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Determination of Dissolved Oxygen in Polluted Waters

By

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Abstract

Winkler, Miller, and polarographic methods for the determination of dissolved oxygen in polluted waters have been critically studied. With waters highly polluted with organic matter, only the polarographic method gives reliable results. It was shown polarographically that the waste from a paper-pulp mill contained much dissolved oxygen though little oxygen could be detected by the other methods.

Introduction

With never-ceasing expansion of industries in recent years, water pollution problems have become of increasing importance in many respects. Among the wastes, those containing much organic matter are of special concern because organic matter undergoes biochemical oxidation in receiving waters and believed to cause dissolved-oxygen deficiency exerting vital effects on fish lives.

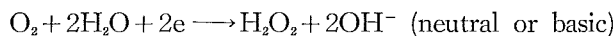
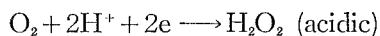
Determination of dissolved oxygen (D.O.) and of biochemical oxygen demand (B.O.D.) is, therefore, regarded as the most reliable method of evaluating the strength of polluted water. However, accurate determination of D.O. is difficult when the water is highly polluted with organic matter. Consequently, uncertainty is involved in the determination of B.O.D., since the latter is obtained from the decrease in the concentration of D.O..

Winkler method¹⁾ is used in most works for the determination of D.O. in surface waters. However, this method is not accurate when applied to polluted waters since organic matter, nitrites and iron salts interfere with the determination. Although several modifications²⁾ have been proposed to reduce or minimize these interferences, most of them are time-consuming and seem to be of no practical importance. Only one exception is the Alsterberg modification involving the decomposition of nitrites by sodium azide. Since the Winkler method involves iodometric titration, it will be easily understood that certain organic compounds capable of reacting with iodine interfere with this

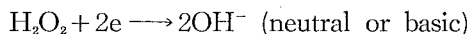
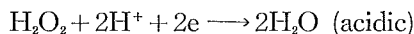
method.

Miller method⁹⁾ is widely used in Japan for the examination of sewages. Although less interferences are encountered with this method, it is also troublesome because titration must be carried out avoiding the contact with air.

On the other hand, voltametric methods,⁴⁻¹⁵⁾ such as the polarographic one, have been developed recently in place of the chemical methods and reported to have many advantages. The voltametric methods are based on the electrochemical reduction of dissolved oxygen at the indicator electrode. The reduction of dissolved oxygen takes place in two stages. The first stage results from reduction to hydrogen peroxide:



and the second corresponds to the reduction of the hydrogen peroxide either to water or hydroxyl ion depending on pH:



The first wave appears at a potential of -0.1 to -0.5 v. and the second at -0.5 to -1.3 v. *vs.* saturated calomel electrode. The rotating platinum^{4,7,10)} or the dropping mercury^{5,6,8,10,13-15)} is most widely used as indicator electrode. Mercury pool or saturated calomel electrode is usually employed as reference electrode. Other electrode systems have also been described in the literature.⁸⁻¹²⁾

A portable D.O.-meter with a dropping mercury electrode was constructed in the present investigation and applied to the examination of several kinds of waters containing much organic matter. Comparisons with the chemical methods indicated that D.O. in polluted water can best be determined by the polarographic method, which is applicable even when the chemical methods are inapplicable because of interferences with organic matter.

Experimental

I. Polarographic Determination of D.O.

Apparatus

A portable D.O.-meter was constructed as shown in Fig. 1 and used in the field tests. The applied potential was measured with Horiba Model H 3 pH-meter, which eliminated the correction for the IR drop across the microammeter. Yanagimoto D.O.-meter was used in the laboratory experiments.

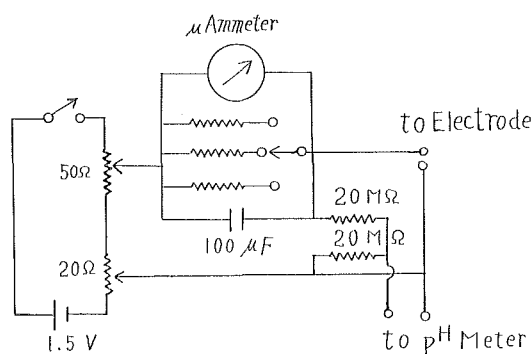


Fig. 1. Portable D.O.-Meter

Reagents

(1) Buffer solution (pH 8).—Dissolve 32 g. of NH_4Cl and 20 g. of KCl in a small volume of water; add 1 ml. of conc. NH_4OH and dilute to 200 ml. with distilled water.

