

# Manual for Dissolved Oxygen Analysis

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## FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

# ANALYSIS PROCEDURE FOR DISSOLVED OXYGEN IN SEA WATER

## SCOPE

1. (a) These methods cover the determination of dissolved oxygen in sea water. Three methods are given, as follows:

	<u>Sections</u>
Method A (High precision, high accuracy)	7 to 14
Method B (Medium precision, medium accuracy)	15 to 22
Method C (Low precision, low accuracy)	23 to 30

(b) These methods provide for the analysis of sea water samples by an optimized Winkler procedure. Samples are collected and fixed under a nitrogen atmosphere according to the classical Winkler chemistry. Excess sodium thiosulfate solution is added to the fixed sample to reduce the iodine generated in the Winkler reaction. An aliquot of this solution is then back titrated amperometrically (constant-current method) under a nitrogen atmosphere. The precision and accuracy of the three procedures differ because of the various levels of care involved in sample handling and measurement of sample and reagent blanks. All three procedures were designed primarily for the analysis of sea water samples containing less than 100 ppb of dissolved oxygen. However, any one of the three may be used in the analysis of sea water samples containing dissolved oxygen concentrations up to saturation or for the analysis of industrial water. Method A is particularly suited for sea water samples containing very low dissolved oxygen contents and samples that may contain uncertain or unknown concentrations of interfering ions. Methods B or C may be used where lesser accuracy and precision can be tolerated and where the composition of the sea water samples is known and constant.

## DEFINITIONS

2. For definitions of terms used in this procedure, refer to the Definitions of Terms Relating to Industrial Water and Industrial Waste Water (ASTM D 1129).

## PURITY OF REAGENTS

3. (a) Reagent grade chemicals shall be used in all tests except in the preparation of the standard potassium iodate solution. That reagent shall be made up from primary standard grade salt.

(b) Unless otherwise indicated, reference to water shall be understood to mean distilled or deionized water.

## REAGENTS

4. (a) Iodine, Standard Solution (0.1 N). - Dissolve 6.346 g of resublimed iodine in a solution of 75 g of KI in 60 ml of water and dilute with water to 500 ml in a volumetric flask. Store in a dark, Polyseal-capped bottle.

(b) Potassium Iodide Solution (1000 g KI per liter). - Weigh out 1000 g of KI and place in a 1 liter volumetric flask. Alternately add water and mix by inversion until all the KI is dissolved, the solution is at room temperature, and the solution has been diluted to the mark. Filter through a Whatman #2 or equivalent filter paper. Store in a dark, Polyseal-capped bottle.

(c) Iodized Alkaline Iodide Solution. - Dissolve 700 g of potassium hydroxide (KOH) in sufficient water (approximately 500 ml) to make approximately 700 ml of solution in a 1-liter volumetric flask. Cool. While this solution is still warm (approximately 35 to 50°C) add 150 ml of the KI solution. Mix. Add 10 ml of 0.1 N iodine solution. After the solution has cooled to room temperature dilute to volume with water and mix. Store the solution in a 2-liter Polyseal-capped reagent bottle.

(d) Manganous Sulfate Solution (364 g per liter). - Dissolve 364 g of manganous sulfate ( $\text{Mn SO}_4 \cdot \text{H}_2\text{O}$ ) in water and dilute to 1 liter. Filter through a Whatman #2 (or equivalent) filter paper. Store the solution in a 2-liter, Polyseal-capped reagent bottle.

(e) Phosphoric Acid Solution (12M). - Add 822 ml of 14.6 M acid (85%  $\text{H}_3\text{PO}_4$ ) to 178 ml of water. Store this solution in a 2-liter, Polyseal-capped reagent bottle.

(f) Potassium Iodate, Standard Solution (0.1 N). - Dissolve 3.5670 g of potassium iodate ( $\text{KIO}_3$ , primary standard) in 800 ml of water, add 0.5 g of sodium bicarbonate ( $\text{NaHCO}_3$ ), and dilute to 1 liter in a Class A volumetric flask.

(g) Potassium Iodate, Standard Solution. (0.01 N). - Using a Class A pipet, transfer 25 ml of 0.1 N potassium iodate solution to a 250-ml Class A volumetric flask. Dilute to the mark with water and mix thoroughly. This solution should be prepared fresh weekly.

(h) Sodium Thiosulfate Solution (0.1 N). - Using a 1-liter, Class A volumetric flask, dissolve 25 g of sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) in 800 ml of water that has just been boiled and cooled.

Stabilize by dissolving 1.0 g of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in this solution. Dilute to the mark with boiled water.

(i) Sodium Thiosulfate Solution (0.005 N). - Using a Class A pipet transfer 10 ml of 0.1 N sodium thiosulfate solution to a 200-ml Class A volumetric flask. Dilute to the mark with water and mix thoroughly. This solution should be prepared fresh daily.

## SAMPLING

5. (a) It is recommended that 300-ml BOD bottles be used as the sample vessels. These should be the special bottles with pointed stoppers, tapered ground-glass stoppers, and flared mouths. The volumes of water contained by the individual bottles should be determined by calibration to the nearest 0.1 ml. The true volume should be recorded for each bottle and be used in any subsequent calculations involving the volume of sample.

