

# Development of a Calibration Module for Trace Oxygen Analyzers

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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.

## ABSTRACT

This report describes the work that was carried out in the development of a calibration module for trace oxygen analyzers. The purpose of the device is to provide a stream of water having an accurately known dissolved oxygen (D. O. ) content for calibration of trace oxygen analyzers in the 0 to 50 ppb range.

Laboratory research was conducted to evaluate methods for deoxygenation and oxygen-addition and to screen analytical methods for accuracy in D. O. analysis. Based on this research a Dissolved Oxygen Calibrator was designed, fabricated, and tested. The calibration module achieves deoxygenation in a two-stage spinning-disc stripper by flowing feedwater and oxygen-free nitrogen gas countercurrently. Oxygen is added by coulometric generation into the second-stage nitrogen purge gas. This instrument gives D. O. contents of 0 to 100 ppb which are accurate to within  $\pm 2$  ppb.

Inasmuch as existing methods for D. O. analysis were of undetermined accuracy, a parallel research was conducted which resulted in the development of an Aerojet-modified Winkler procedure. The novel features of this improved method include (1) sampling, fixing, and titrating under a nitrogen atmosphere, (2) treating the sample by a novel combination of single and double, normal and reverse mode of reagent additions to obtain data for the absolute determination of sample D. O. content, and (3) measuring and correcting for certain errors in the D. O. procedure. This has resulted in a procedure with demonstrable accuracy. The improved method has a precision and accuracy which is better than  $\pm 2$  ppb.

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## I. INTRODUCTION

Corrosion inevitably results during the handling of brines and other process waters because of the oxidizing effect of the dissolved oxygen (D.O.). In evaporative desalination processes, for example, corrosion is a problem even when the D.O. content is reduced by mechanical stripping to the low parts per billion (ppb) level. Attempts to correlate the corrosion rates with D.O. content have, heretofore, been unsuccessful because of uncertainty in the value for D.O. content derived by chemical analysis or instrumental techniques. The magnitude of the problem is illustrated by the fact that different types of monitoring instruments used in the measurement of the D.O. content of a given brine stream, or of identical parallel streams may, and more than likely will, furnish highly different read-outs. Although it is not clear whether any confidence can be placed in even the relative value of such measurements, it is obvious that reliable calibration techniques must be developed if the attainment of real accuracy is to be achieved.

Aerojet-General's Contract D. I. 14-01-0001-2127, with the Office of Saline Water, was aimed at the development of this capability in the form of a calibration module to be used on stream with existing commercial trace oxygen analyzers. Although the primary application was to enhance accuracy in the D.O. monitoring of evaporative desalination process-brines, it is believed that the equipment developed will have a much wider use, extending to any situation where D.O. analysis or monitoring is required.

Inasmuch as D.O. analyzers are typically designed for continuous stream analysis, the research and development of the calibration module was oriented toward an instrument that would operate in the continuous rather than an intermittent mode. The principal design objectives were that:

- (1) The calibration stream be a liquid having an accurately known D.O. content;

(2) This calibration liquid be essentially (excepting D. O. content) the sample stream itself, in order to eliminate chemical and physical errors arising from dissimilarities in media; and

(3) The calibration module feed-liquid be completely deoxygenated or completely equilibrated with any (accurately known) oxygen-containing gas, as determined by the nature of the oxygen-injection step.

Accordingly, laboratory tests were conducted to evaluate techniques appropriate for incorporation in the ultimate calibrator design. The experimental work thus included the examination of methods for complete water deoxygenation, the evaluation of oxygen-addition techniques through gas equilibration and by direct injection for the production of stable, accurately-known D. O. concentrations. Concurrently a screening review of various analytical methods was made so that the D. O. levels produced by calibration test systems could be verified. The program culminated in the design, fabrication, testing, and delivery of a calibration module which produces a product stream having a D. O. content of 0 to 100 ppb that is accurate to ± 2 ppb.

## II. SUMMARY

The work performed under this contract fell logically into three separate tasks beginning with research and ending in equipment delivery. The initial task was to evaluate various methods for deoxygenation and oxygen addition, the second involved the evaluation and development of analytical procedures for obtaining precise and accurate determinations of the D. O. content of treated feedwater streams, and the third was the design, fabrication, and testing of a calibration module based on the results of the preceding tasks. The investigations carried out under this contract began with an evaluation of several deoxygenation methods with relative efficiency values being determined by standard (ASTM) Winkler analyses. As the efficiency of deoxygenation increased so that water having D. O. contents of less than 100 ppb were apparently routinely produced, it became necessary to proceed with the evaluation of analysis methods to insure that techniques of demonstrable accuracy were being employed. This did not prove to be the case, so an improved method was developed, based on the Winkler titration. When the deoxygenation and analysis problems were finally resolved satisfactorily, the work proceeded to the investigation of oxygen-addition methods. Necessarily, the first two tasks were conducted and advanced more or less concurrently. After these two tasks had been successfully completed, the effort was then directed toward the design, development, fabrication, and testing of the calibrator which was delivered at the conclusion of this program. The results of these efforts are summarized below and discussed in detail in the body of this final report.

During the course of the first task, five separate deoxygenation methods were evaluated. These five methods were:

1. Vacuum degassing under mechanical agitation.
2. Purging by the evaporation of dry ice.
3. Stripping in a packed column.
4. Deoxygenation by membrane permeation.
5. Oxygen removal in a spinning-disc stripper.

Each of these techniques was first evaluated in a preliminary screening which indicated the relative merit and potential for reducing the D. O. content to less than 1 ppb. Although all these methods furnished some D. O. removal, this preliminary screening evaluation indicated that the spinning-disc stripper provided the simplest route to achieving the desired efficiency. Further experimental and theoretical studies of the spinning-disc stripper demonstrated that the D. O. removal efficiency is directly related to the rotational speed of the discs and to the flow-rate ratio of stripping gas to feedwater. Calculations indicated that a feedwater stream saturated with  $O_2$  at atmospheric pressure and flowing at a rate of 100 ml/min could be deoxygenated to a D. O. content of less than 0.1 ppb in a two-stage stripping operation in which  $O_2$ -free  $N_2$  was passed countercurrently at a flow rate of 1000 ml/min. This was confirmed experimentally by means of the Aerojet-modified Winkler method developed during the second task of the program.

Methods for oxygen injection were also investigated during the first task. Candidate methods for producing an  $O_2/N_2$  stream having an accurately known composition included: (1) dilution of air with  $N_2$  in successive dilute-split-dump stages to achieve a final concentration of  $O_2$  in  $N_2$  in the range of 0 to 4000 ppm, and (2) constant-current coulometric (electrical) generation of  $O_2$  into a  $N_2$  stream. Prior experience and literature searching showed that accurate mixing of air and  $N_2$  to give the desired dilution of  $O_2$  in  $N_2$  would be very difficult to achieve. Coulometric generation was investigated in laboratory experiments in which  $O_2$  was produced electrically and then transferred into an  $O_2$ -free  $N_2$  stream. The mixed-gas stream was then equilibrated with the deoxygenated feedwater stream in a second-stage spinning-disc stripper. Calculated values based on rate of  $O_2$  generation,  $N_2$  flow rate, and  $O_2$  solubility values were within 0.1 ppb of measured values obtained by means of the Aerojet-modified Winkler method, the development of which is next discussed.

In the second task several standard analytical procedures for D. O. analysis were evaluated as candidate methods for establishing the true D. O. content of the calibrator-processed feedwater stream after complete deoxygenation and after O<sub>2</sub> addition. In initial screening tests the Winkler method (Alsterberg modification per ASTM D1589) had been used to measure the relative efficiency of the various deoxygenation methods.

The analysis methods of ASTM D888A (colorimetric, indigo carmine) and ASTM D888C (Winkler method) were evaluated after the spinning-disc stripper had been improved to the point that it routinely produced water having a D. O. content of less than 100 ppb. Our experience demonstrated that results obtained by the indigo carmine method were dependent upon the flow rate of the sample and other indeterminate factors. It was therefore not further considered. Each of the two Winkler procedures tested exhibited advantages and shortcomings, but neither appeared to offer the data quality required to prove out the calibrator. Furthermore, none of the three procedures produced values whose accuracy could be reliably verified. The investigation then turned to the development of a modified Winkler procedure incorporating the sought-for features of other Winkler methods and resulted in the inclusion of several special adaptations.

Basically, the Aerojet-modified Winkler analysis involves collecting the sample in a N<sub>2</sub>-purged BOD bottle, fixing under N<sub>2</sub> according to the Winkler chemistry, and titration of the prepared sample to a potentiometric endpoint, again under a N<sub>2</sub> blanket. Through a novel combination of single and double reagent additions in the normal and reverse mode, it proved possible to derive nearly absolute values for D. O. content of the sample, D. O. content of reagents, and net redox of the sample and the reagents. A characterization of the new procedure, as limited by program requirements, indicated that there is negligible interference from ion concentrations which normally affect the iodine-thiosulfate reaction. It can be stated with confidence that the newly developed procedure furnishes D. O. values which are precise and accurate to 2 ppb.

In the third task a calibration module was designed, fabricated, and tested to establish its performance characteristics. The calibrator incorporates the same design employed in the bench investigations. Feedwater and purified  $N_2$  are flowed continuously through the two-stage spinning-disc stripper. Feedwater flow to the first stage is automatically controlled by means of a level controller/solenoid valve arrangement so as to maintain a constant liquid level. The partially deoxygenated feedwater stream from Stage 1 flows by gravity to Stage 2 where further stripping and/or  $O_2$  addition occurs. The calibration stream then flows out of the second stage to the D.O. analyzer or sample container.

The  $N_2$  supply is divided into two streams. One passes countercurrently through the first stage and is discharged with entrained  $O_2$  to the atmosphere. The other is directed through a third disc stripper which acts as an electrolysis cell, from which it passes with a fixed amount of  $O_2$  (including zero) through stripper Stage 2 counter-current to the flow of water and thence to the atmosphere. The temperature of the feedwater and calibration stream are monitored and indicated continuously by means of narrow-range dial thermometers. Rotational speed of the discs in all three strippers is adjusted by means of an electronic speed controller and is indicated by a tachometer. Oxygen added to the  $N_2$  stream in the third disc stripper is generated electrically by a constant-current power supply. The  $O_2$  level in the calibration liquid is calculated from instrument panel readings for coulometric current,  $N_2$ -flow rate, the temperature of the calibration stream, and from tabulated  $O_2$  solubility data. A correction must be applied for barometric pressure.

After the fabrication of the calibration module was completed, it was tested to verify the accuracy of the calibration fluid and to determine its response characteristics. The D.O. content of the calibration stream was determined in a series of tests using sea water as the feedwater stream. For nine values obtained at the 0, 25, 50, and 100 ppb level, the measured D.O. content differed from calculated values by an average of 0.26 ppb. The standard deviation of the nine measured values averaged 1.7 ppb, the maximum deviation being 3.1 ppb. The response time to stepwise increases in the rate

of  $O_2$  generation was found to be in good agreement with theory and to be dependent only upon the volume of feedwater in Stage 2 and upon the flow-rate of the calibration stream. Under typical conditions in which Stage 2 contains 500 ml of feedwater, the calibration stream is flowing at 70 ml/min, and a step change in the  $O_2$  content of the  $N_2$  stream occurs, the 90%, 99%, and 99.9% responses in the D. O. content of the calibration stream are 16.5 min, 32.5 min, and 49.5 min, respectively. (The response time is slower for stepwise decreases in the  $O_2$ -generation rate.) The response time is inversely related to the flow rate of the calibration stream. Step changes in the salinity of the feedwater require approximately twice this length of time for corresponding responses in the calibration stream, inasmuch as the change has to be effected in both stripper stages.

### III. CHEMICALS AND EQUIPMENT

Many chemicals and pieces of equipment were used extensively in the course of studies involving deoxygenation, oxygen addition, and analysis. Some pieces of equipment were designed and fabricated specially for certain portions of the laboratory research; these items are described later in appropriate sections of this report. The materials described in this section were used more or less continuously throughout all three tasks of the program. Detailed descriptions of chemicals and equipment used are given in Appendix I.