(2) Thymol blue solution.—Dissolve 0.1 g. of thymol blue in 5 ml. of ethanol and dilute to 100 ml.

(3) Sodium sulfite solution.—Freshly prepared, saturated solution.

(4) H_2 gas.—Prepare by electrolysis.

Procedure

Take 1 drop of thymol blue and 0.5 ml. of buffer in a polarographic cell. Insert the dropping mercury electrode in the cell in such a way that the end of the electrode is located 2 cm. below the water level when sample is added. Take 10 ml. of sample in the cell by flowing down on the walls. Read the diffusion current at 0.6 v. vs. mercury pool.

It is advisable to calculate the D.O. content from measurements of diffusion current before and after saturation of sample with air, since fine adjustment of drop-time of mercury is difficult in the field tests. Water is easily saturated with air by taking one-fourth fill of it in a small stoppered bottle and by shaking vigorously for 20–30 seconds. Effect of shaking time on the dissolution of oxygen into D.O.-deficient water is

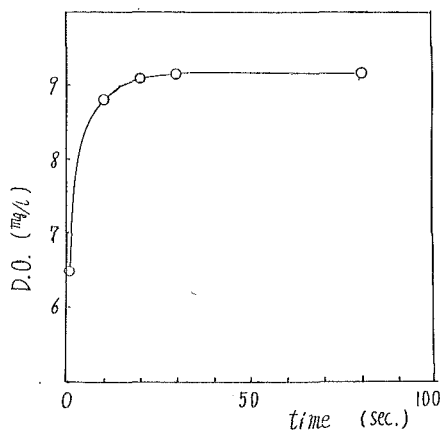


Fig. 2. Effect of shaking time on the dissolution of oxygen

shown in Fig. 2.

The solubility of oxygen at various temperatures and salt concentrations is shown in Table I,¹⁶⁾ and was used in the calculation of D.O. concentration.