(b) A glass-coated magnetic stirring bar should be placed in the BOD bottle before sampling is begun. (Caution. The glass coating breaks easily.) These should be approximately 1-1/4-in. long and 1/4-in. in diameter. The volume of water displaced by the stirring bar should be determined to within 0.1 ml. This may be measured by observing the difference in the meniscus level in a 10-ml graduated cylinder with and without the stirring bar. It is best to purchase a dozen or more stirring bars and to calibrate them all. Then select for use only those which have a displacement volume of, say,  $2.0 \pm 0.1$  ml.

(c) It is recommended that glass tubing be used for the sampling line. Connections should be made by inserting the tubing ends into short sections of heavy-walled (vacuum) rubber tubing until they touch. Stainless steel tubing may also be used.

(d) A nitrogen-purged sampling vessel is required to protect the sea water sample from exposure to atmospheric concentrations of oxygen. This sampling vessel should be constructed of acrylic plastic. The recommended size and configuration is shown in Figure 1.

(e) The nitrogen for purging the sampling vessel should not contain excessive amounts of oxygen. Cylinder nitrogen (water or oil pumped) or nitrogen gas derived from the vaporization of liquid nitrogen is acceptable so long as the oxygen content of the gas phase is less than approximately 1000 ppm (0.1%).

(f) The sampling time will depend upon the flow rate of the sample. Generally speaking the sea water should flow through the BOD bottle long enough to provide at least 8 to 10 changes of water. If the sample line is used intermittently, allow sufficient time to flush the sample line so that a representative sample is obtained.

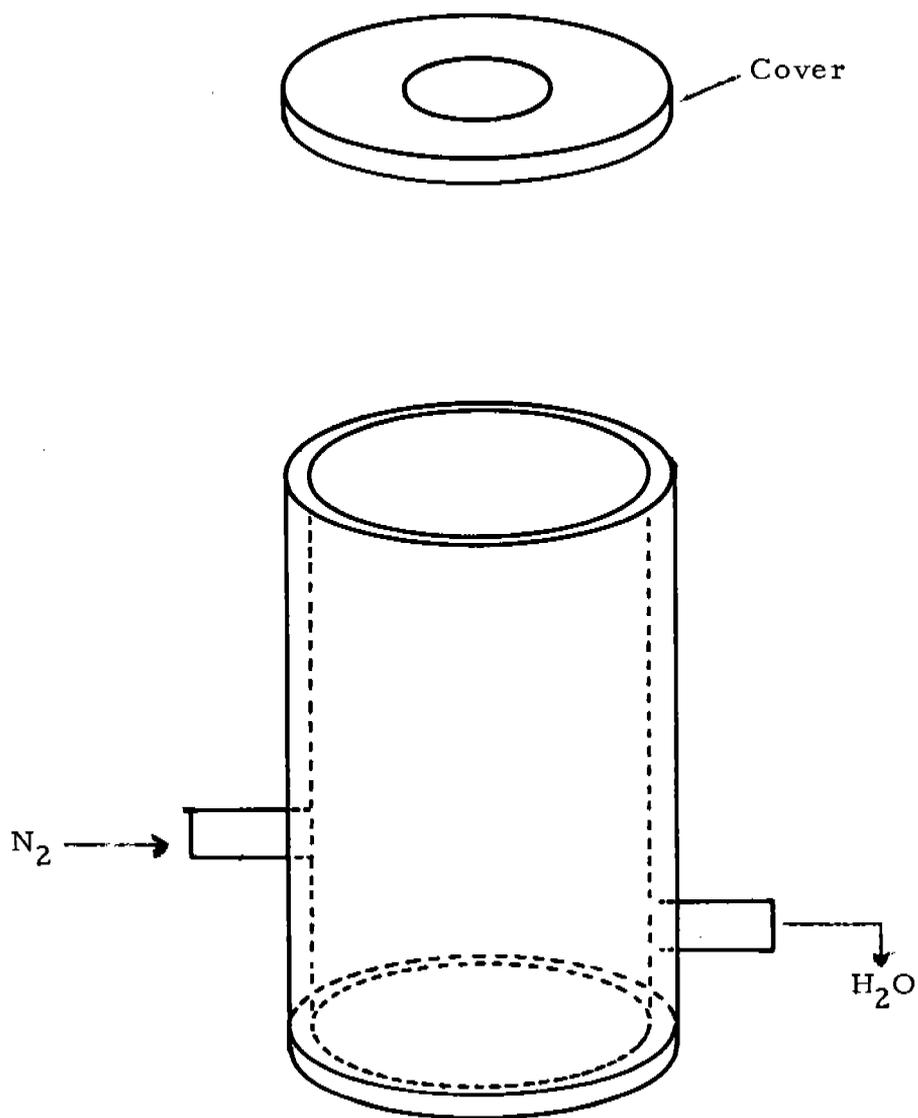


Figure 1. Container for Sampling and Fixing Under Nitrogen

(g) Further details on sampling are given in the individual procedures.

## TITRATION

6. (a) A titration shield such as shown in Figure 2 should be constructed to maintain the titration vessel and solution under a nitrogen blanket.

(b) A 200-ml tall-form Berzelius beaker is recommended as the titration vessel.

(c) The nitrogen for purging should be as described in Section 5(e).

(d) The end point in the titration is detected amperometrically. The titration may be performed manually or automatically. If the titration is conducted automatically, the instrument may record the titration curve or may simply stop at a preset end point, in which case the end point must then be read from the chart or buret. Any of these methods for end-point detection are acceptable. However, it should be understood that the precision, and perhaps the accuracy, will vary depending upon the characteristics of the specific method used for end-point sensing. The precision of the procedure following the fixing step may be estimated by titrating several aliquots of a fixed sample.