#### IV. EVALUATION OF DEOXYGENATION METHODS

The experimental work of this program was organized around the premise that the calibration module should generate a calibration stream by the addition of  $O_2$  to completely deoxygenated water. Such an instrument would make it possible to provide a true zero D.O. level for calibration of D.O. analyzers. A completely deoxygenated stream would serve as a convenient medium for checking out existing analysis methods and for developing and proving the absolute accuracy of data derived by such methods. Complete deoxygenation is desirable from the standpoint that it is easier to maintain a constant "zero" than it is to maintain a constant D.O. level other than zero when the actual value is dependent upon liquid and gas flow rates, temperature, pressure, salinity, and other factors. Thus, evaluation of deoxygenation methods was considered to be a necessary first task upon which other tasks would depend.

##### A. INTRODUCTION

In the initial work, five methods for oxygen removal were investigated. Simple laboratory setups were utilized to produce comparative data on:

- a. Vacuum degassing with mechanical agitation.
- b. Purging with evaporating dry ice.
- c. Stripping on a packed column
- d. Permeation through a membrane.
- e. Disc stripping

The first two methods are batch processes and were therefore given only preliminary consideration. The last three involve continuous methods of counter-current gas and liquid flow; these were given primary consideration during the evaluation.

The laboratory investigations reported here were carried out using distilled water at laboratory temperatures, generally  $23.0 \pm 1.0^\circ C$ . Williams and Miller (Reference 1) report that there is no difference in the degassing rates of distilled versus saline water. Thus, the efficiency results obtained with distilled water should be valid, especially because the greater solubility of  $O_2$  in distilled water involves removing larger amounts of  $O_2$  than would

be the case in the deoxygenation of sea water under the same conditions of temperature, pressure, and flow rate.

Samples of deoxygenated water were collected in 300-ml BOD bottles, except as otherwise noted. A few of the preliminary samples were collected in BOD bottles containing air, but because it was anticipated that deoxygenated water would pick up a considerable amount of oxygen from this air blanket, the sampling procedure was modified to include purging of the empty sample bottles with inert, dry gas. For the data reported here, a stream of  $\text{CO}_2$  from subliming dry ice was used to sweep oxygen from the sample bottles, except as noted.

In all the initial measurements of D.O. content, ASTM D1589 (Alsterberg Modification) Method was followed. The analysis is capable of measuring a range of values from 10,000 ppb down to less than 100 ppb. Inasmuch as the initial tests were exploratory and there was no way of knowing what D.O. levels would be achieved as a result of the deoxygenation experiments, this broad-range procedure was considered appropriate. Samples with D.O. values of 8000 ppb were titrated with 0.025 N thiosulfate solution. As the D.O. content was reduced to lower and lower concentrations, the titrant was diluted appropriately to 0.010, 0.005, and 0.0025 N. In some cases titrations with 0.001 and 0.00025 N thiosulfate solution were attempted, but these titrant concentrations bordered on being so dilute that visual end point detection was not reliable.

The procedure of ASTM D1589 does not provide for a correction for the  $\text{O}_2$  content of the Winkler reagents, inasmuch as the correction is small by comparison with the total amount of  $\text{O}_2$  normally measured. Typically, the D.O. content of the water sample would be 8000 ppb as compared to a reagent correction of approximately 20 ppb, a negligibly small interference. In the preliminary evaluations conducted during this report period the D.O. levels, for the most part, were sufficiently high so as to make the reagent correction unnecessary. In any case, the intent was to obtain relative values for comparing stripping efficiencies; the data may be compared with or without this reagent correction. The data of Tables 1 through 8 have

not been corrected, except where noted. Obviously, for more accurate determination of the deoxygenation effect, the reagent correction needs to be determined and applied, especially when the true D. O. content of the deoxygenated water is less than 500 ppb. In tests made subsequent to the preliminary evaluation of deoxygenation methods, this reagent correction was measured and applied.

#### B. VACUUM DEGASSING

In this series of tests distilled water was vacuum degassed in a 500 ml Erlenmeyer flask modified as shown in Figure 1. Water was introduced into the flask, stirring was begun, and the flask evacuated for a specific length of time. The vacuum obtained at the surface of the sample corresponded to the vapor pressure of water at the sample temperature, 24°C (22.4 torr). At the end of the degassing period the vacuum was interrupted, the degassed water was pressurized at 4 to 5 psig with purified nitrogen and the sample transferred to a 300-ml BOD bottle. These samples were then analyzed by titration to a visual end point (starch-iodine) with 0.0255 N sodium thiosulfate solution. The results of this series of tests are shown in Table 1. These data indicate that much of the dissolved oxygen can be removed in 5 minutes (or probably less), but that continued vacuum degassing does not reduce the D.O. concentration to an adequate degree. This method was not considered worth further study.

#### C. DRY ICE OXYGEN REMOVAL

The effectiveness of using evaporating dry ice for deoxygenation was investigated by introducing roughly weighed quantities of the finely powdered material into 1-liter quantities of distilled water contained in large filter flasks. These were set aside (without stirring) and the dry ice allowed to evaporate. As the last of the solid disappeared, the treated water was transferred to BOD bottles and then analyzed. Expectedly, the water temperature was lowered in proportion to the amount of dry ice added. As shown in Table 2, this method of treatment is surprisingly efficient in reducing D.O. content; however, the solution effervesces when acidified, which poses problems of analysis and in the potential use of the liquid as a calibration medium. In any case, the still unacceptably high residual D.O. content made this (batch) method unsuitable for further consideration.

#### D. PACKED COLUMN

Feed water and purified  $N_2$  were flowed countercurrently through a column containing an inert packing to effect transfer of oxygen from the liquid to the gas phase. Ideally, the bed is a water-wettable, non-reactive material of large surface area. In passing over such a bed, the water is distributed in a thin, uniform layer and thus presents a large transfer surface to the gas phase. If the gas and liquid film transfer coefficients favor it, complete deoxygenation can be achieved by properly dimensioning the process.

The packed column used in this series of tests consisted of a 1-inch I. D. by 22-inch long glass column packed with a 9-inch section of small Raschig rings. There were an estimated 534 Raschig rings each having approximately  $2.19 \text{ cm}^2$  of surface area; this corresponds to  $1169 \text{ cm}^2$  of available transfer surface. Details of the column are shown in Figure 2. Purified nitrogen gas was introduced below the Raschig rings and allowed to flow upward through the column and to vent at atmospheric pressure, except in one test when the  $N_2$  was vented through a 2-inch head of mercury (about 1 psig of pressure). Water introduced at the top of the column was allowed to flow downward over the Raschig rings, and finally was collected in a BOD bottle as it flowed out the bottom of the packed column. The inlet and outlet flow of water was adjusted by means of two stopcocks to give the desired flow rate and to avoid flooding. The D.O. content of the samples was determined immediately after collection. In this series of tests both the liquid and gas flow rates were varied over a limited range to show the effect of the flow rate ratios. The data obtained in this series of tests are given in Table 3.

In view of the probability that the packed column was not ideally dimensioned for efficient deoxygenation, the fact that it lowered the D. O. content from 7700 to 1000 (vented to 2-in. Hg pressure) or to 1500 ppb (vented to atmosphere) was considered encouraging. It is apparent from the data that by optimizing the flow rate ratios, selecting appropriate packing column diameters and lengths, perhaps incorporating a more efficient packing material such as Intalox saddles or Pall rings, and

choosing a higher (but practical) vent pressure, the D. O. content could be reduced to well below 1000 ppb. It was believed, however, that the transfer surface area possible in a practically sized packed column could not begin to compare with the larger transfer surface area attainable in a similarly dimensioned spinning-disc stripper.

#### E. MEMBRANE PERMEATION

Transfer of D. O. from a feedwater stream to a stripping gas by membrane permeation depends largely upon the characteristics of the membrane separating the two phases. The membrane should possess the ability to pass oxygen selectively in relatively large quantities, and it should be as thin as mechanical strength requirements permit to provide maximum O<sub>2</sub> transfer. Deoxygenation occurs because the O<sub>2</sub> migrates from the feedwater to the stripping gas at a rate depending upon the O<sub>2</sub> permeability of the membrane and on the O<sub>2</sub> concentration gradient existing across the membrane.

The intention was to examine the permeation characteristics of two membranes - FEP Teflon and a newer experimental "copolymer of silicone rubber with polycarbonate resins." The latter, a membrane developed by General Electric Company (Reference 2), was reported to diffuse gases up to 30 times faster than materials previously tested. Attempts to acquire samples of this copolymer were unsuccessful inasmuch as General Electric Company has, for the present time, suspended all plans to make the membrane commercially available. The membrane permeation tests were confined, therefore, to FEP Teflon film and tubing. This material has a reported O<sub>2</sub> permeability of  $1.045 \mu l / (cm^2) / (min) / (mil)$  at room temperature.

The test setups employed in our laboratory for preliminary evaluation of film and tubing permeation are shown in Figure 3. For the tubing permeation study, 1/8-inch diameter (I. D.) FEP Teflon tubing having a 10-mil wall thickness (the thinnest wall commercially available) was used. The test apparatus had 4 tubes, each having a 22-inch effective length. This corresponds to 223 sq. cm. of active exchange area. For the film tests the

liquid and gas phases were separated by 1-mil thick FEP Teflon film. The films were separated and held in place by ring-type spacers cut from a 4-in. (I. D.) Plexiglas tube. Each film was 4 inches in diameter, giving  $81 \text{ cm}^2$  of active surface per film or  $162 \text{ cm}^2$  for both films. The data reported in Table 4 are for single and paired film surfaces.

In both tubing and film tests, water and purified nitrogen gas were flowed countercurrently. These data showed that only 4 to 5 per cent of the D. O. was removed by this treatment. From these data alone this approach would appear to be impractical. But, calculating the theoretical amount of  $\text{O}_2$  that should have been removed indicated a different picture. For a permeation rate of  $1.045 \mu\ell/(\text{cm}^2)/(\text{min})(\text{mil})$  of thickness gave calculated removal values which compared with those experimentally derived as follows:

Configuration	Flow Rates, ml/min ( $\text{N}_2$ /Feedwater)	Reduction D. O. Content, ppb	
		Experimental	Theoretical
Tubing	100/85	390	391
2 Films	100/78	325	3100

The very good agreement between theoretical and experimental removal values for tubing permeation indicated that further tests were warranted.

One can calculate theoretical maximum removal rates for various lengths of tubing at the same temperature. For example, 100 ft of tubing\* should allow the D. O. content to be lowered by as much as 5332 ppb. This does not necessarily mean that feedwater containing 5332 ppb of D. O. could be completely deoxygenated, for as the D. O. content of the sample is reduced, a smaller concentration gradient across the membrane would cause a reduced rate of permeation. In the subsequent tests, 1/8-in dia. (I. D.) tubing was inserted into 3/8-in dia. (O. D.) polyethylene tubing.

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It would, of course, be advantageous to use a thinner-walled tube of a proportionally shorter length, but thinner-walled FEP-Teflon tubing is not commercially available.

End connections were made using appropriate Swagelok connections. A total of 30 ft. each of FEP Teflon and polyolefin tubing was used. Distilled water was passed through the Teflon tubing at a rate of 100 ml/min and purified N<sub>2</sub> was flowed countercurrently in the annular space between the Teflon and polyolefin tubing at 1000 ml/min. Under these conditions the D.O. level in the distilled water could theoretically be reduced by as much as 1600 ppb. In actual measurements, however, the D.O. content was reduced from 7772 to 7468 ppb, a net removal of only 304 ppb. Thus, it was concluded that further tubing permeation experiments would not be profitable.

#### F. DEOXYGENATION WITH THE SPINNING-DISC STRIPPER

The spinning-disc stripper provides a means for distributing O<sub>2</sub> between a gas and liquid phase. The device consists of a large number of parallel shaft-mounted discs cross-sectionally arranged in a trough or horizontal cylinder. Water is flowed through the bottom of the cylinder while a stripping gas passes countercurrently in the upper portion. As the shaft rotates, the wettable discs pick up a thin film of water which can then transfer the D.O. into the stripping gas. The advantage of the disc stripper is that a relatively small area of discs can, through the rotational process, provide a highly effective surface for gas-liquid exchange.