Current-voltage curve was obtained in various buffer systems. The results,

TABLE I. Solubility of Oxygen in Fresh Water and in Sea Water.¹⁶⁾

| C° | Chlorides in Sea Water (parts per million) | | | | | Difference per 100 ppm Cl | Dissolved Oxygen in Chloride-free Water | |
|----|-------------------------------------------------|-------|-------|-------|-------|---------------------------|-----------------------------------------|-----|
| | 0 | 5000 | 10000 | 15000 | 20000 | | C° | ppm |
| °C | Dissolved oxygen in parts per million by weight | | | | | ppm | C° | ppm |
| 0 | 14.62 | 13.79 | 12.97 | 12.14 | 11.32 | 0.0165 | 30 | 7.6 |
| 1 | 14.23 | 13.41 | 12.61 | 11.82 | 11.03 | .0160 | 31 | 7.5 |
| 2 | 13.84 | 13.05 | 12.28 | 11.52 | 10.76 | .0154 | 32 | 7.4 |
| 3 | 13.48 | 12.72 | 11.98 | 11.24 | 10.50 | .0149 | 33 | 7.3 |
| 4 | 13.13 | 12.41 | 11.69 | 10.97 | 10.25 | .0144 | 34 | 7.2 |
| 5 | 12.80 | 12.09 | 11.39 | 10.70 | 10.01 | .0140 | 35 | 7.1 |
| 6 | 12.48 | 11.79 | 11.12 | 10.45 | 9.78 | .0135 | 36 | 7.0 |
| 7 | 12.17 | 11.51 | 10.85 | 10.21 | 9.57 | .0130 | 37 | 6.9 |
| 8 | 11.87 | 11.24 | 10.61 | 9.98 | 9.36 | .0125 | 38 | 6.8 |
| 9 | 11.59 | 10.97 | 10.36 | 9.76 | 9.17 | .0121 | 39 | 6.7 |
| 10 | 11.33 | 10.73 | 10.13 | 9.55 | 8.98 | .0118 | 40 | 6.6 |
| 11 | 11.08 | 10.49 | 9.92 | 9.35 | 8.80 | .0114 | 41 | 6.5 |
| 12 | 10.83 | 10.28 | 9.72 | 9.17 | 8.62 | .0110 | 42 | 6.4 |
| 13 | 10.60 | 10.05 | 9.52 | 8.98 | 8.46 | .0107 | 43 | 6.3 |
| 14 | 10.37 | 9.85 | 9.32 | 8.80 | 8.30 | .0104 | 44 | 6.2 |
| 15 | 10.15 | 9.65 | 9.14 | 8.63 | 8.14 | .0100 | 45 | 6.1 |
| 16 | 9.95 | 9.46 | 8.96 | 8.47 | 7.99 | .0098 | 46 | 6.0 |
| 17 | 9.74 | 9.26 | 8.78 | 8.30 | 7.84 | .0095 | 47 | 5.9 |
| 18 | 9.54 | 9.07 | 8.62 | 8.15 | 7.70 | .0092 | 48 | 5.8 |
| 19 | 9.35 | 8.89 | 8.45 | 8.00 | 7.56 | .0089 | 49 | 5.7 |
| 20 | 9.17 | 8.73 | 8.30 | 7.86 | 7.42 | .0088 | 50 | 5.6 |
| 21 | 8.99 | 8.57 | 8.14 | 7.71 | 7.28 | .0086 | | |
| 22 | 8.83 | 8.42 | 7.99 | 7.57 | 7.14 | .0084 | | |
| 23 | 8.68 | 8.27 | 7.85 | 7.43 | 7.00 | .0083 | | |
| 24 | 8.53 | 8.12 | 7.71 | 7.30 | 6.87 | .0083 | | |
| 25 | 8.38 | 7.96 | 7.56 | 7.15 | 6.74 | .0082 | | |
| 26 | 8.22 | 7.81 | 7.42 | 7.02 | 6.61 | .0080 | | |
| 27 | 8.07 | 7.67 | 7.28 | 6.88 | 6.49 | .0079 | | |
| 28 | 7.92 | 7.53 | 7.14 | 6.75 | 6.37 | .0078 | | |
| 29 | 7.77 | 7.39 | 7.00 | 6.62 | 6.25 | .0076 | | |
| 30 | 7.63 | 7.25 | 6.86 | 6.49 | 6.13 | .0075 | | |

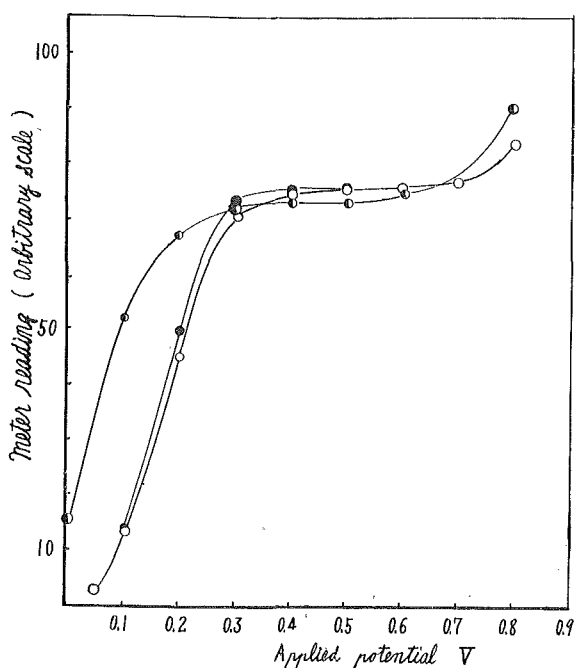


Fig. 3. Polarogram different fuffer systems

- pH 4.0, acetic acid-sodium acetate buffer
- pH 8.0, Ammonia-ammonium chloride buffer
- ◐—◐— pH 9.7, ammonia-ammonium chloride buffer

which are shown in Fig. 3, indicate that pH has little effect on the diffusion current of dissolved oxygen.

Meter-reading is generally corrected for the residual current, which can be measured by reading the meter after removal of D.O. from the sample by bubbling H_2 or N_2 gas or by adding sodium sulfite. When an acetic acid-sodium acetate buffer was used, diffusion current was increased by the addition of sodium sulfite, giving rise to a difficulty in the use of the latter in the determination of residual current. Consequently, an ammonia-ammonium chloride buffer was used in the present investigation. Since, however, the residual current is about the same for different wastes at 0.1–0.2 μA , corresponding to 0.3–0.6 mg./l. of dissolved oxygen, the measurement of residual current can be omitted in most determinations.