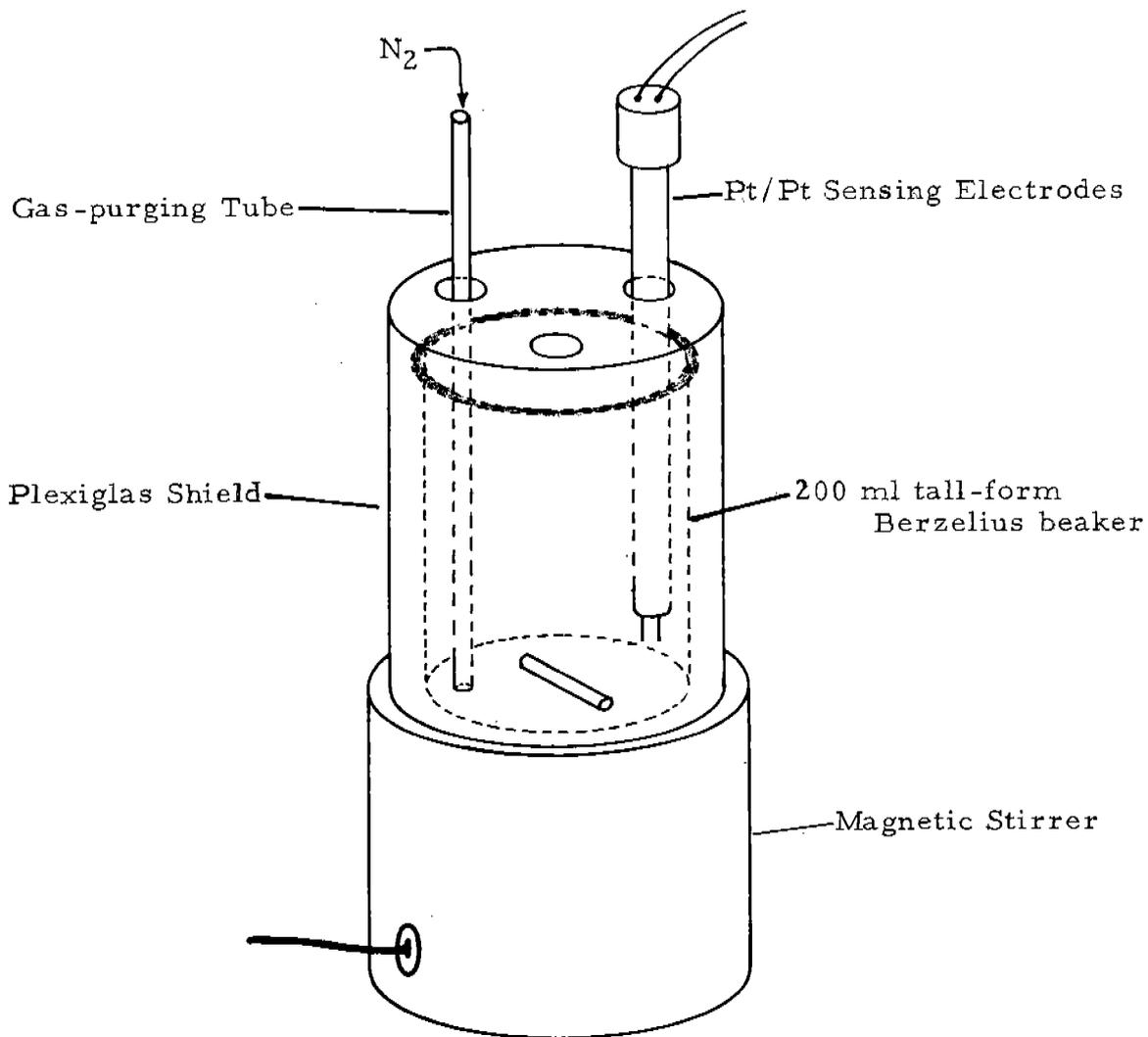


Figure 2. Assembly for Titration of Samples in Controlled Atmospheres

## METHOD A

### (HIGH PRECISION, HIGH ACCURACY)

#### APPLICATION

7. This method is applicable to sea water or other samples having dissolved oxygen concentrations from 0 to 500 ppb; higher oxygen concentrations, to saturation, may be analyzed by appropriately increasing the concentration of the sodium thiosulfate and potassium iodate solutions.

#### INTERFERENCE

8. If the sample contains nitrite or nitrate and ferrous iron, their interference is overcome by adding 1% of sodium azide (1.0 g  $\text{NaN}_3$  per 100 ml iodized alkaline iodide solution) to the iodized alkaline iodide solution. Large quantities of reducing substances are compensated by increasing the amount of iodine in the iodized alkaline iodide solution to maintain an excess of  $\text{I}_2$ . Making these adjustments allows the analysis to be made accurately in the presence of up to 1000 ppb of  $\text{Fe}^{+++}$ ,  $\text{Fe}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Cu}^+$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_3^{=}$ ,  $\text{S}^{=}$ , and  $\text{N}_2\text{H}_5^+$ .

#### APPARATUS

9. (a) Beaker - One 200-ml, tall-form Berzelius beaker.
- (b) Stirrer - One variable-speed, motor-driven stirrer with on-off switch.
- (c) Sample Bottle - One 300-ml BOD bottle. See Section 5(a) for specifications.
- (d) Stirring Bar - One glass-coated stirring bar. See Section 5(b) for specifications.
- (e) Pipets - One 1-ml, three 2-ml, one 3-ml, and one 100-ml (Class A) pipets.