The spinning-disc stripper was used by Williams and Miller (Ref. 1) for stripping dissolved gases from sea water into a stream of helium for subsequent gas chromatographic analysis. In view of their claim that "water can be completely purged of its gas content in a single pass through this unit," it seemed worthwhile to fabricate and evaluate such a device for these deoxygenation studies. For the first experimental run dimensions were selected that seemed appropriate. Fortuitously, the dimensions and numbers selected proved nearly ideal for these deoxygenation studies and essentially no changes or modifications were subsequently required.

The disc stripper used in these preliminary studies (see Fig. 4) consists of an acrylic tube (1/4-in. wall) envelope 12-3/4-in. long and 4-in. I. D. The ends are capped with 1/4-in. thick acrylic plates fitted with Teflon supports to allow the free rotation of the center shaft. The latter, constructed of 1/4-in. O. D. stainless steel tubing holds thirty 3-1/2-in. diameter Mylar discs; the latter are separated by spacers consisting of 1/4-in. lengths of polyethylene tubing. The shaft and discs are rotated by a variable speed electric motor. Water and gas connections (inlet and outlet) are also provided.

Data taken in the preliminary evaluation of this device are shown in Table 5. These values were obtained with the discs rotating at poorly controlled speeds, probably ranging from between 100 and 400 rpm. The data shown in Table 5 represent samples successively taken; i. e., in the order listed. It may be noted that the early samples show higher residual D. O. contents; the gradual lowering of D. O. content is no doubt attributable to the purging of air from the system at startup. In any case, the data indicated clearly that increasing the flow rate of the stripping gas should enable one to lower the residual D. O. content much further.

Based on the preliminary results reported above, test emphasis was placed on developing and improving the spinning-disc stripper.

## V. DETAILED EVALUATION OF THE DISC STRIPPER

### A. PARAMETERIZATION

Further tests were conducted to determine the effects of variables which might have a bearing on the stripping efficiency and, more importantly, on the lower attainable limit of  $O_2$  concentration. In considering the principle of operation of the disc stripper, one can conclude that the most important parameters are: (1) flow rate of gas and liquid or, perhaps, the ratio of these flow rates, and (2) the rate of surface area exposure of the discs and, for high rotational speeds, the rate at which the water of this surface exchanges its D. O. with the  $N_2$ . Flow rates and flow-rate ratios are easily controlled and measured. Surface and exchange characteristics are more difficult to parameterize, because the total effective surface area and the rate of exchange between gas and liquid phases are difficult to determine. Using a fixed stripper design (30 discs) and operating at constant temperature ( $23^\circ C$ ), transfer characteristics may be evaluated in an indirect way as a function of superficial contact area by measuring the effect of rotational speed of the discs. This section presents experimental and theoretical analyses of both of the parameters mentioned; i. e., flow rate ratios and speed of rotation.

### B. FLOW RATE RATIO EFFECTS

This series of tests was run at constant disc speed and water flow rate; the nominal values were 390 rpm and 98 ml/min. The gas/liquid flow rate ratios were varied over the range of approximately 1:1 to 12:1 by adjusting the  $N_2$  flow. The experimental values for flow rate ratios and measured residual D. O. contents of the water samples are given in Table 6. From the data it can be seen that the first sample of a series at a single flow-rate ratio is not consistent with subsequent values obtained. This is believed to be attributable to the fact that a measurable time is required to reach a new steady-state condition at a higher or lower D. O. content based on different flow rate ratios. Additionally, the data show that the residual D. O. content is inversely proportional to the gas flow rate.

On eliminating the first sample of each series, correcting for reagent D. O., and averaging the data in Table 6, the values shown in Table 7 result. These adjusted data show that the D. O. content has been reduced

to fairly low values at the higher flow rate ratios. It is also interesting to note that the value of the blank increases as the water is stripped to lower residual D. O. contents. This should be expected in that the lower the oxygen content of the water, the greater the driving force will be to acquire any available oxygen. These data will be further discussed in Section V, D where theoretical efficiency values are considered.

### C. EFFECT OF ROTATIONAL SPEED

After the preliminary evaluation of the disc stripper had been completed, the motor driving the rotating discs was replaced with a more powerful one whose speed could be adjusted and controlled in the range from approximately 0 to 500 rpm. Distilled water was passed through the disc stripper countercurrent to a flow of purified  $N_2$  stripping gas. While the discs were being rotated at various speeds, the product water was collected and analyzed. The results of these tests are given in Table 8. The data indicate that stripping efficiencies at rotational speeds of 378 and 518 rpm (measured with a Veeder counter) do not significantly differ, and speeds as low as 250 rpm apparently do not influence the efficiency of the stripper. However, at 172 rpm deoxygenation is noticeably less effective. From these tests one can conclude that above about 400 rpm, oxygen transfer is essentially independent of shaft velocity.

### D. THEORETICAL ANALYSIS OF FLOW RATE RATIO EFFECTS

The operational efficiency of the disc stripper depends upon several parameters; namely, D. O. concentrations and per cent saturation, flow rates, temperature, pressure, and feedwater salinity. If these quantities are appropriately defined and related mathematically, one should be able to calculate the D. O. in the product from the disc stripper under different operating conditions. The key parameters are symbolized and defined as follows:

- $C_f$  = D.O. content of feedwater, ppm  
 $C_{s, w, p}$  =  $O_2$  solubility in feedwater at temperature, T, pressure, P, and salinity, S, mg/l (ppm)  
 $C_a$  = Concentration of  $O_2$  in atmosphere, 20.946 vol%  
 $F_g$  = Flow rate of  $O_2$ -free nitrogen stripping gas, ml/min  
 $F_w$  = Flow rate of feedwater through the spinning-disc stripper, ml/min  
 $T$  = Temperature of feedwater in the spinning-disc stripped,  $^{\circ}C$   
 $S$  = Salinity of feedwater, ppt  
 $d_T$  = Density of water at temperature, T, and salinity, S, g/ml  
 $T_g$  = Temperature of  $N_2$  stripping gas (assumed to be identical with T),  $^{\circ}C$   
 $C_g$  = Concentration of  $O_2$  in the  $N_2$ , vol%  
 $C_w$  = D.O. concentration in the water, mg/l (ppm)

In order to develop an understanding of the operation of the spinning disc stripper, it is convenient to begin by considering a closed, static system in which volumes,  $V_g$  and  $V_w$ , replace flow rates  $F_g$  and  $F_w$ , respectively. If, for example, a theoretical vessel initially contains 100 ml of feedwater ( $V_w$ ) having a D.O. content of 8.000 ppm ( $C_f$ ) and 100 ml of  $O_2$ -free  $N_2$  ( $V_g$ ), one can calculate the distribution of  $O_2$  that would result after equilibration. The total volume of  $O_2$  ( $V$ ) present in the 100 ml of feedwater is:

$$V = \frac{C_f \times d_T \times V_w}{1.4277 \times 1000} \times \frac{273 + T}{273} \quad (1)$$

In this equation, 1.4277 is the factor for converting from ml  $O_2$  to mg  $O_2$ . Assuming the feedwater to be distilled water at  $20^{\circ}C$ ,  $V$  is found to be 0.600 ml. At equilibrium, the  $O_2$  will be distributed between the two phases, with the largest percentage appearing in the gas phase.

The solubility of  $O_2$  in water obeys Henry's law; i. e. :

$$C = \alpha p \quad (2)$$

where:  $C$  = concentration of  $O_2$  in solution, ppm

$\alpha$  = solubility coefficient, ppm/atm

$p$  =  $O_2$  pressure in gas phase, atm

In more conventional oceanographic terms the equation is expressed:

$$C_{s, w, p} = \alpha C_a \quad (3)$$

where, now:  $\alpha$  = solubility coefficient, ppm/vol%

or, more generally:

$$C_w = \alpha C_g \quad (4)$$

Combining equations 3 and 4 gives the more general equation:

$$C_w = \frac{C_g \times C_{s, w, p}}{C_a} \quad (5)$$

Considering again, the example, if the 0.600 ml of  $O_2$  were all to end up in the 100 ml of  $N_2$ , the gas phase composition,  $C_g$ , would be:

$$C_g = \frac{0.600 \times 100}{100 + 0.600} \approx 0.60 \text{ vol\%} \quad (6)$$

From Equation 5 one calculates the D. O. content of the distilled water (at  $20^\circ C$ ,  $C_{s, w, p} = 9.40$ ) to be:

$$C_w = \frac{0.60 \times 9.40}{20.946} = 0.269 \text{ ppm} \quad (7)$$

Thus, the original 8.000 ppm has now been reduced to 0.269 ppm. This means that 3.4% of the D.O. remains in the water and that 96.6% has been transferred to the gas phase. Continuing the example of the static system, if the volume of nitrogen were increased to 200 ml, the per cent O<sub>2</sub> would be halved and the D.O. content of the water (at equilibrium) would be similarly reduced. Similar dilutions would occur for still larger volumes of N<sub>2</sub>. Tabulated, the values would be approximately as follows:

<u>V<sub>g</sub>, ml</u>	<u>C<sub>g</sub>, vol%</u>	<u>C<sub>w</sub>, ppm</u>	<u>% D.O. removed</u>
100	0.60	0.269	96.6
200	0.30	0.135	98.3
500	0.12	0.054	99.3
1000	0.06	0.027	99.7

The foregoing discussion has dealt with equilibrium in a static system. The dynamic system represented by the disc stripper may be treated in an analogous manner using N<sub>2</sub> and feedwater flow rates instead of volumes. The analogy can be very illuminating and helpful in understanding the operation of the disc stripper, but it should be understood that while in a flowing system the transfer of O<sub>2</sub> tends toward equilibrium, it does not necessarily attain it.

The static system used in the foregoing discussion would represent one theoretical plate. If a disc stripper of a length, L, were constructed that gave exactly the values obtained in the example cited previously, L would be the height equivalent to one theoretical plate (H E T P). In the disc stripper, where O<sub>2</sub> is transferred by a differential rather than by a step-wise action, it is theoretically correct to speak of L as being the height equivalent to one transfer unit (H T U). HETP and HTU may be, but are not necessarily, equal for the disc stripper.

Using flow rates in place of volumes would give approximate equations for  $C_g$  and  $C_w$ , as follows:

$$C_g = \frac{C_f \times d_T \times F_w}{14.277 \times F_g} \times \frac{273 + T}{273} \quad (8)$$

$$\text{and: } C_w = \frac{C_g \times C_{s,w,p}}{C_a} = \frac{C_{s,w,p} \times C_f \times d_T \times F_w}{C_a \times F_g \times 14.277} \times \left( \frac{273 + T}{273} \right) \quad (9)$$

Using the conditions of the experiment involving flow rate ratios given in Table 7, one can calculate theoretical values with which to compare the experimental data. The comparison is shown in Table 9. The reasonable agreement between theoretical and experimental values indicate that the disc stripper used in this experimental work has the efficiency of approximately one transfer unit; i. e., it is equivalent to 1 HTU. Although 1 transfer unit is usually considered unimpressive, the distribution here favors the transfer of D. O. to the gas phase, and a single transfer unit under practical flow conditions can effect 99.7% D. O. removal. Obviously, increased efficiency could be achieved by adding another transfer unit to the single spinning-disc stripper.

#### E. SOME THEORETICAL CONSIDERATIONS RELATED TO ROTATIONAL SPEED

For a fixed design the exchange characteristics of the disc stripper are a function primarily of water and  $N_2$  flow rates and the rotational speed of the discs. The rate of area exposure in gas-liquid exchange is:

$$A = 2RN \times 3.14 \left[ \left( \frac{d_2}{2} \right)^2 - \left( \frac{d_1}{2} \right)^2 \right]$$

where:  $A$  = rate of area exposure of the Mylar discs,  $\text{cm}^2/\text{min}$   
 $R$  = rotational speed, rpm  
 $N$  = number of discs  
 $d_2$  = outside diameter of the Mylar disc, cm  
 $d_1$  = diameter of hole at center of Mylar disc, cm.