Calibration of D.O.-meter.

The D.O.-meter was calibrated by comparing the diffusion current obtained in a solution with the dissolved oxygen content as determined by the Winkler

method. Solutions of D.O. were prepared by the following procedure.

An appropriate amount of deoxygenated water was taken in a separating funnel containing a few glass beads. The separating funnel was filled with distilled water containing much D.O. and stoppered with precautions to completely exclude air bubbles. The contents were mixed by inverting the separating funnel several times.

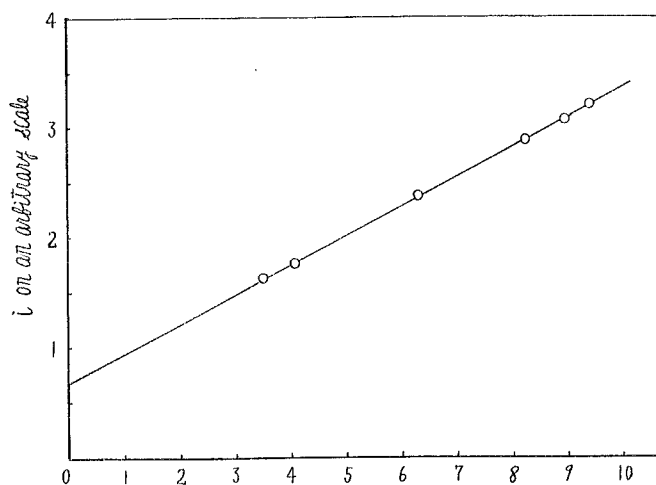


Fig. 4. Calibration curve at 23°C

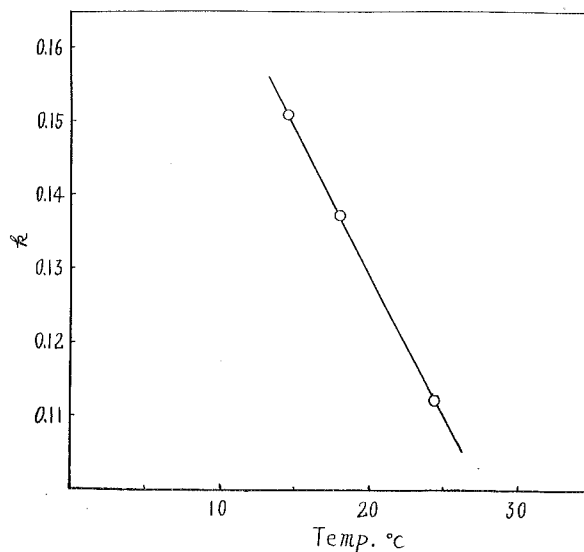


Fig. 5. Temperature coefficient for k

Diffusion current as a function of dissolved oxygen concentration is plotted in Fig. 4. Calibration constant, $k = \frac{\text{D.O.}}{\text{Diffusion current}}$, was determined from the slope of the calibration curve at different temperatures and is shown in Fig. 5 as a function of temperature.

II. Winkler Method (Alsterberg Modification)

Reagents

(1) Manganous sulfate solution.—Dissolve 48 g. of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in sufficient water to make up 100 ml. solution.

(2) KI-KOH- NaN_3 solution.—Dissolve 70 g. of KOH, and 15 g. of KI in water. Add to this, 1 g. of NaN_3 dissolved in a small volume of water and dilute to 100 ml.

(3) Sulfuric acid, concentrated.

(4) Starch indicator solution.

(5) Standard $\text{Na}_2\text{S}_2\text{O}_3$ solution, 0.0250 N.—1 ml. of this solution is equivalent to 0.2 mg. of dissolved oxygen.

Procedure

To the sample as collected in a Winkler bottle, add 2 ml. of MnSO_4 followed by 2 ml. of KI-KOH- NaN_3 solution well below the surface of the liquid, stopper with care to completely exclude air bubbles, and mix by inverting the bottle several times. When the precipitate is settled, carefully remove the stopper and immediately add 2.0 ml. of concentrated sulfuric acid by allowing the acid to run down the neck of the bottle, restopper and mix by gentle inversion until solution is complete. Take an appropriate amount of the solution and titrate the liberated iodine with thiosulfate using starch as indicator.