(f) Titration Apparatus - The preferred instrument for titration is the Metrohm Potentiograph Recording Titrator, Model E-436, with a 1-ml buret on the micro-titration stand. Equivalent or other available titration apparatus and accessories may be used so long as it is understood that the precision and perhaps the accuracy may be different from that obtained by the use of the Metrohm Potentiograph. The sensitivity in the end-point region should be at least 300 mv per 0.1 ml of 0.005 N titrant and it should be possible to estimate the titration volume to within  $\pm 0.0002$  ml.

The Metrohm Potentiograph should be fitted with EA-240 platinum/platinum electrodes and should be operated voltametrically at 1 microampere current and 100 mv full scale sensitivity. Consult the instruction manual for operating instructions. The instrument is complete with titrant reservoir, delivery tube, magnetic stirrer, and Teflon-coated stirring bar. A titration shield such as described in Section 6(a) should be fabricated for use in the analysis.

(g) Deoxygenation Apparatus. - A system for deoxygenating the sample water stream should be assembled as shown schematically in the flow diagram given in Figure 3. Stage 1 and Stage 2 each are spinning-disc strippers in which the transfer of oxygen into the nitrogen stripping gas occurs. Details of these stripper units are given in Figure 4. Deoxygenation is effected by counter-current flow of nitrogen and the water sample. The water-wettable Mylar discs are rotated at approximately 300 rpm by means of an adjustable-speed electric motor. Water flowing through the stripper units is picked up on the surface of the Mylar disc and exposed to the oxygen-free nitrogen gas flowing countercurrently. Oxygen in the water is transferred to the nitrogen stream, tending toward equilibrium. In the completion of each rotation of the Mylar discs, this deoxygenated water is replaced by a new, oxygen-rich film of sample water and the process is repeated. Where the ratio of nitrogen-gas to sample flow is maintained at or above 10 to 1, two stages operated in series as shown in the schematic diagram are capable of lowering the dissolved oxygen content of an air-saturated sample stream to less than 0.1 ppb, assuming, of course, that the nitrogen is suitably pure.

The nitrogen stream is purified by passing it over a copper/copper oxide bed maintained at  $525 \pm 25^\circ\text{C}$ . A suitable purification train is prepared by packing a combustion tube (3/8-in. ID by 10-in. long) loosely with very fine copper wire or turnings (2/3 full) and copper oxide wire (1/3 full). The tube is then positioned in a tube furnace in such a manner that portions of both packing materials are in the heated zone. Only the nitrogen passing through Stage 2 needs to be purified in this manner.

The flow of nitrogen through the deoxygenation system should be monitored by means of appropriately located calibrated rotameters or other reliable flowmeters. Sample entering Stage 1 will be delivered under pressure, but beyond that point the flow to Stage 2 and thence to the sample container will be by gravity flow. Thus, it is desirable to elevate Stage 1 above Stage 2, and Stage 2 above the point of sampling. The water level in Stages 1 and 2 should be maintained constant at approximately one-half inch below the rod supporting the Mylar discs in order to achieve maximum transfer efficiency.