Using values from the experimental work with 30 discs having a diameter of 3-1/2 in. (9.0 cm) and a negligibly small center hole, at 400 rpm, the rate of area exposure is 1,520,000 cm<sup>2</sup>/min. This area is far larger than could be provided by a similarly sized packed column.

This calculation only shows how much surface area is available; it does not tell how efficiently it is used. It could be assumed that all the area is wetted and exposed for gas-liquid transfer, but this is not necessarily true. Further, it does not help establish the rate at which O<sub>2</sub> is exchanged between the feedwater and the N<sub>2</sub> gas. The rate of exchange is determined by diffusional processes in the gas, liquid, and interface phases. In the two-film concept, where there is exchange without chemical reaction, the interface phase is considered to offer no resistance to the passage of the slightly soluble O<sub>2</sub>. The resistance to transfer lies within the gas or liquid phases; the higher resistance may be in either the gas or the liquid phase, in which case the transfer may be gas-phase limited or liquid-phase limited. The rate of transfer is also dependent upon the driving force; i. e., the concentration gradients in the gas and/or liquid phases. In the disc stripper the composition of the N<sub>2</sub> and the water vary continuously as they pass through it, and consequently the driving force also varies. It is conventional to employ the concept of a mean driving force rather than actual point-to-point concentration gradients.

In a stripping operation, gas diffusivity in the liquid is probably the limiting factor in liquid-gas transfer. Thus, the rate of stripping, written on a liquid-phase basis, may be described for our system by the equation:

$$W = KA\Delta C \quad (11)$$

where: W = rate of O<sub>2</sub> removal, ppb/min  
K = stripping coefficient, ppb/cm<sup>2</sup>/ppb  
A = rate of area exposure, cm<sup>2</sup>/min  
ΔC = concentration gradient (mean driving force), ppb

Conventionally the stripping coefficient,  $K$ , is given in units of mass/area/unit time/concentration, but in the disc stripper the units listed above, although not rigorously correct, are more directly applicable. The concentration gradient,  $\Delta C$ , in the above equation is related to the operation of the disc stripper in the following manner:

$$\Delta C = \frac{C_f - C_w}{2}$$

$$\text{Thence: } W = \frac{KA}{2} \left[ C_f - C_w \right] \quad (12)$$

where  $A$  and  $C_w$  are the quantities given by equations 10 and 9, respectively. This equation, then, relates the stripping action to the number and size of the discs, the rotational speed of the discs, and flow rate of  $N_2$  and feedwater. No doubt the equation will have to be modified and refined to give a quantitative description of the disc stripper operation. For example, at the present time the value of  $K$  is not known, and the upper and lower limits of operation have not been established. No doubt the upper limit on rotational speed, insofar as increasing D. O. removal, is established by the liquid-phase diffusion coefficient of  $O_2$ ; the lower limit is probably a function of  $N_2$  and feedwater flow rate.

This is a very interesting problem and, obviously, more experimental data needs to be obtained before any detailed comparison between calculated and experimental values can be made.

#### F. TWO-STAGE STRIPPING

The experimental and theoretical values suggested that the total removal of  $O_2$  from water samples might be accomplished more easily by employing a second stripping stage rather than by further increasing the gas/liquid flow rate. For example, if the incoming water contains 8000 ppb of D. O. and is flowing at 100 ml/min, the product D. O. content (at 20°C) should be, after a single pass, 269 ppb for a gas flow of 100 ml/min, 26.9 ppb for a gas flow of 1000 ml/min, and 2.69 ppb for a gas flow of 10,000 ml/min. Obviously, gas flows as high as 10,000 ml/min would be impractical

and could possibly lead to unstable conditions. Alternatively, one might operate two stages, each having water and gas flow rates of, say, 100 and 1000 ml/min, respectively. The water coming into the first stage at 8000 ppb of D. O. would enter the second stripper with a D. O. content of 26.9 ppb. This water would, in turn, exit from the second stripper, operated under the same flow conditions, with a D. O. content of .090 ppb. Water with such a low residual D. O. content would be adequately deoxygenated for use in the contemplated calibration module.

Two disc strippers were, therefore, set up to operate as just indicated. Water samples were collected as they exited from the second stage of stripping and analyzed. The indication was that the D.O. content was essentially zero. However, the accuracy and precision of the analytical procedure used were such as to render the results uncertain. The further evaluation of two-stage stripping thus became involved with the task of developing a method for more accurate D. O. analysis.

## VI. EVALUATION OF CANDIDATE ANALYTICAL METHODS

### A. INTRODUCTION

Three ASTM methods (ASTM D888A, ASTM D888C, and ASTM D1589) for D. O. measurement were evaluated in conjunction with the deoxygenation experiments carried out during this report period. ASTM D1589 (Alsterberg modification) is the Winkler method for dissolved oxygen in industrial waste water. Although this method is not primarily intended for measuring D. O. at the ppb level, it is well-suited to our application because by selecting the appropriate titrant strength one can quantify deoxygenation effects from 8 ppm down to the low ppb level. ASTM D888 Referee Method C is the Winkler titration with a potentiometric end point. This method is described as being: "applicable to the determination of dissolved oxygen in steam condensate, boiler feedwater, and industrial water having oxygen concentrations below 1 ppm." ASTM D888 Referee Method A, a colorimetric indigo carmine procedure is: "applicable to water containing less than 0.06 ppm of dissolved oxygen, such as steam condensate and deaerated boiler feedwater."

Most of the analyses conducted during these preliminary evaluations of deoxygenation procedures were performed by ASTM D1589. The method is versatile, allowing measurement over a wide range of D. O. values. As the oxygen stripping capability was improved to give less than 100 ppb of residual oxygen, the procedure was modified to permit D. O. quantification at these low levels. The two referee methods (ASTM D888A and ASTM D888C) were compared with it at various times during the laboratory studies. The ASTM D1589 procedure, as modified in our laboratory, is our choice for the analyses, even at the low ppb level. The primary reason is that, among other complications, the referee methods give good results only when the deoxygenated water is sampled at a high flow rate; in our tests the typical flow rate for the stripped water is 100 ml/min. It has been our experience that this flow rate is too low to provide adequate rinsing under the sampling conditions specified in ASTM D888A and ASTM D888C.

## B. ASTM D888A, COLORIMETRIC INDIGO CARMINE

This method is reportedly quite sensitive to the D. O. content and to slight changes in the D. O. level. It was our experience that this procedure consistently gave higher values than did ASTM D1589, as modified in our laboratory. For example, in a series of runs in which samples were collected in 300-ml BOD bottles, results from the two methods compared as shown in Table 10. The samples were taken intermittently in a single stripping run and analyzed alternately by ASTM D1589 and ASTM D888A. Thus, there should have been no bias introduced by the sampling technique. It is believed the consistently higher results by ASTM D888A are attributable to problems associated with reagent introduction -- problems that cannot be overcome at the low sample flow rates. Furthermore, the ASTM method makes no claim as to the absolute accuracy of results derived and it is difficult to imagine how absolute values could be obtained and verified. Thus, after this preliminary evaluation the method was not considered further.

## C. ASTM D888C, POTENTIOMETRIC WINKLER

For this series of evaluations, water was deoxygenated in the disc stripper, collected, and analyzed following the procedure of ASTM D888C, except that samples and blanks were taken sequentially instead of simultaneously. The analyses for these tests are given in Table 11. It will be noted that two of the four experimental values agree very well with calculated values; Sample 1 shows reasonable agreement and it appears that the measured value for Sample 5 may be grossly in error.

Sample and blank were sampled sequentially rather than simultaneously because the deoxygenated water was flowing at only 100 ml/min. This means that in order to change the water 10 times in the 500 ml McLean sampling bottle, the water sample would have to flow through a single flask 50 minutes or through two parallel flasks for 100 minutes. The samples were actually taken after 30 min of flushing, which means that there were only an equivalent of 6 changes of water in the single McLean bottle. Much higher sample flow rates would be required if the 10-fold volume change were to be achieved.

Our practice in adding the reagents was to rinse the calibrated 2-ml tip with distilled water prior to or between additions and to dry with a slow stream of nitrogen gas. This represents a modification of the recommended ASTM procedure - a modification which should improve the results derived by this method of D. O. analysis.

The two chief advantages of the method are potentiometric end-point detection and the use of iodized alkaline iodide solution to lower or eliminate interferences from reducing agents. The disadvantages for the present application are the need for a high sample flow rate and the loss of a small portion of the precipitate during acidification. After weighing the advantages and disadvantages, it appeared advisable to incorporate the advantages into a modification of the ASTM D1589 procedure.

#### D. ASTM D1589, WINKLER TITRATION (ALSTERBERG MODIFICATION)

In this procedure the liberated iodine is titrated with an 0.025 N thiosulfate solution to a visual end point using the starch-iodine indicator. For low D. O. contents (less than 1000 ppb) it was convenient to dilute the thiosulfate titrant to 0.01, 0.005, 0.0025, or 0.0001 N as lower and lower D. O. levels were attained. In some cases titrant with a normality as low as 0.00025 was tried. These analyses with decreasing titrant normalities were made with a view to improving the precision of the visual end-point titration. As it turned out, the color change at the very low normalities - 0.001 and 0.00025 N - became less distinct so that there was no real benefit from the use of the more dilute titrants. The optimal titrant concentration appeared to be 0.0025 or 0.0050 N; these normalities were used in a majority of the tests reported herein. Each of the standard Winkler methods evaluated possessed advantages and shortcomings. For ASTM D888C the advantages were: potentiometric titration and the use of iodized alkaline iodide to take care of negative blanks; the disadvantages were: loss of precipitate during acidification and the need for a high sample flow rate. In the case of ASTM 1589 the advantage was the use of a convenient sample bottle which prevents loss of precipitate. Thus, the research was directed to the development of a modified Winkler procedure that would incorporate the desirable features and avoid the undesirable points of the two methods.

## VII. DEVELOPMENT OF THE AEROJET-MODIFIED WINKLER METHOD

The Winkler analysis, as commonly practiced, involves sampling, fixing, and titration. Water is collected in an appropriate sample bottle from which extraneous  $O_2$  can be excluded or purged. Following that, the fixing step involves several chemical reactions by means of which D.O. is converted to an equivalent amount of  $I_2$ ; the latter is then titrated with a standard sodium thiosulfate solution to an appropriate end point. In the fixing step typically 2.0 ml of an alkaline iodide solution and 2.0 ml of a  $MnSO_4$  solution are added to the water sample and allowed to react. During this first step the D. O. oxidizes Mn(II) to a higher valent state. Then 2.0 ml of  $H_2SO_4$  is added to acidify the mixture and dissolve the precipitated hydroxides. In the acid solution the higher valent manganese ions oxidize iodide to iodine. It is this liberated iodine which is then measured in the subsequent titration with thiosulfate solution. Being an iodometric method, the Winkler analysis is subject to the errors and interferences of the iodine-thiosulfate titration. Two important sources of error are air oxidation of iodide in an acid solution and loss of iodine by volatilization. Certain ions can catalyze the air oxidation of iodide or can, of themselves, act as oxidizing or reducing impurities. These and other problems associated with the Winkler method have been reviewed and investigated by White, Leland, and Button (Reference 3).

The third source of error is in the titration and end point detection. It has been shown by those authors that the visual end point and the potentiometric end point do not coincide; our investigations corroborated this finding. They also demonstrated that  $O_2$  of the atmosphere can react with iodide during the titration to give high results.

In the development of an improved method, consideration was given to each step in the process and to an evaluation of the various ways in which errors and inaccuracies could occur. Three areas must be considered in any such analysis; namely, sample handling, reagent blanks, and chemical interferences and errors. Handling routines were designed to exclude extraneous  $O_2$  wherever it might interfere. Reagent problems were investigated

with a view to reducing, eliminating, or measuring and compensating accurately for blank values. Chemical interferences and errors were evaluated with a view to nullifying or correcting for their effects. These various areas of the research and development are considered in this order, although it should be noted that this is not necessarily the order in which the problems were attacked. Consequently, the data presented does not show the step by step improvement achieved.