When the sample is highly colored, the end-point of Winkler titration cannot be detected with starch as indicator. It is advisable to use an electrochemical device for the detection of end point in these cases. The end point is noticed by a sudden inflexion of the pH-meter readings.

Polluted water generally consumes a considerable amount of iodine, causing error in the Winkler method. To minimize such an effect, the results were corrected in some

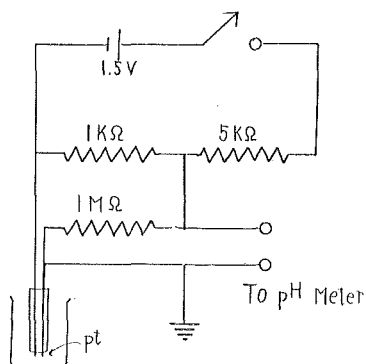


Fig. 6. Apparatus for dead-stop method

determinations for the iodine consumption as determined on a separate portion of sample (stated in each case).

III. Miller Method

Reagents

(1) Rochelle salt solution.—Dissolve 350 g. of Rochelle salt and 100 g. of NaOH in water and dilute to 1 l.

(2) Standard ferrous ammonium sulfate solution.—Dissolve 5.38 g. of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in a small volume of water. Add 5 ml. of conc. H_2SO_4 and dilute to 1 l. Standardize against a saturate solution of D.O.

(3) Methylene blue solution, 0.1% aqueous solution.

(4) Liquid paraffin.

Procedure

Take a 50-ml. portion of sample in a 80-ml. cylinder. Add two drops of methylene blue and 5 ml. of Rochelle salt. Cover the surface of the mixture with liquid paraffin. Titrate with a standard ferrous ammonium sulfate solution until the blue color of methylene blue turns to yellow, keeping the tip of the buret well below the surface of the liquid.

Results

Using several kinds of wastes and polluted waters, polarographic method was compared with Winkler (Alsterberg modification) and Miller methods.

Table II shows the results obtained with the waste from a paper pulp mill

TABLE II. Determinations with Waters Polluted mainly by Paper-Pulp Mill Waste.

| Sample | Temperature (°C) | D.O. Found (mg./l.) | | |
|------------------------------------------------|---------------------|-------------------------|----------------|---------------|
| | | Polarographic method | Winkler method | Miller method |
| Combined waste from Kokusaku Parupu Mill | 19.5 | 8.05 | 0.00 | 1.10 |
| Ishikari River* (Asahibashi) | 22.0 | 7.02 | 4.33 | |
| Ishikari River (Takikawa) | 18.0 | 9.16 | 7.35 | |
| Ishikari River (Ebetsu) | 17.5 | 7.10 | 7.19 | |

* Determination was made on a sample brought to the Laboratory, Kokusaku Parupu Mill.

and with waters polluted with it. It is surprising that polarographic method indicated the presence of much D.O. in the waste though little oxygen was detected by the chemical methods. Although errors are encountered also in the polarographic method, there seems to be no other method which is more reliable than the polarographic one, as will be discussed later. It is also shown in Table 2 that Winkler method is unreliable even for the water sample taken at Takikawa, some 40 kilometers down the point where the waste is discharged. At Ebetsu, 120 kilometers down the point of discharge, polarographic and Winkler methods gave consistent results.

Presented in Table III are determinations carried out on several dilutions

TABLE III. Results with Diluted K. P. Waste.

| Dilution | D.O. Found (mg./l.) | | |
|----------|----------------------|----------------|---------------|
| | Polarographic method | Winkler method | Miller method |
| 5 | 7.05 | 2.96 | 6.10 |
| 10 | 7.30 | 4.63 | 7.43 |
| 50 | 7.89 | 7.68 | 7.85 |

Temperature, 25°C; KMnO_4 consumption of the original waste, 8.4g./l.

of the waste from a kraft-pulp mill. The waste was diluted with distilled water, saturated with air by shaking in a bottle, allowed to stand for about 10 minutes to effect separation of air bubbles and then subjected to D.O. determinations. It is clearly shown in the table that Miller method agrees considerably well with the polarographic method unless the strength of polluted water is extremely high, while the Winkler method does not give consistent results until the original waste is diluted more than 50 times or to a potassium-permanganate consumption of about 160 mg./l.