## REAGENTS

10. The reagents are those described in Section 4.

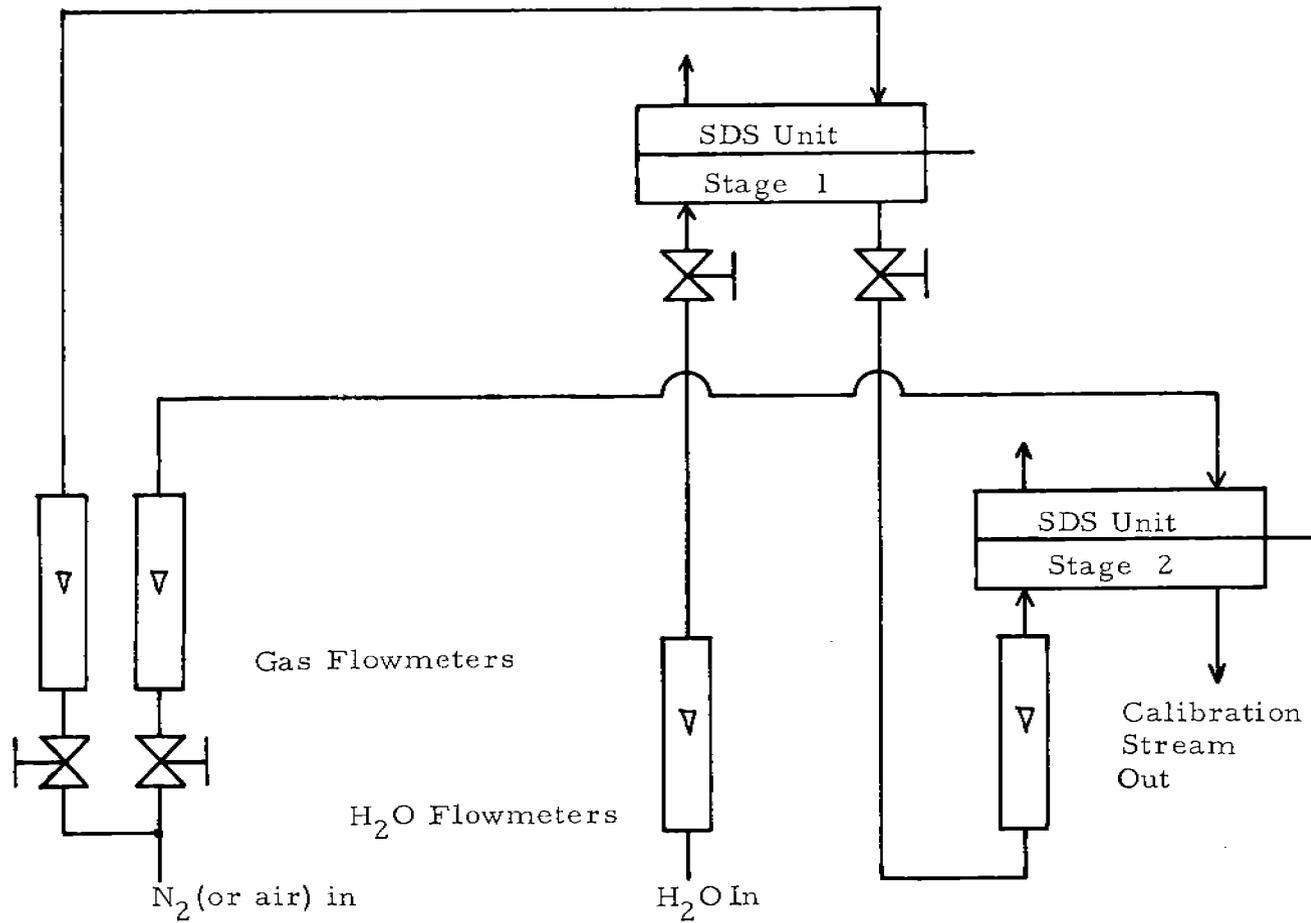
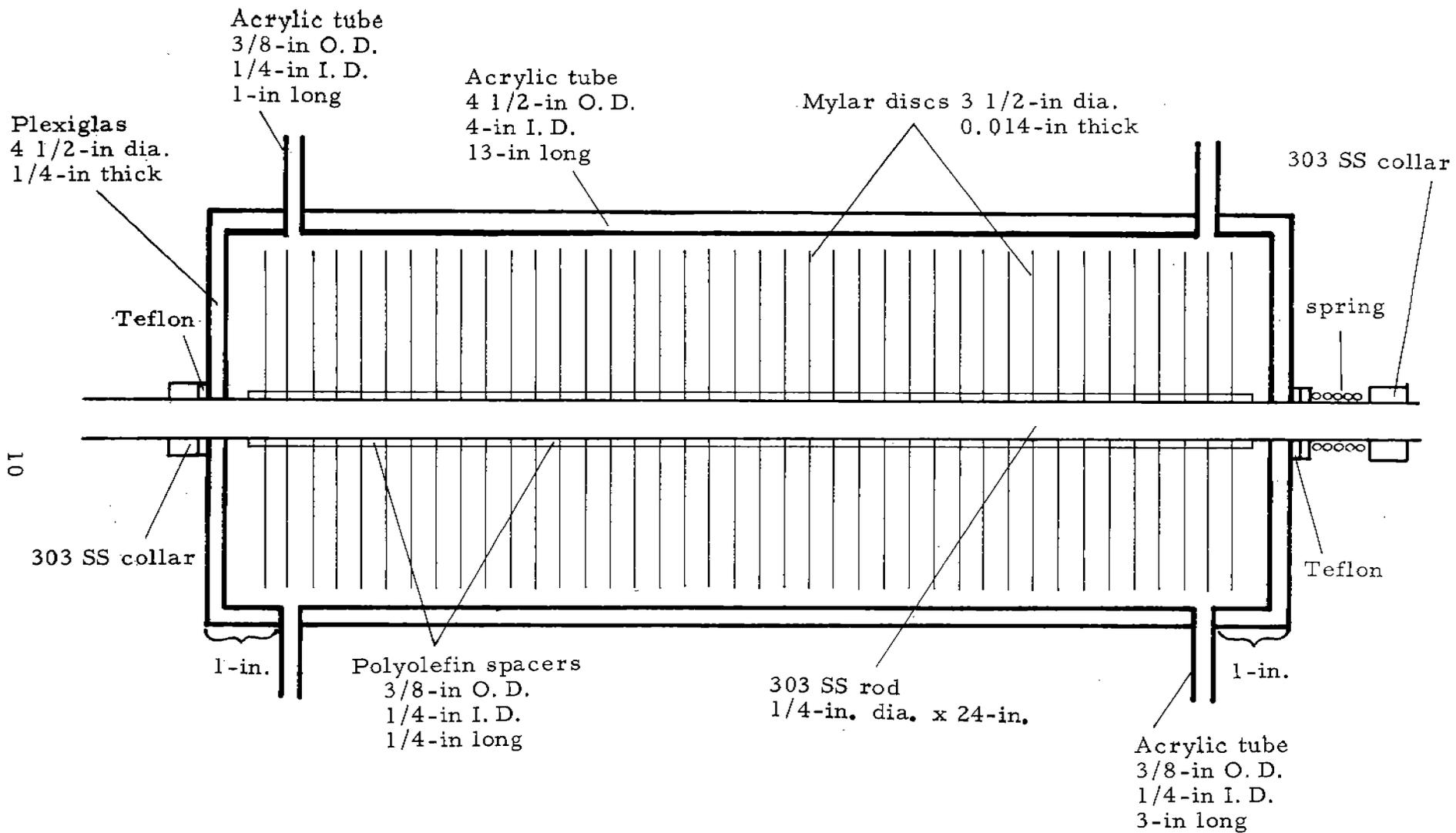


Figure 3. Schematic Diagram of Dissolved Oxygen Calibrator



Details of the Spinning-Disc Stripper

Figure 4

11. Procedure. (a) Starting Deoxygenation Apparatus. - The deoxygenation apparatus should be started up at least one hour before sampling is to begin. Turn on the tube furnace. Flow sample into Stage 1 and Stage 2 to the desired levels. Begin the flow of nitrogen to both stages and adjust to the appropriate rate. Adjust the flow of sample through the two stages and to the sampling point. Turn on the electric motor(s) connected to the shaft supporting the Mylar discs and adjust the rotational speed to approximately 300 to 350 rpm.