#### A. MODE OF REAGENT ADDITION

The key to the success of the developmental work was the formulation of a unique set of measurements. By using a novel combination of single and double reagent volumes added in the normal and reverse modes, it was possible to derive the four quantities which characterize the sample-reagent system; namely, (1) the D. O. content of the sample, (2) the D. O. content of the reagents, (3) the net oxidizing or reducing capability of the sample, and (4) the net oxidizing or reducing capability of the reagents; these are designated, respectively,  $H_{O_2}$ ,  $R_{O_2}$ , H, and R.

In the conventional Winkler procedure of ASTM D 888C, two samples are collected simultaneously. One is designated as the blank and the other as the sample. The reagents are added to the sample in the order: 2.0 ml iodized alkaline iodide solution, 2.0 ml manganese (II) sulfate solution, and 2.0 ml sulfuric acid solution. When reagents are added to determine the blank, the order of addition of the acid and manganese reagents are reversed. In the case of the sample, the reagent addition (normal) order allows D. O. to react, eventually converting it to an equivalent amount of  $I_2$ . The total  $I_2$  titrated is the sum of: (1)  $I_2$  added with the alkaline iodide solution; (2)  $I_2$  formed due to the D. O. present in the water sample and added with the reagents; and (3)  $I_2$  liberated by any net oxidizing ability (exclusive of the D. O. moiety) or consumed by any net reducing ability of the sample itself. Expressed as an equation this becomes:

$$NR = R + H + R_{O_2} + H_{O_2} \quad (13)$$

where: NR = total I<sub>2</sub> titrated: normal reagent (NR) mode, ppb\*  
 R = net redox of the Winkler reagents, ppb\*  
 H = net redox of the water sample, ppb\*  
 R<sub>O<sub>2</sub></sub> = D.O. content of Winkler reagents, ppb  
 H<sub>O<sub>2</sub></sub> = D.O. content of the water sample, ppb.

Free iodine is added to the alkaline iodide solution to insure that there will be a net oxidizing ability, even if the other reagents and the water sample have residual reducing capacities. It is possible, for example, for H to have a negative value.

In the case of the blank, the last two reagents (MnSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>) are added in the reverse order so that the D.O. in the water sample and reagents cannot react. Consequently, this reverse reagent (RR) mode gives a measure of the net redox capacity of reagents and water sample. Expressed as an equation, this becomes:

$$RR = R + H \quad (14)$$

where: RR = total I<sub>2</sub> titrated; reverse reagent (RR) mode, ppb\*

In ASTM D 888C the calculation of the net D.O. content of the water sample is obtained by difference. In terms of the quantities defined above:

$$H_{O_2} = NR - RR - R_{O_2} \quad (15)$$

R<sub>O<sub>2</sub></sub> is assumed to be 10.4 ppb where 500 ml McLean bottles are used for sample and blank. This is equivalent to 17.3 ppb for the same amounts of reagents handled in a 300 ml BOD bottle.

\*Calculated as D.O. content

The goal of our research was to prove that two-stage deaeration in the spinning-disc stripper lowers the D. O. content of the water sample ( $H_{O_2}$ ) to essentially 0 ppb, and, secondarily, to verify the reagent blank of 17.3 ppb for  $R_{O_2}$ . An added benefit developed, that of being able to calculate the separate residual redox contributions of the water sample and of the Winkler reagents. The procedure employed was to obtain NR and RR values, and additionally to secure similar titration values for the addition of double reagent volumes in the normal (DNR) and reverse (DRR) reagent modes. In so doing one measures the following quantities:

$$DNR = 2R + H + 2R_{O_2} + H_{O_2} \quad (16)$$

$$\text{and } DRR = 2R + H \quad (17)$$

where: DNR = total  $I_2$  titrated: double normal reagent  
(DNR) mode, ppb\*

DRR = total  $I_2$  titrated: double reverse reagent  
(DRR) mode, ppb\*

Values for the four unknowns ( $R$ ,  $H$ ,  $R_{O_2}$ ,  $H_{O_2}$ ) can then be derived from the following four equations:

$$R = DRR - RR \quad (18)$$

$$H = 2RR - DRR \quad (19)$$

$$R_{O_2} = DNR - NR - R \quad (20)$$

$$H_{O_2} = 2NR - DNR - H \quad (21)$$

Thus, it is readily apparent that this set of determinations provides a means for characterizing the reagents and the water sample.

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\*Calculated as D. O. content.

## B. TEST PLAN

A test plan was devised to include series of measurements in which selected volumes of the Winkler reagents would be added either in the NR or RR mode. The purpose of this test plan was to organize a systematic approach to the examination of various reagent, sample, handling, and titration parameters. The set of tests is shown in Table 12. Although not all possible combinations of reagents are included here, this series does allow the variables of immediate interest in this program to be examined.

## C. HANDLING PRECAUTIONS

From the very beginning of the test program it was believed necessary that the water sample be collected in a container that had been purged of air with an inert gas. In early tests, especially during the evaluation of deoxygenation techniques,  $\text{CO}_2$  (from dry ice) was used to sweep  $\text{O}_2$  from the BOD sample bottles. Later this was abandoned in favor of  $\text{N}_2$  purging simply because  $\text{N}_2$  was readily available and at a higher flow velocity. The studies covered in this section dealt primarily with collecting, fixing, and titrating in a protected atmosphere and with magnetic stirring versus mixing by inversion.

### 1. Sampling and Fixing in an Inert Atmosphere

A series of tests were made in order to assess the value of protecting the sample from atmospheric oxygen during sampling and fixing. Two sets of samples were treated identically except that "regular" samples were collected and fixed in air and "protected" samples were collected and fixed in a BOD bottle bathed in an  $\text{N}_2$  stream. The special container used to accomplish this protected sampling is shown in Figure 5. Distilled water samples were taken from the second stage disc stripper. Data obtained for the two techniques (Table 13) represent actual volumes of 0.0051 N thiosulfate solution required to reach the potentiometric end point. Regular and protected samples were taken randomly throughout a given run to avoid possible systemic errors. The data show that titration volumes for protected samples are much

lower and more reproducible. In fact, the D.O. contents of the protected samples were so low that no starch-iodine color appeared when the indicator (potato starch in these tests) was added. The volumes given in Table 13 - 0.228 and 0.07 ml - correspond to 46.5 and 14.3 ppb D.O., respectively. The difference (32.2 ppb) probably represents the oxygen picked up in the handling procedure. It should be noted that these values are not corrected for the D.O. content of the reagents.

## 2. Titration in an Inert Atmosphere

Inasmuch as iodometric analyses are subject to errors because of air oxidation, it was believed possible to improve the precision and accuracy of the Winkler method by carrying out the titration, as well as the sampling and fixing, in an inert atmosphere. Accordingly, a special container was fabricated that would accept a standard 250-ml beaker. The container (Figure 6) was designed so that the beaker could be purged with  $N_2$  before the sample was pipetted in and a  $N_2$  blanket could be maintained over the solution during the titration. The cover of this vessel contains ports through which the electrodes (platinum-calomel pair) and buret tip can be inserted into the solution being titrated. By having the buret tip inserted below the surface of the sample, it is not necessary to rinse the drops of titrant into the solution with distilled water, another source of  $O_2$  introduction. During this program over 95% of the more than 400 samples analyzed were titrated in an inert atmosphere using the special vessel described above. Inasmuch as the parameters investigated here also are concerned with impurity and pH interferences, iodine loss, the details of laboratory investigations involving inert atmosphere titrations are presented later in Section VII, E.

## 3. Magnetic Stirring

In the conventional Winkler procedure (ASTM D 1589) mixing is effected after reagent addition by repeated inversion of the BOD bottle. As handling procedures were modified to include sampling and fixing in an  $N_2$  atmosphere, the BOD bottle was removed from the  $N_2$  environment to accomplish mixing in this manner.

It is possible, of course, for  $O_2$  to be picked up by the sample-reagent mixture in this manipulation even though it is contained in the tightly stoppered BOD bottle. The logical way to anticipate this problem would be to stir the sample magnetically under the  $N_2$  blanket, thus avoiding any possible air exposure. Tests were made in which Teflon-, Tygon-, and Pyrex-coated magnetic stirring bars were used. The higher D.O. results obtained with the Teflon and the Tygon stirring bars indicated that the coatings contain a measurable amount of absorbed  $O_2$ . The Pyrex-coated stirring bar proved satisfactory, but values obtained with its use were only slightly lower ( $\sim 1.4$  ppb) than those derived when mixing was achieved by inversion. These data are shown in Table 14.

Assuming the net D.O. content to be the difference between tests TP-13 and TP-1 (obtained by inversion), it is estimated that the Teflon and Tygon coatings contained, respectively, 3.2 and 2.1  $\mu$ l of absorbed or dissolved  $O_2$ . It was noted that if a given Teflon-coated (or Tygon-coated) stirring bar were used in successive tests, the amount of coating-contained  $O_2$  gradually decreased. Thus, it would be difficult to make an accurate correction for this source of interference.

In cases where the water sample is at a temperature lower than room temperature, the slight warming that tends to occur during fixing would help to exclude atmospheric  $O_2$  during inversion mixing. However, if the sample temperature is higher than room temperature, some cooling is likely to occur during the fixing step and air might be drawn into the sample. The problem can be avoided by stirring magnetically in the  $N_2$  environment. Thus, it was concluded that the more favorable (and convenient) procedure would be to stir magnetically in all cases.

#### D. EVALUATION OF REAGENT PARAMETERS

In an ideal analytical titration the blank is zero and the titration volume is stoichiometrically proportional (without correction) to the quantity being determined. In the Winkler procedure the primary titration (NR) gives

a total of R, H,  $R_{O_2}$ , and  $H_{O_2}$ ; the latter is the actual quantity of interest. Thus, if the titration were to be made ideal it would be necessary to reduce R, H, and  $R_{O_2}$  to zero. However, it is probably not practical to adjust R or H to zero. The evaluations of reagent parameters reported here were therefore aimed at measuring R and H and at reducing  $R_{O_2}$  to the lowest possible value.

#### 1. Characteristics of Iodized Alkaline Iodide

In some of the preliminary measurements, iodized alkaline iodide was evaluated in the Winkler chemistry with and without added sodium azide. Inasmuch as azide is capable of behaving as either a reducing or as an oxidizing specie, it seemed advisable to omit it from the iodide reagent to avoid possible ambiguity. The alkaline iodide solution contained 700 g KOH and 150 g KI per liter. The solution was "iodized" by adding an appropriate volume of 0.1000 N  $I_2$  solution (6.346 g  $I_2$  + 75 g KI in 500 ml solution). The appropriate volume was found to be about 8 ml of the  $I_2$  solution per liter of alkaline iodide solution; this was sufficient to react with reducing materials present in the latter and to leave a slight excess over any reducing materials that might be present in the  $MnSO_4$  solution,  $H_2SO_4$ , and water sample. The amount of  $I_2$  added is theoretically equivalent to 42.3 ppb of D.O. in the Winkler titration. The amount actually found in excess varied from as low as 6.5 ppb to as high as 35.5 ppb. Tests indicated that the reducing materials responsible for the differences noted were largely present in the alkaline iodide solution and their level varied widely from batch to batch.

Tests conducted over a long period of time indicated that alkaline iodide solution treated with iodine was stable with respect to further chemical reaction and physical loss of  $I_2$ . When stored in air, under vacuum (water aspirator),\* or under an  $N_2$  purge, the concentration of the

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\*The vacuum provided by the water aspirator would be the vapor pressure of water. Neglecting salt effects, a solution at the same temperature would have the same vapor pressure.

solution remained constant. This indicates that there is sufficient excess of KI to tie up the  $I_2$  as the  $I_3^-$  complex so as to prevent its physical loss. The iodized alkaline iodide containing azide showed a corresponding reducing-impurity loss and stability against  $I_2$  loss. Typically, the reverse-reagent titration volume would agree to within  $\pm 0.002$  ml (0.4 ppb) after 5 days of storage in air or after 24 hours in vacuo or  $N_2$  purging.