TABLE IV. Determination of D.O. in Effluent from Potato-Starch Preparation.

| Dilution | I_2 consumption as O_2 (mg./l.) | Polarographic method | Winkler method correction for I_2 consumption | Miller method |
|----------|---------------------------------------------------|----------------------|--------------------------------------------------------|---------------|
| 10 | | 7.28 | —* | —* |
| 20 | 0.58 | 7.75 | 6.62 | 5.99 |
| 50 | 0.23 | 8.14 | 6.61 | 7.17 |
| 100 | 0.11 | 8.96 | 8.42 | 8.28 |

* End-point detection impossible by the usual method.

KMnO_4 consumption and total solid content of original effluent, 135 g./l. and 64 g./l., respectively (Much more concentrated than those discharged from ordinary plants).

Table IV collects the results obtained with several dilutions of a potato-starch waste prepared in the laboratory and stored in an open vessel for about 3 days. Comparisons between figures in this table indicate that agreement between the methods is obtained when the waste is diluted to about 1 g./l. in potassium-permanganate consumption.

Table V shows determinations carried out on waters polluted with wastes

TABLE V. Results obtained with Waters Polluted by Wastes from Coal-Preparation Plants.

| River | Temp. | KMnO ₄ consump. (mg./l.) | I ₂ consump. as mg./l. of D.O. | D.O. Found (mg./l.) | | |
|-------------------------|-------|-------------------------------------|-------------------------------------------|----------------------|-----------------|---------------|
| | | | | Polarographic method | Winkler* method | Miller method |
| Sorachi River (Akabira) | 13.7 | 62 | 0.71 | 9.57 | 9.48 | 11.19 |
| Yubari River (Ebetsu) | 14.8 | 53 | 0.42 | 9.94 | 9.72 | 9.92 |
| Horomui River | 14.8 | 41 | 0.61 | 9.20 | 9.15 | 9.25 |
| Ikushunbetsu River | 18.0 | 33 | 0.61 | 9.88 | 9.95 | 10.08 |
| Penke River** | 18.0 | 1670 | 0.20 | 7.43 | —*** | 7.33**** |
| Bibai River** | 20.0 | 1600 | 0.34 | 8.32 | —*** | 8.27**** |

* Corrected for I₂ consumption.

** Determination was made on a sample brought to the laboratory.

*** End-point detection impossible.

**** Dead-stop end point.

from coal-preparation plants. For these waters, disagreement between the methods is not so great as for the waste from paper pulp mills. When the water is highly polluted with the waste from coal-preparation plants, chemical methods cannot be applied because of interfering color and turbidity, which make it difficult to detect the end point of titration by the usual method. Such a difficulty is overcome, however, by employing the dead-stop method of end point detection.

Surface waters streaming in peat bogs have been reported to contain much organic matter.¹⁷⁾ For these waters, however, polarographic, Miller, and Winkler methods give fairly consistent results, as will be seen in Table VI.

Comparisons between the polarographic and the Miller methods were made also for the determination of D.O. in B.O.D. dilutions. The results are shown in Table VII. Figures in this table indicate that although polarographic and Miller methods give consistent results, small discrepancies still exist at smaller

TABLE VI. Results Obtained with Peaty Waters
(Laboratory Experiment)

| Sample | Temp. | KMnO ₄ consump. (mg./l.) | I ₂ consump. as mg./l. of D.O. | D.O. Found (mg./l.) | | |
|---------------------------------------------------|-------|-------------------------------------------|-------------------------------------------------|---------------------------|------------------|--------------------|
| | | | | Polarogra- phic method | Miller method | Winkler method* |
| Barato Lake A drain (Nibandori, Shinoro) | 15.0 | 65 | 0.24 | 7.70 | 7.41 | 7.38 |
| | 13.5 | 117 | 0.18 | 6.87 | 6.80 | 6.13 |
| A drain (Bannaguro) | 13.5 | 15 | 0.14 | 3.39 | 3.26 | 3.17 |
| Drain A | 13.8 | 65 | 0.14 | 10.72 | 10.50 | 10.83 |
| Drain B | 14.2 | 67 | 0.13 | 9.69 | 9.94 | 9.91 |

* Corrected for I₂ consumption.