(b) Preparing Titration Apparatus. - Turn on the Metrohm Potentiograph (or other titration device) at least 30 minutes prior to use. Fill the titration reservoir with 0.01000 N  $\text{KIO}_3$  solution. Flush the delivery system with titrant several times to rinse and observe that there are no air bubbles in the delivery tube. Connect and position the platinum/platinum electrodes. Position the titration shield, magnetic stirrer, and titrant-delivery tube. Adjust the flow of nitrogen to 100 ml/min and position the nitrogen-delivery tube.

(c) Preparation for Fixing. - Select the pipets to be used for addition of the Winkler reagents and the sodium thiosulfate solution. Rinse the pipets with the respective solutions to be delivered.

(d) Preparation for Sampling. - At least 15 min before sampling is to begin, select a clean 300-ml BOD bottle, insert a Pyrex-coated stirring bar, stopper, and place in a sample container which is being purged with nitrogen flowing at 8 to 10 liters per min. Ten minutes before sampling is to begin, remove the stopper of the BOD bottle and insert a purge tube. Purge five minutes with nitrogen flowing at 8 to 10 liters per min. Then remove the purge tube, restopper, and continue flowing nitrogen through the sample container.

(e) Sampling. - Remove the stopper of the BOD bottle and quickly position the BOD bottle/nitrogen-purged sample container under the sample line so that the sample is delivered near the bottom of the BOD bottle. Continue purging the sample container with nitrogen during the sampling period. Allow sample water to flow a sufficient time so that at least ten volumes of water (3000 ml) have passed through the BOD bottle. Then, quickly remove the sample line and restopper the BOD bottle. Do not allow drops of water to fall from the sample line into the BOD bottle. Be careful not to trap gas bubbles in the BOD bottle.

(f) Fixing. - Continue the nitrogen purge through the sample container during the fixing step. Carefully draw all the excess sample from around the stopper of the BOD bottle with a plastic-tipped syringe, water aspirator, or other suitable means. Fix sample in the following manner. Draw iodized alkaline iodide reagent (See Section 4(c)) to above the line of the 2.0 ml pipet. Carefully wipe the tip of the pipet with a clean, lint-free wiper and wait for any bubbles in the aliquot to rise to the top. Lower the meniscus slowly to the mark. Remove the stopper from the BOD bottle and

position the tip of the pipet just at the surface of the sample. Add the reagent, allowing a 1-minute drain time. Wipe the stopper of the BOD bottle until it is visibly clean and dry. Insert the stopper carefully so as to trap no gas bubbles inside the BOD bottle. Set the magnetic stirrer to a medium speed, turn on, and stir for 30 seconds. Turn off the stirrer. Remove excess liquid from around the stopper of the BOD bottle, as above. Add 2.0 ml of manganous sulfate solution (See Section 4(d)), stopper, and stir in the manner described above. Remove excess liquid, add 3.0 ml of phosphoric acid solution (See Section 4(e)), stopper, and stir in the manner described above. (Allow a 2-minute drain time.) Remove excess liquid. Then, after the fixing steps are completed, pipet 2.0 ml of 0.005 N sodium thiosulfate solution into the fixed sample. Allow a 30-second drain time. Do not restopper the BOD bottle. Stir for 30 seconds.

(g) Titration. - Lower the beaker away from the electrodes and titrant delivery tube and rinse with distilled water. Position the titrant delivery tube to approximately 1/2-in. below (downstream) the electrodes. Deliver a small quantity of titrant from the buret tip or titrant delivery tube and wipe away the pendant drop in a reproducible manner. Place a clean, dry 200-ml Berzelius beaker on the titration stand. Insert the nitrogen purge tube to within 1/2 to 1-in. from the bottom of the beaker. Transfer a 100-ml aliquot of the fixed sample to the titration vessel by means of a 100-ml pipet. Carefully fill the pipet, wipe the tip, and lower the meniscus to the mark. Insert the pipet tip into the Berzelius beaker, raise the nitrogen-purge tube to approximately 1-in. below the top of the titrant vessel, and allow the sample to flow in. Turn on the stirrer and set the stirring speed so that cavitation draws the center of the sample down approximately 1/2-in. Titrate the sample to the end point following the procedure that is appropriate for the instrument used. In the case of the Metrohm Potentiograph, set the titration speed to 4, the sensitivity to 100 mv full scale, compensation to -400 mv, voltametric current ( $I_{pol}$ ) to  $-1 \mu a$ , and then turn to titration selector to  $I_{pol}$ . Press the titrate button and allow titrant to flow back into the reservoir until the indicator light on the titrant delivery unit (titration stand) goes out, indicating that any slack in the drive train has been eliminated. Press the titrate button again to stop delivery. Set the three-way stopcock to deliver titrant to the titration vessel. Lower the recorder pen to the chart paper and position the chart paper so that the pen begins at precisely 0. Press the titrate button. When the end point has been reached or passed, press the titrate button to stop the titration. Turn the titration selector to off. Raise the titrant delivery tube to above the surface of the titrated sample to avoid contamination of titrant resulting from back diffusion of sample.