## 2. Redox of the Winkler Reagents

A series of determinations encompassing Test Plan tests No. 0 through 5 were made to measure the residual redox capacities of each of the three Winkler reagents. The water samples used here were deoxygenated distilled water. The results of these tests are given in Table 15. It will be noted that the average titration volumes for tests TP-0, 1, and -2 agree quite well (RR mode), as do those for TP-3, 4, and 5 (DRR mode). As shown in the table, the variable in TP-0, -1, and -2 is the amount of  $MnSO_4$  solution added, and in 3, 4, and 5 the variables are the amount of  $MnSO_4$  solution and  $H_2SO_4$  added. Taken as groups, the first three tests average out at 0.1329 ml, with an average deviation of  $\pm 0.0017$  ml (27.2  $\pm$  0.3 ppb) and the second group at 0.2530 ml  $\pm$  0.0023 ml (52.8  $\pm$  0.5 ppb). These series of tests indicate that there is no significant redox capacity in either the  $MnSO_4$  solution or the  $H_2SO_4$ . From these values one calculates R to be 25.6 ppb ( $R = DRR - RR$ ) and H ( $H = 2RR - DRR$ ) to be 1.6 ppb. This R would, then, represent the net redox of the iodized alkaline iodide solution. Values for R will, of course, be a function of the amount of  $I_2$  added. Values of H for distilled water were typically found to fall within the range of 0  $\pm$  2 ppb.

## 3. D. O. Content of the Winkler Reagents

A reagent  $O_2$  correction of 10.4 ppb in 500 ml samples, as specified by ASTM D 888C, would correspond to a correction of 17.3 ppb for 300 ml samples if identical volumes of reagents are used. Attempts were made to reduce this reagent-contained  $O_2$  blank to zero by deoxygenation, first by evacuation and then by  $N_2$  stripping of the iodized alkaline

iodide and  $\text{MnSO}_4$  solutions. No attempt was made to deoxygenate the  $\text{H}_2\text{SO}_4$  (which reportedly has a very low D. O. content), and because it is added at such a point in the titration as to make a negligible effect on the titer even if some  $\text{O}_2$  is introduced.

Although it was possible to reduce the D. O. content of the two reagents by approximately 75%, apparently the conditions necessary to achieve complete deoxygenation were never reached. A D. O. content equivalent to approximately 5.0 ppb or less was obtained, but it was difficult to maintain this low level throughout the day while the two reagents were being manipulated within the special reagent-handling systems.

Vacuum degassing proved difficult to reproduce and was soon abandoned. Reagent deoxygenation by  $\text{N}_2$  stripping was accomplished in the apparatus shown in Figure 7. Its use would typically result in  $R_{\text{O}_2}$  values ranging from 4 to 9 ppb. This variable  $\text{O}_2$  content caused poor precision in the analyses. The data in Table 16 show typical data for RR, NR, DRR, and DNR; and for R, H,  $R_{\text{O}_2}$ , and  $H_{\text{O}_2}$  where the reagents were (1)  $\text{N}_2$  purged overnight and during the time of use, and (2) air purged to saturation. In comparing values for R, H,  $R_{\text{O}_2}$ , and  $H_{\text{O}_2}$ , it will be noted that R and  $H_{\text{O}_2}$  agree very well for the two series, and that H is comparable for the two series, and that  $R_{\text{O}_2}$  shows a high value for the air-saturated reagents and a lower value for the  $\text{N}_2$ -purged reagents. These values, all of which are reasonable, help demonstrate that the single- and double-reagent modes of analysis, when used comparatively, are useful in establishing the absolute accuracy of the results.

It will be noted that the sea water values for H are on the order of  $13 \pm 2$  ppb as compared to  $0 \pm 2$  ppb for distilled water. The average deviations for all values are less than 2.0 ppb. It is believed, however, that this does not represent the ultimate precision obtainable from this method. Nonetheless, it is well within the 2 ppb precision reported for ASTM D 888C.

The D. O. contents of the individual reagents were not determined during this program. A series of tests involving TP-1, 2, 3, 8, 13, 14, 15, and 20, would give values for the D. O. content of the individual reagents. According to White, Leland, and Button (Reference 4), the D. O. content of the various reagents is as follows:

<u>Reagent</u>	<u>D. O. Content, mg/l</u>	<u>D. O. Error Introduced in Sample Analysis, ppb</u>
Alkaline Iodide Solution	128	0.9
Sulfuric Acid	57	0.4
Manganese (II) Chloride	<u>2370</u>	<u>16.0</u>
Total	2555	17.3

If the D. O. concentration of the  $MnSO_4$  solution used in our procedure is the same as in the  $MnCl_2$  solution used by White, et al, then nearly all the reagent-contained D. O. would have to come from the  $MnSO_4$  solution. Yet in all the tests that were made using air-saturated reagents, an  $R_{O_2}$  value as low as the 17.3 ppb reported by these authors was never obtained. Perhaps this may be attributed to the fact that  $MnSO_4$ , not  $MnCl_2$ , solution was used in our studies.

In view of the results obtained in these tests and considering the extra equipment and manipulation involved in deoxygenating the Winkler reagents, it was concluded that the use of air-saturated reagents is preferable. It is, however, recommended that these reagents be handled in, and delivered from, Koch-type automatic burets. This topic will be further discussed in Section VII, F.

#### E. INTERFERENCES AND ERRORS

A number of factors are reported or have been shown to lead to errors or to be potential sources of error in the Winkler analysis. A large percentage of these have to do with the titration step. The tests and data discussed here were aimed at evaluating and eliminating or correcting for

these effects. Specifically, the problem areas included (1) rate of air oxidation, (2) pH effects, (3) ion interferences, (4) end point characteristics, and (5) iodine loss. While it is realized that the results and conclusions presented here are not in all cases supported by exhaustive studies nor a statistically adequate degree of replication, it is believed that further experimentation would confirm and strengthen the findings presented.

#### 1. Rate of Air Oxidation

The rate of air oxidation of iodide was estimated from a single test. After the titration of sample #47 (TP-1) under  $N_2$ , a slight excess of thiosulfate was added beyond the end point. The sample was then exposed to air and stirred magnetically until the starch- $I_2$  color reappeared. The rate of air oxidation was estimated from the known excess of thiosulfate (0.140 ml = 27.3 ppb D. O.) and the time to the reappearance of the indicator color (1.0 hr). This corresponds to a rate of air oxidation of approximately 0.5 ppb/min. A normal titration takes about 4 minutes; thus up to 2 ppb error could result for titrations done in air.

Subsequent tests indicate that any problems associated with air oxidation of iodide during the titration step could probably be avoided by the simple expedient of performing the operation in an  $N_2$  atmosphere. The relatively small amounts of  $O_2$  that might be introduced or admitted aside from that reacted during the fixing step should produce an air-oxidation error less than 0.1 ppb.

#### 2. Effect of pH

A series of tests were conducted to determine the effect of pH on the stoichiometry. The results of these tests are shown in Table 17. In all these tests the samples were deoxygenated distilled water. The three series were run on different days. The variation in titer from one series to the next, as for example in TP-1, is primarily because of differences in the amount of  $I_2$  in the iodized alkaline iodide solution. The pH values varied by less than 0.02 units for replicates and from the beginning to the end of the

titrant addition. It will be noted that Series "a" shows a regular increase in titer in going from a pH of 1.72 to a pH of 0.73; this is as expected. The largest change occurs in the first step - in going from a pH of 1.72 to 1.20. The other three data points obtained at pH values from 1.20 to 0.73 compare as well as would replicates. In the case of Series "b" and "c" (except for what is probably an anomalous value at a pH of 0.93 in Series "b"), the data seem to indicate that, at worst, there is only a small difference in the titration volume required at the various pH values. Most importantly, these tests indicate that under routine analytical conditions, where repeatable amounts of reagents are added to give essentially the same pH for each titration, the titer will be reproducible.

### 3. Effect of Ion Impurities

The effect of  $\text{Fe}^{+++}$ ,  $\text{Cu}^{++}$ , and  $\text{NO}_3^-$  on the titration was examined using the apparatus for titration in an  $\text{N}_2$  atmosphere. These three oxidizing impurities were selected because, if they interfere, they should give a higher titer. The sample employed for these tests was distilled water to which a measured quantity of stock ferric chloride and cupric nitrate solutions had been added. Ten ml of the  $\text{FeCl}_3$  solution and 10 ml of the  $\text{Cu}(\text{NO}_3)_2$  solution were added to 5 gallons of distilled water. The resulting solution contained 100 ppb of  $\text{Fe}^{+++}$ , 30 ppb of  $\text{Cu}^{++}$  (in each case, 10 times the quantity normally found in sea water) and 58.8 ppb of  $\text{NO}_3^-$ . These correspond, respectively, to 14.3, 3.77, and 22.8 ppb of D.O. if the ions reacted stoichiometrically with iodide. The data of Table 18, obtained on disc stripper deoxygenated water samples, show that the contaminants had no detectable effect on the titration, and thus did not react with iodide to form  $\text{I}_2$ . These tests probably should be repeated using sea water samples to establish conclusively that no interference is caused. Additionally, the effect of other ions, such as  $\text{Fe}^{++}$ ,  $\text{Cu}^+$ , and  $\text{NO}_2^-$ , should also be tested.

### 4. End Point Characteristics

Several factors having to do with the end point of the  $\text{I}_2^-$  thiosulfate titration were investigated or observed while developing the Aerojet-modified Winkler titration. It was noted, for example, that the

end-point potential is inversely proportional to the concentration of KI added in the iodized alkaline iodide and that the potentiometric end point break is not always sharp in the presence of starch indicator. Details of further investigations of these characteristics are presented below.

a. End-Point Potential

In the measurement of emf with the platinum-calomel electrode pair during titrations, it was observed that increasing the amount of iodized alkaline iodide added to the samples caused the end point break to occur at lower emf values, and conversely. At first this change in potential was thought to be the result of pH changes caused by the KOH in the reagent. However, experiments in which only the amount of acid was varied (reported in Section VII, E, 2 above) did not show corresponding end-point potential shifts. The tests reported here showed that the end-point potential is a function of the KI concentration in the sample. Typical data are given in Table 19 and shown graphically in Figure 8. These values are for distilled water; this same general dependence was also observed for sea water samples. The KI concentrations correspond to 0.018, 0.0060, and 0.0036 M for the 100, 300, and 500 ml samples, respectively. From the Nernst relationship ( $E = E^{\circ} - \frac{0.059}{2} \log \frac{(I_3^-)}{(I^-)^3}$ ), the calculated potential shifts would be 42 and 20 mv, as compared to observed shifts of 18 and 11 mv, respectively. The differences between theoretical and observed are probably attributable to the presence of other ions which might associate or complex with the free iodide to alter its concentration in the sample. Although not verified, manganous ion appears the most likely to bring about this deviation from theoretical in that it is added in excess in the fixing step and both  $Mn^{++}$  and  $I^-$  are known to form complex ions.

b. Starch Interference

In some of the earlier tests starch solution was added routinely so that a visual indication of the progress of the titration was available to accompany the measured potentiometric change. This was particularly convenient because of the fact that the starch end point occurred some .02 to

.08 ml before the potentiometric end point. It was observed, however, that many of the potentiometric titration curves were skewed and indistinct when starch was present. The curves plotted in Figure 9 illustrate this behavior. In order to avoid any possible error from this source, the use of starch indicator was discontinued. No attempt was made to determine the reason for this phenomenon; it may, perhaps, be attributable to a slow desorption of  $I_2$  from the starch at the very low concentrations existing in the end point region.

### c. Method of End Point Determination

The volume of sodium thiosulfate solution required in the titration was derived from the characteristics of the ml-emf data. Volumetric increments of titrant and emf were read and recorded through the end point region and somewhat beyond in order to obtain full curve definition. The volume of titrant corresponding to the inflection point in the ml-emf curve was estimated visually from a graph of the data and also by mathematical interpolation between data points. On the average, the titration volumes obtained by the two methods differed by approximately 0.001 ml (0.2 ppb).

## 5. Iodine Volatilization Loss

Attempts have been made by several investigators over the past half-century to derive highly accurate values for the saturation concentration of oxygen in sea water in equilibrium with air. For years the commonly accepted solubility data were those of Fox (1909). More recent determinations by Truesdale, et al (Reference 4) showed solubilities that were on the order of 3% lower than the data of Fox. Still more recent investigations by Montgomery, et al (Reference 5) confirmed the data of Fox. Their investigations indicated that the solubilities published by Truesdale, et al, were in error because of  $I_2$  losses introduced by a variant in the Winkler method which they employed. The notable fact here is that  $I_2$  losses can cause errors on the order of several per cent. Several series of analyses were therefore made specifically to measure the  $I_2$  loss under the conditions employed in our laboratory.

