis justifies the relationship of equation-11.

- potentiometric technique of DO analysis and
- Winkler's titrimetric technique.

In the present work, we have adopted both these techniques of DO analysis using the same two-in-one cell set up (figures 1 and 4). Experimentally, the amount of iodine liberated due to redox reaction (8) is titrated against standard $\text{Na}_2\text{S}_2\text{O}_3$ and the amount dissolved oxygen (mg/L) is evaluated.

Curiously enough, it is observed in potentiometric analysis that the observed [$E_1 - E_2$] millivolts of the redox reactions (4) and (8) are found to be quantitatively related to the amount dissolved oxygen (mg/L) present water at laboratory temperature (TABLE 3).

A linear plot is obtained when [$E_1 - E_2$] millivolts of redox reactions (5) and (9) plotted against DO mg/L at laboratory temperature (figure 2). This linear plot is identified as the calibration plot for DO determination. If [$E_1 - E_2$] millivolts for a unknown water sample is measured, it is possible to report the DO of water at laboratory temperature from the graph (figure 3). The potentiometric technique of DO analysis of water determination is unique, which was adopted by Bharath N and Palanna O.G to determine DO of water (communicated to Indian Patent 2007) for the first time; and is also successfully adopted again for the determination of DO and BOD of waste water (Madival lake) sample in the present work. The data obtained from potentiometric analysis is further corroborated by the investigation of the samples of water by Winkler's titrimetric method (TABLE 4). A notable feature of the present investigation is that one can record simultaneously both [E_1 , millivolts] by a potentiometric technique and the end point volume (ml) of Standard thiosulphate by Winkler's titrimetry; wherein the liberated iodine is titrated against standard sodium thiosulphate solution using starch as an indicator.

The Dissolved oxygen (DO) obtained by these techniques are comparable to any known techniques^[6-8] of analysis and the results are reproducible with great success. Moreover, the present technique is simple, unique, easy to handle and inexpensive to determine the DO

and BOD of water samples.

These encouraging results of DO of water determination has prompted us to investigate the BOD of waste water samples, too. As described in the procedure, the dissolved oxygen (D_1) of waste water sample at laboratory temperature is evaluated on the same day (Ist day) soon after the collection of sample of water and carefully introduced into a closed cell for DO data in a set up as shown in figure 3; and equilibrium potential values E_1 and E_2 are recorded as usual for the waste water sample. The difference [$E_1 - E_2$] millivolts for the waste water (Madivala lake) sample is noted. From graph (figure 3), DO of waste water is noted for the corresponding value of [$E_1 - E_2$] millivolts. This is referred to as D_1 (mg/L) of waste water on the first day of investigation. The same waste water sample is isolated and kept in a closed container at constant temperature ; and DO of this waste water sample is similarly obtained by noting [$E_1 - E_2$] millivolts on the 5th day and recorded as D_2 (mg/L) from the figure 3. The BOD of the waste water (madivala lake) sample at the temperature is calculated thus:

25ml of waste water (Madivala) sample is diluted to 250 ml and 25 ml this waste water is taken for DO and BOD measurements of Madival lake water.

$$\text{Volume fraction, } P = \frac{25}{250} = 0.1$$

- (i). Draw a line horizontally for [$E_1 - E_2$] mv on the DO calibration graph of water for the Ist day and note the corresponding value of D_1 .
- (ii). Draw a line horizontally for [$E_1 - E_2$] mv on the DO calibration graph of water corresponding to the 5th day and note the corresponding value of D_2
- (iii). Find the difference $D_1 - D_2$ from graph (figure 3)

The BOD of waste water (Madivala lake) is calculated thus

$$\text{BOD}_5 = \frac{D_1 - D_2}{P}$$

The BOD of Madivala lake water measured by potentiometric analysis is 31.6 mg/L (TABLE 5) at the laboratory temperature. Since the above electrochemical set up has two-in-one provision, BOD₅ of madivala lake waste water is also simultaneously obtained as 31.6 mg/L by Winkler's titration method. The values of BOD₅ obtained from these two techniques of analysis are in excellent agreement (TABLES 5 and 6) pointing out that potentiometric analysis as a valid technique for the determination of BOD of any waste water sample.

ACKNOWLEDGMENTS

We are very much indebted and grateful to Prof M.R.Holla, Director, for his stimulating encouragement and the permission to carry out this work in the laboratory. I profusely thank with gratitude to Prof Dr H N Shivashanker, Principal, RNSIT for his untiring encouragement through out this investigation. we thank sincerely, H.C.Anandamurthy and Dr Subha Ramesh, departmental colleagues for their valuable help and involvement.

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