(h) Blank. - The blank is collected in exactly the same manner as the sample except that the blank is collected at the outlet delivery tube of the deoxygenation apparatus. See Section 11(e).

(i) Fixing the Blank. - The blank is fixed according to the procedure of Section 11(f).

(j) Titrating the Blank. - The blank is titrated according to the procedure of Section 11(g)..

#### CALCULATION

12. Calculate the dissolved oxygen content of the sample ( $H_o$ ), in parts per billion, as follows:

$$\text{Dissolved Oxygen } (H_o), \text{ ppb} = 80,000 n \left[ T_B \left( \frac{V_B + 9}{V_B} \right) - T_S \left( \frac{V_S + 9}{V_S} \right) \right]$$

where:

$n$  = normality of the  $KIO_3$  solution

$T_B$  = volume of  $KIO_3$  solution required for titration of the blank, ml.

$V_B$  = total volume of blank, ml (volume of BOD bottle minus volume of stirring bar).

$T_S$  = volume of  $KIO_3$  solution required for titration of the sample, ml.

$V_S$  = total volume of sample, ml (volume of BOD bottle minus volume of stirring bar).

#### PRECISION

13. The precision of the method is 0.75 ppb of oxygen.

#### ACCURACY

14. The accuracy of the method is 0.5 ppb of oxygen or 1%, whichever is greater.

## METHOD B

### (MEDIUM PRECISION, MEDIUM ACCURACY)

#### APPLICATION

15. This method is applicable to sea water or other samples having dissolved oxygen concentrations from 0 to 500 ppb. Higher oxygen concentrations, to saturation, may be analyzed by appropriately increasing the concentration of the sodium thiosulfate and potassium iodate solutions.

#### INTERFERENCES

16. The precision and accuracy of this method are essentially unaffected by the presence of up to 1000 ppb of  $\text{Fe}^{+++}$ ,  $\text{Fe}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Cu}^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_3^-$  ions. Nitrite or nitrate and ferrous ion combinations are overcome by adding 1% of sodium azide (1.0 g  $\text{NaN}_3$  per 100 ml of iodized alkaline iodide solution) to the iodized alkaline iodide reagent. Large quantities of reducing substances are compensated by increasing the amount of iodine in the iodized alkaline iodide reagent to maintain an excess of iodine at the end of the fixing process. Sulfide and hydrazine interfere in proportion to their concentrations, but this interference is cancelled out by the method used here for determining the reagent blanks. In order for the blank to compensate for the effects of interferences, it is necessary for the levels of these interferences to be constant throughout the period for which the blank is used and assumed valid.

#### APPARATUS

17. The apparatus required here is described in Section 9.

#### REAGENTS

18. The reagents required here are described in Section 10.

#### PROCEDURE

19. (a) Starting up Deoxygenation Apparatus. - See Section 11(a).
- (b) Preparing Titration Apparatus. - See Section 11(b).
- (c) Preparation for Fixing. - See Section 11(c).
- (d) Preparation for Sampling. - See Section 11(d).
- (e) Sampling. - See Section 11(e).
- (f) Fixing the Sample. - See Section 11(f).

(g) Titration of Sample. - See Section 11(g)

(h) Redox Blank. - The redox blank is collected as in 11(e).

(i) Reaction of the Redox Blank. - The redox blank is reacted (not fixed) by adding reagents in a reverse order so that the dissolved oxygen does not react. Continue the nitrogen purge through the sample container during the reaction step. Carefully draw the excess liquid from around the stopper of the BOD bottle with a plastic-tipped syringe, water aspirator, or other suitable means. Draw iodized alkaline iodide reagent (See Section 4(c)) to above the line of the 2.0 ml pipet. Carefully wipe the tip of the pipet with a clean, lint-free wiper and wait for any bubbles in the aliquot to rise to the top. Lower the meniscus slowly to the mark. Remove the stopper from the BOD bottle and position the tip of the pipet just at the surface of the liquid. Add the reagent, allowing a 1 minute drain time. Wipe the stopper of the BOD bottle until it is visibly clean and dry. Insert the stopper carefully so as to trap no gas bubbles inside the BOD bottle. Set the magnetic stirrer to a medium speed, turn on, and stir for 30 seconds. Turn off the stirrer. Remove excess liquid from around the stopper of the BOD bottle, as above. Add 3.0 ml of phosphoric acid solution. (See Section 4(e)), stopper, and stir in the manner described above. (Allow a 2-minute drain time.) Remove excess liquid. Add 2.0 ml of manganous sulfate solution (Section 4(d)) (1-min drain time), stopper, and stir in the manner described above. Remove excess liquid. Then, after these reaction steps are complete, pipet 2.0 ml of 0.005 N sodium thiosulfate solution into the reacted solution. Allow a 30-second drain time. Do not restopper the BOD bottle. Stir for 30 seconds.

(j) Titration of the Redox Blank. - The redox blank is titrated as in Section 11(g).

(k) Reagent Oxygen Blank. - The reagent oxygen blank is collected as in Section 11(h).

(l) Fixing the Reagent Oxygen Blank. - See Section 11(i).

(m) Titrating the Reagent Oxygen Blank. - See Section 11(g).