TABLE VII. Determination of D.O. in B.O.D. Dilutions

| Sample | Dilution | D.O. Found (mg./l.) | | |
|-----------------------------------------------------------------|----------|-------------------------|---------------|------------|
| | | Polarographic method | Miller method | Difference |
| Combined waste from Kokusaku Parupu Mill | 80 | 4.07 | 4.40 | -0.37 |
| | 100 | 4.85 | 5.12 | -0.27 |
| | 160 | 6.05 | 6.20 | -0.15 |
| Waste containing ash from boiler, Kokusaku Parupu Mill | 28.6 | 5.10 | 4.68 | 0.42 |
| | 40 | 5.90 | 5.64 | 0.26 |
| | 50 | 6.08 | 5.95 | 0.13 |
| | 100 | 7.18 | 7.11 | 0.07 |
| Waste from a gas works | 80 | 1.46 | 1.48 | -0.02 |
| | 160 | 5.14 | 4.75 | 0.39 |
| | 200 | 5.50 | 5.39 | 0.11 |
| | 267 | 6.05 | 5.95 | 0.10 |

dilutions.

Comparisons are also made between the polarographic and the Winkler methods. Remainders of B.O.D. dilutions were combined, shaken for 1 minute to saturate with air, allowed to stand for about 10 minutes and examined by the stated methods. The results are shown in Table VIII. It is very interesting to note in this table that with incubated waters, Winkler method gives higher values.

TABLE VIII. Results obtained with B.O.D. Dilutions

| Waste | Polarographic method | Winkler method | |
|--------------------------------------------------------|----------------------|------------------------------------------------|---------------------------------------------|
| | | Without correction for I ₂ consump. | With correction for I ₂ consump. |
| Combined waste from Kokusaku Parupu Mill | 7.40 | 8.78 | 9.00 |
| Waste containing ash from boiler, Kokusaku Parupu Mill | 7.20 | 7.78 | 8.58 |
| Waste from a gas works | 7.20 | 8.48 | 8.67 |

Discussion

It is very interesting to point out that much D.O. has been detected in the waste from a paper pulp mill only by the polarographic method, or, little D.O. has been found by the other methods.

When the concentration of organic matter is very high, polarographic method would also be interfered with by alteration of the drop-time of mercury and of the diffusion coefficient of D.O., caused by the viscosity change, and by compounds which are also reduced at the electrode. However, since the diffusion current is decreased to a very low value by bubbling hydrogen or nitrogen gas through the waste sample, and since it is re-increased by re-aeration, it may be reasonable to assume that much D.O. has been present in that waste.

Errors owing to the change of drop-time and of diffusion coefficient may be small when the waste is diluted, or if any, they can be eliminated by calculating the D.O. content from measurements of diffusion current before and after the aeration unless the oxygen uptake of the organic matter is extremely rapid.

It will be clear from the foregoing results that Winkler method is seriously interfered with in some instances and should not be used for the examination of polluted waters, although this method is used in most works. For freshly discharged wastes, low values are generally obtained by the Winkler methods, as shown in Tables II, III, and IV. However, high values were obtained for incubated samples, as will be seen in Table VIII, for an unknown reason. This indicates that the Alsterberg modification of Winkler method should not be used in B.O.D. determinations.

Although less interferences are encountered with Miller method, it is also

unreliable when applied to highly polluted waters. It is very important to point out that in some cases where titration is delayed, the color of methylene blue faded before the addition of standard ferrous ammonium sulfate, indicating the presence of substances which react with methylene blue.

In conclusion, the authors strongly recommend the use of a voltametric technique for the determination of D.O. in polluted waters containing much organic matter, since this method is simple and rapid, and seems to be most reliable.

Finally it should be pointed out that the B.O.D. determination is over-emphasized in most works as a measure of water pollution. It would be easily accepted that the D.O. content is not directly connected to the B.O.D. value. Much D.O. would even be found in waters with very high B.O.D. values, if the rate of aeration is sufficiently high, as in the case of the waste from Kokusaku Parupu Mill. Thus sufficient D.O. is found in most streaming waters. It would therefore be apparent that water pollution cannot be evaluated from the measurement of B. O. D. alone.

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