Iodine losses are believed to occur primarily in the titration step inasmuch as at this point the free  $I_2$  in solution (as evidenced by the brown or yellowish tinge) can be lost through volatilization into the slow stream of  $N_2$

purge gas. The extent of this loss was measured by adding excess thiosulfate solution (0.005 N) and back-titrating with iodate solution (approx. 0.005 N); then excess iodate solution (which liberates  $I_2$ ) was added and back-titrated with thiosulfate solution. In the first case, where excess thiosulfate was titrated with iodate, no  $I_2$  loss should be possible. In the second case, the excess iodate liberates  $I_2$  which might be lost during the back titration with thiosulfate. The  $I_2$  loss should then be calculable from these titration data.

The first tests were made with a flowing  $N_2$  blanket over the solution being titrated. The titration volumes showed  $I_2$  losses on the order of 5 to 6% at levels equivalent to a D. O. content of 100 ppb in sea water. Further tests were then made in which the  $N_2$  blanket was not flowing. These tests showed  $I_2$  losses of approximately 3% at similar D. O. levels. The data for these tests and for determination of losses at other D. O. levels and for distilled water are given in Table 20. One particularly interesting feature of these data is the indication that there is no  $I_2$  loss when larger quantities of KI are present (i. e., when 4.0 ml of iodized alkaline iodide was added). This means, then, that in correcting data involving both single and double reagent volumes (under a stagnant  $N_2$  blanket), a 2.9% correction would be applied to the former and no correction to the latter. The result of this type of correction is demonstrated in Table 21. The values given there indicate that there was a 5% loss of  $I_2$ , provided, of course, that this is the only correction to be applied and that the value for  $H_{O_2}$  for this deoxygenated sample is truly zero. This value is in reasonable agreement with the values measured directly by titration.

One might ask why  $I_2$  is lost during the titration of sample, but not in the purging of the iodized alkaline iodide reagent itself (see Section VII, D, 1) and not when 4 ml instead of 2 ml of the iodized alkaline iodide solution are added to the sample. The theoretical free  $I_2$  concentration can be calculated for each solution, based on the amounts of KI and  $I_2$  added or generated. These are calculated to be, respectively,  $6.2 \times 10^{-7}$  M,  $8.4 \times 10^{-6}$  M, and  $4.6 \times 10^{-6}$  M for the three conditions: (1) iodized alkaline iodide,

(2) sample containing  $I_2$  equivalent to 100 ppb of D. O. and with 2.0 ml iodized alkaline iodide per 300 ml of sample, and (3) the same as (2) but with 4.0 ml iodized alkaline iodide. These calculations are based on the reaction:



$$\text{where: } K = \frac{(I^-)(I_2)}{(I_3^-)} = .0014 \quad (23)$$

The data indicate that loss is minimal when the free  $I_2$  concentration is less than approximately  $5 \times 10^{-6}$  M, and becomes noticeable at concentrations somewhat greater than that. Certainly this is not a sharp dividing line between loss and no-loss conditions.

The important factor in determining the free  $I_2$  concentration and thus the loss of  $I_2$  is the ratio of  $I_3^-$  to  $I^-$ , as indicated by Equation 23. For example, when the  $(I_3^-)/(I^-)$  ratio is  $10^{-1}$ , the free  $I_2$  concentration is  $1.4 \times 10^{-4}$  M and when the ratio is  $10^{-6}$  the free  $I_2$  concentration is  $1.4 \times 10^{-9}$  M. Thus, the losses can probably be avoided if the  $(I_3^-)$  to  $(I^-)$  ratio is less than  $5 \times 10^{-4}$  (i. e., the iodide concentration is at least 2000 times that of the  $I_3^-$  or  $I_2$ ); otherwise,  $I_2$  loss corrections will be necessary. Although Carritt and Carpenter (Reference 6) mention the problem of iodine loss and the possibility of its control via the iodide ion concentration, they do not give data on  $I_2$  loss vs  $I^-$  concentration. Inasmuch as our research in this area was incomplete because of insufficient time, further investigations need to be conducted to determine optimum  $I^-$  concentrations at various D. O. ( $I_2$ ) levels.

#### F. DATA CORRECTION

The data obtained in the Winkler analysis are titration volumes; in the Aerojet-modified Winkler method four values are obtained, corresponding to titration volumes derived by procedures TP-1, TP-13, TP-5, and TP-17. These volumes are then calculated as equivalent ppb of D. O., giving values designated respectively as RR, NR, DRR, and DNR (discussed in Section VII, A). In order to obtain values which accurately represent the

ppb of D. O. and redox (as D. O.) of reagents and sample, there are three corrections that must be applied in converting from ml to accurate ppb values. One correction is for  $I_2$  loss, the second deals with the dilution of the sample because of reagent addition, and the third involves a correction for the exact amount of reagent added.

In the case of  $I_2$  loss, the correction amounts to approximately  $\pm 3\%$ , as discussed in the preceding section. The addition of reagents (6 ml total) to 300 ml of sample requires a  $+2\%$  correction; in the double reagent mode a  $+4\%$  correction is necessary. The third involves the correction of the quantity of reagent to a specified volume. It has been noted previously that the net redox of the reagents (R) is contained in the iodized alkaline iodide solution and the D. O. content ( $R_{O_2}$ ) resides chiefly in the  $MnSO_4$  solution. Typically, R has a value of 36<sup>2</sup> ppb and  $R_{O_2}$  a value of 24 ppb. If 1.990 ml of each reagent is added instead of the intended 2.000 ml, a correction must be added to make up for the  $I_2$  and  $O_2$  not added in the 0.010 ml of each reagent (2.000 - 1.990). In the case of the iodized alkaline iodide solution this correction amounts to 0.18 ppb and for  $MnSO_4$  it amounts to 0.12 ppb. If the added volume had been 2.010 ml in each case the correction would be subtracted. If the dispensing error had been greater or less, the correction would be correspondingly larger or smaller. If the values of R and  $R_{O_2}$  were sufficiently small and/or if the volume added were sufficiently close to 2.00 ml, a correction would not be needed. Our experience has been, however, that the volume of iodized alkaline iodide added from a buret is typically reduced by approximately 0.04 ml after allowance for wall drainage. This corresponds to a correction of 0.7 ppb. Similarly, in the addition of the  $MnSO_4$  solution, the correction may be of the same order of magnitude. The need for this type of correction points up the advantage and even the necessity of adding reagents from burets rather than from pipets if one is to obtain accuracy as well as precision.

The effects of these three correction steps on a series of data is shown in Table 22. In this specific instance, the change in going from uncorrected values to ones corrected for all three factors is, in each case,

less than 2 ppb; R increased by 1.4 ppb, H by 1.9 ppb,  $R_{O_2}$  by 0.9 ppb, and  $H_{O_2}$  not at all. However, the magnitude and absolute value of the correction, especially for reagent volumes, will not always be the same, and so larger or smaller corrections may be encountered. These corrections have essentially no effect upon the precision of the values, but do have a significant effect upon the accuracy.

## VIII. DETAILED AEROJET-MODIFIED WINKLER METHOD

A detailed procedure was worked out for the analysis of sea water samples based upon the research conducted in the course of the program, as described in the preceding section. The method discussed here is the detailed procedure as developed and used in the latter part of the program. The results given here include those obtained in the evaluation of the calibrator fabricated and delivered under this program.

### A. METHOD

The procedure for the Aerojet-modified Winkler method has been committed to the general format of an ASTM method. It has been shown to give good precision and accuracy so long as the details and manipulations are carefully followed. It is believed that both the precision and the accuracy can be further improved by additional development work. The complete procedure is given in Appendix II.

### B. RESULTS

The Appendix II procedure and minor modifications thereof were used to obtain several sets of values for R, H,  $R_{O_2}$ , and  $H_{O_2}$  at various times throughout the latter part of the program. These data are shown in Table 23, which also gives the special conditions for each series of tests. These data show that an experienced analyst can routinely obtain data permitting R, H,  $R_{O_2}$ , and  $H_{O_2}$  values to be derived whose precision (based on the average deviation) is better than 2.0 ppb of D. O. The data of this table show good consistency for values for R,  $H_{O_2}$ , and reasonable consistency for H; the average deviations are, respectively, 1.8, 1.1, and 2.5 ppb. Note also that there is good agreement among comparable  $R_{O_2}$  values derived by each of three methods for each series; the deviations are not greater than 1.0 ppb for any series and average 0.4 ppb for all 6. The accuracy of the values is indicated for the  $H_{O_2}$  values.

In passing through the two stages of the spinning disc stripper, the D. O. content should theoretically be reduced to less than 0.1 ppb as shown previously in Section V, F. The  $H_{O_2}$  values have an average value of -1.0 ppb and an average deviation of 1.7 ppb. Thus it can be concluded that the accuracy is at least as good as the precision of the method.

## IX. OXYGEN ADDITION

Experiments were conducted to evaluate the addition of  $O_2$  to deoxygenated distilled water and sea water. The laboratory setup used in these experiments is shown in Figure 10. The  $O_2$  was generated electrically at a constant current in a disc-stripper cell so as to effect quantitative  $O_2$ -transfer into the  $N_2$  carrier gas. The purified  $N_2$  from the combustion furnace was passed first through the electrolysis cell wherein it acquired the generated  $O_2$  and then through the second stage stripper wherein the gas mixture equilibrated with the water sample to give appropriate D. O. contents. The first stage spinning-disc stripper was used only for sample stream deoxygenation. Although the output water was not completely freed of  $O_2$  in the first stage, the D. O. content of the water passing to the second stage was sufficiently low to allow the D. O. concentration to be brought up or down to a saturation value corresponding to the volume composition and pressure of the  $O_2$ - $N_2$  mixture from the electrolytic generation and to the temperature and salinity of the water.

It is important to realize that the water entering the second stage stripper does not have to be completely freed of its D. O. content for the oxygen addition to be accurate. D. O. contents as low as 0 ppb would, of course, be acceptable. The upper D. O. limit will depend on a number of operational characteristics such as the flow rate of the feedwater and the nitrogen, the D. O. level desired, longitudinal mixing in the spinning-disc stripper, and probably other factors. From a practical standpoint the D. O. level must be low enough so that the stripper can further reduce the  $O_2$  content in the front section and still have adequate length in the back section of the stripping stage to equilibrate with the  $O_2$ - $N_2$  mixture produced by electrical generation. That is to say, whatever the concentration profile of the D. O. content vs distance traveled may look like in the stripper, the composition at the exit end is the value of importance. This concentration profile may decrease and level, decrease and increase, or increase and level; at the present this characteristic is not known. Inasmuch as the D. O. level is low enough so that the second stage can further reduce the oxygen content to 0, the problem is not one of having too much  $O_2$  in the water entering the second

stage. And, inasmuch as the amount of  $O_2$  available in the  $O_2$ - $N_2$  mixture generated electrically is sufficient to bring the D. O. content of approximately 500 ml/min. of completely deoxygenated water up to that representing equilibrium, the problem is not one of having too little  $O_2$  available to supply the amount required by the sample stream.

Generally speaking, the D. O. content measured by the Winkler method was within 2 to 5% of the theoretical values calculated from the measured and corrected electrolysis current,  $N_2$  flow rate, salinity, barometric pressure, and sample temperature. Differences between measured and theoretical values could result from errors in the measurement of: (1)  $O_2$  generation rate, (2) rate of  $N_2$  flow, (3) equilibration temperature and pressure in the second stage disc-stripper, or (4) the actual D. O. content determination by the Winkler method. The agreement between measured and theoretical values is considered adequate for the intended application.