(n) Reagent Redox Blank. - The reagent redox blank is collected as in Section 11(h).

(o) Reacting the Reagent Redox Blank. - See Section 19(i).

(p) Titrating the Reagent Redox Blank. - See Section 11(g).

## CALCULATIONS

20. (a) Calculation of Reagent Oxygen Blank. - Calculate the correction for reagent-contained oxygen ( $R_o$ ) in parts per billion, as follows:

$$\text{Reagent Oxygen Blank (R}_o\text{), ppb} = 80,000 n \left[ T_{B4} \left( \frac{V_{B4} + 9}{V_{B4}} \right) - T_{B3} \left( \frac{V_{B3} + 9}{V_{B3}} \right) \right]$$

Where:

$n$  = normality of the  $\text{KIO}_3$  solution.

$T_{B4}$  = volume of  $\text{KIO}_3$  solution required for titration of the reagent redox blank, ml.

$V_{B4}$  = total volume of reagent redox blank, ml (Volume of BOD bottle minus volume of stirring bar).

$T_{B3}$  = volume of  $\text{KIO}_3$  solution required for titration of the reagent oxygen blank, ml.

$V_{B3}$  = total volume of reagent oxygen sample, ml. (Volume of BOD bottle minus volume of stirring bar).

(b) Calculation of the Dissolved Oxygen Content of the Sample  
Calculate the dissolved oxygen content of the sample, ( $H_o$ ) in parts per billion, as follows:

$$\text{Dissolved Oxygen (H}_o\text{), ppb} = 80,000 n \left[ T_{B2} \left( \frac{V_{B2} + 9}{V_{B2}} \right) - T_S \left( \frac{V_S + 9}{V_S} \right) \right] - R_o$$

where:

$n$  = normality of the  $\text{KIO}_3$  solution.

$T_{B2}$  = volume of  $\text{KIO}_3$  solution required for titration of the redox blank, ml.

$V_{B2}$  = total volume of redox blank, ml (volume of BOD bottle minus volume of stirring bar).

$T_S$  = volume of  $\text{KIO}_3$  solution for titration of the sample, ml.

$V_S$  = total volume of sample, ml (volume of BOD bottle minus volume of stirring bar).

$R_o$  = reagent oxygen blank, ppb.

## PRECISION

21. The precision of the method is 2.0 ppb of oxygen.

## ACCURACY

22. The accuracy of the method depends upon the frequency with which the reagent oxygen blank is determined and the constancy of the sample composition. If the blank is determined daily and the water has a constant composition, the accuracy is 1.0 ppb or 2%, whichever is greater.

## METHOD C

### (LOW PRECISION, LOW ACCURACY)

#### APPLICATION

23. This method is applicable to sea water or other samples having dissolved oxygen concentrations from 0 to 500 ppb. Higher oxygen concentrations, to saturation, may be analyzed by appropriately increasing the concentrations of the sodium thiosulfate and potassium iodate solutions.

#### INTERFERENCES

24. The precision and accuracy of this method are essentially unaffected by the presence of up to 1000 ppb of  $\text{Fe}^{+++}$ ,  $\text{Fe}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Cu}^+$ , and  $\text{SO}_3^-$ . Interferences due to nitrite are avoided by adding 1% of sodium azide (1.0 g  $\text{NaN}_3$  per 100 ml of iodized alkaline iodide solution) to the iodized alkaline iodide reagent. Large quantities of some reducing substances may be compensated by increasing the amount of iodine in the iodized alkaline iodide reagent. The presence of nitrate at 1000 ppb gives an interference of +4.25 ppb. Sulfide and hydrazine interfere in proportion to their concentrations. At concentrations of 133 ppb, the measured values will be, respectively 11.4 and 36.1 ppb too high.

#### APPARATUS

25. The apparatus required here is that described in Section 9(a) through (f). The deoxygenation apparatus of Section 9(g) is not required.

#### REAGENTS

26. The reagents required here are described in Section 10.

#### PROCEDURE

27. (a) Preparing Titration Apparatus. - See Section 11(b).
- (b) Preparation for Fixing. - See Section 11(c).
- (c) Preparation for Sampling. - See Section 11(d).
- (d) Sampling. - See Section 11(e).
- (e) Fixing the Sample. - See Section 11(f).
- (f) Titration of Sample. - See Section 11(g).

- (g) Blank. - The blank is collected as in 11(e).
- (h) Reaction of the Blank. - See Section 19(i).
- (i) Titration of the Blank. - See Section 11(g).

## CALCULATIONS

28. Calculate the dissolved oxygen content of the sample ( $H_O$ ), in parts per billion, as follows:

$$\text{Dissolved Oxygen } (H_O), \text{ ppb} = 80,000 n \left[ T_B \left( \frac{V_B + 9}{V_B} \right) - T_S \left( \frac{V_S + 9}{V_S} \right) \right] - 17.8$$

where:

- $n$  = normality of the  $KIO_3$  solution.
- $T_B$  = volume of  $KIO_3$  solution required for titration of the blank, ml.
- $V_B$  = total volume of blank, ml (volume of BOD bottle minus volume of stirring bar).
- $T_S$  = volume of  $KIO_3$  solution required for titration of the sample, ml.
- $V_S$  = total volume of sample, ml (volume of BOD bottle minus volume of stirring bar).

## PRECISION

29. The precision of the method is 4 ppb of oxygen.

## ACCURACY

30. If the sample is free of certain interfering ions the accuracy is probably in the order of 5 ppb or 5%, whichever is greater.