#### A. OXYGEN GENERATION

Oxygen for these experiments was produced electrically in an  $O_2$ -generation apparatus (described in Appendix I), which was constructed like the spinning-disc stripper shown in Figure 4. The function of the  $O_2$ -generation apparatus is to introduce  $O_2$  at a known rate into a stream of  $N_2$  flowing at a known rate. In this series of tests the  $N_2$  flow rate was measured by means of a wet-test meter connected to the  $N_2$  exit line from the second stage stripper. (In the calibration module the  $N_2$  flow rate is read from accurate, calibrated rotameters.) The rate of  $O_2$  production was based on the electrolysis current. From these two quantities, and the temperature and pressure, it was possible to calculate the vol-% of  $O_2$  in the  $N_2$  stream passing to the second stage for equilibration.

Oxygen is generated coulometrically at a rate of 3.482 ml (STP) per ampere per minute. Correcting to laboratory temperature and pressure, gives the following current-volume relationship:

$$F_{O_2} = 3.482 I \left( \frac{273 + T}{273} \right) \times \left( \frac{760}{P} \right) \quad (24)$$

where:  $F_{O_2}$  = rate of  $O_2$  generation at temperature, T,  
and pressure, p, ml/min

I = generating current, amperes

T = temperature, °C

P = barometric pressure, torr.

The volume per cent  $O_2$  in  $N_2$  is the quantity which actually determines the D. O. content that will result from a given rate of  $O_2$  generation. This quantity is a function of the rate of  $O_2$  generation and of the  $N_2$  flow rate in the system, thus:

$$C_g = (F_{O_2} / F_{Total}) \times 100 \quad (25)$$

where:  $C_g$  = concentration of  $O_2$  in carrier gas, vol %

$F_{Total}$  = total volume of gas passing through the  
spinning-disc stripper, ml/min.

In this case:

$$F_{Total} = F_{O_2} + F_{N_2} + F_{H_2O} \quad (26)$$

where:  $F_{N_2}$  =  $N_2$ -flow rate at temperature, T, and pressure,  
P, ml/min.

$F_{H_2O}$  = volume flow of water vapor through the spinning-  
disc stripper, ml/min.

In our laboratory work the purified nitrogen carrier gas was passed through a pressure regulator and rotameter before it was directed through the spinning-disc stripper. The flow rate was controlled by means of a needle valve. The gas passing through the rotameter was purified nitrogen only. The total volume of gas passing through the system was

measured by means of a wet-test meter connected at the vent of the spinning-disc stripper. This measured volume of gas corresponded, then, to  $F_{\text{total}}$ . The concentration of oxygen in the carrier gas was then determined by means of equations (24) and (25), above.

It is important to note that the rotameter was read in terms of the total volume of gas passing through the spinning-disc strippers even though only purified nitrogen actually flowed through the rotameter. It is important to note further that if the flow-rate measurements were made with no oxygen being generated, the wet-test meter values would be the same for readings taken (1) at the exit of the spinning-disc stripper, and (2) just after the rotameter. In the former case the gas sample is nitrogen gas saturated with water vapor and in the latter case the sample is nitrogen gas only. However, gas samples passing through the wet-test meter become saturated with water vapor before being measured, and no distinction is made between wet or dry samples. Further note, if the flow-rate measurements are made without oxygen being generated, the measured flow rate must be increased by the volume of oxygen produced per minute to get  $F_{\text{total}}$ .

## B. SOLUBILITY DATA

In Section VI, E, 5, it was mentioned that there is some uncertainty as to the true solubility of  $O_2$  in distilled water and sea water at various salinities and temperatures. Riley and Skirrow (Ref. 7) have reviewed the oxygen solubility data of various researchers and indicated that the values derived by Fox are probably the most accurate of those currently published. The values adopted as the standards for this work were the solubility data of Fox (from Reference 7) given in part in Table 24.

It should be borne in mind that the accuracy of the D. O. content of the calibration liquid will depend not only upon the accuracy of the solubility data but also upon the reliability with which solubility data derived at oxygen levels corresponding to atmospheric composition can be applied at lower  $O_2$  contents, down to zero oxygen. The theoretical values used for

comparison in our laboratory investigations were derived based on the assumption that Henry's law (Equation 2) is valid over the oxygen vapor pressure range corresponding to a D.O. content of 0 to 15000 ppb. Generally, Henry's law is valid in dilute solutions and so long as the dissolved gas does not undergo association or ionization. Inasmuch as our experimental conditions meet the requirements for conforming to Henry's law, the assumption should certainly be valid.

Fox's solubility data in Table 24 are expressed in ml of O<sub>2</sub> (STP) per liter of water in equilibrium with a dry atmosphere at 760 torr at sea level and 45° N latitude. These solubility data fit the equation:

$$C_{s,v} = 10.291 + (-0.2809T + 0.006009 T^2 - 0.00006320 T^3) \quad (27) \\ - (0.1161 - 0.003922 T + 0.00006310 T^2) Cl$$

where:  $C_{s,v}$  = solubility of O<sub>2</sub> (STP) in water equilibrated with dry air at a total pressure of 760 torr at sea level and 45°N latitude, ml/l

Cl = chlorinity, ppt.

From the standpoint of conditions and units employed, a more practical form of the equation would express the solubility in terms of the weight of O<sub>2</sub> per liter of water in equilibrium with a water-vapor-saturated atmosphere at 760 torr (sea level and 45°N latitude) as a function of the salinity of the sea water.

The volume-to-weight conversion involves multiplying by 1.4277, the weight in mg of 1 ml of O<sub>2</sub> (STP).

The conversion from a dry atmosphere to a water-vapor-saturated atmosphere involves compensating for the vapor pressure of water which, in turn, is a function of the water temperature and salinity. In the case of distilled water, the vapor pressure is given by the equation:

$$\log P_d = 9.1642 - \frac{2322}{273 + T} \quad (28)$$

where:  $P_d$  = vapor pressure of distilled water at temperature, T, torr.

The vapor pressure of sea water is close to that of distilled water. It is lowered in proportion to the salinity by a factor of  $1 - 0.000537 S$ . A more general equation for the vapor pressure of the water sample would then be:

$$\log P_w = \left( 9.1642 - \frac{2322}{275 + T} \right) \left( 1 - 0.000537 S \right) \quad (29)$$

where:  $P_w$  = vapor pressure of the water sample at temperature, T, and salinity, S, torr.

The correction of the solubility equation for the vapor pressure of the water sample has the form:  $\frac{760 - P_w}{760}$

The conversion from a chlorinity factor to a salinity terms involves simply the empirical equation relating the two terms:

$$S = 1.805 Cl + .030 \quad (30)$$

Thus, the equation fitted to Fox's solubility data has the expression  $\frac{S - 0.030}{1.805}$  in place of Cl.

Application of these corrections results in the following equations:

$$C_{s,v} = 10.291 + (-0.2809 T + 0.006009 T^2 - 0.00006320 T^3) - (0.1161 - 0.003922 T + 0.00006310 T^2) \left( \frac{S - 0.030}{1.805} \right) \quad (27a)$$

$$\text{and } C_{s,w} = 1.4277 C_{s,v} \left( \frac{760 - P_w}{760} \right) \quad (31)$$

where:  $C_{s,w}$  = solubility of  $O_2$  in water equilibrated with air saturated with water vapor at a total pressure of 760 torr at sea level and  $45^\circ N$  latitude, mg/l (ppm)

This latter equation was solved by computer at temperatures from 0 to 30°C and at salinities from 0 to 39 ppt in integer steps. The computer program and the data print-out for these 1240 points are given in Table 25. Values at temperatures or salinities between these points can be obtained by interpolation.

In order for these solubility data to be used in the derivation of calculated D. O. values in the O<sub>2</sub>-addition experiments, the listed (Table 25) or interpolated values for C<sub>s,w</sub> must be further corrected to the local barometric pressure. The equation for making these corrections is:

$$C_{s,w,p} = C_{s,w} \left( \frac{B + l + a + b}{760} \right) \quad (32)$$

where: B = measured barometric pressure, torr  
 l = latitude correction, torr (-0.8 torr)  
 a = altitude correction, torr (-0.1 torr)  
 b = barometer scale correction, torr (-2.7 torr)

Correction to the local barometric pressure involves several factors, expressed in the above equation as the factor: (B + l + a + b)/760. The local barometric reading needs to be corrected for the temperature, altitude, and latitude at which the barometric reading was made. In our laboratory (approx. 34°N latitude) the latitude correction is -0.80 to 0.82 torr. The altitude (250 meters) correction is -.06 torr. The temperature correction for the barometer reading (brass scale) amounts to -2.7 ± 0.3 torr (750 torr, 20 to 25°C). Correcting sea-level data to our location involved applying all three of these corrections to the barometric readings.

For the conditions prevailing in our laboratory the equation was simplified to:

$$C_{s,w,p} = C_{s,w} \left( \frac{B - 3.6}{760} \right) \quad (33)$$

At typical barometric pressures in our laboratory (740 to 750 torr), this represented a further correction of 1.8 to 3.1%.

### C. RESULTS OF OXYGEN-ADDITION EXPERIMENTS

Experiments were conducted in which O<sub>2</sub> was added to distilled water and to sea water. In these tests the rate of O<sub>2</sub> generation was selected to give approximately 20 to 25 ppb, 50 ppb, and 100 ppb. No attempt was made to obtain these values precisely, although this could have been done. The electrolytic current required varies with sample temperature and salinity and with the N<sub>2</sub> flow rate, thus making the generation of arbitrarily preset O<sub>2</sub> levels somewhat inconvenient. Oxygen was generated into the N<sub>2</sub> stream and this O<sub>2</sub>-N<sub>2</sub> mixture was then equilibrated with the deoxygenated water in the second-stage spinning disc stripper. The water issuing from this disc stripper was collected in a 300-ml BOD bottle and analyzed by the Aerojet-modified Winkler method. The D. O. content obtained by the Winkler procedure was designated as the measured value. The theoretical D. O. content was calculated from the O<sub>2</sub>-generation and flow parameters measured during the run, from the equation:

$$C_{\text{out}} = \frac{1000 C}{20,946} \times C_{s,w,p} \quad (34)$$

where:  $C_{\text{out}}$  = D. O. content of the product water, ppb.

Theoretical and measured values were then compared.

The experimental data presented in Table 23 and discussed in Section VIII, B, showed that complete deoxygenation can be achieved. The water flowing from the second-stage spinning-disc stripper contains 0 ppb of D. O. when the N<sub>2</sub> carrier gas contained no O<sub>2</sub>. The measured D. O. content of samples during O<sub>2</sub>-addition experiments can be determined by either of two analytical approaches. One method is to run a series of analyses by the RR, NR, DDR, and DNR modes at a single generation rate and from the derived values calculate H<sub>O<sub>2</sub></sub>, the D. O. content of the water sample. Inasmuch as no O<sub>2</sub> generation gives a D. O. content of 0 ppb, the value for H<sub>O<sub>2</sub></sub> will be the true D. O. content produced by O<sub>2</sub> generation. A simpler approach is to calculate H<sub>O<sub>2</sub></sub> from the difference between the NR value with and without O<sub>2</sub> generation. In the case of NR without O<sub>2</sub> generation, the quantity derived

represents a blank which is the sum of R, H, and  $R_{O_2}$ ;  $H_{O_2}$  is 0. With  $O_2$  generation,  $H_{O_2}$  takes on the value corresponding to the D.<sup>2</sup>O. content of the product water and the measured value of NR increases accordingly. The situation is as follows:

$$H_{O_2} = NR(\text{gen}) - NR \quad (35)$$

where: NR(gen) = total  $I_2$  titrated; normal reagent (NR) mode with  $O_2$  generation, ppb (calculated as D. O. content)

In a series of tests where R, H, and  $R_{O_2}$  are constant, this method will give the true D. O. content of the sample more rapidly than the first-described procedure.

The values for  $H_{O_2}$  obtained during these  $O_2$ -addition experiments were, with one exception, obtained by difference as in Equation 35. A single value for  $H_{O_2}$  obtained from the RR, NR, DRR, DNR mode of measurement agreed quite well with the theoretical and the by-difference values.

The data obtained for  $O_2$ -addition to distilled water and sea water are given in Table 26. The sea water data shown there were obtained using the laboratory model and later using the calibration module fabricated for delivery under this contract. The values within the individual groups were obtained in a relatively short period of time (i. e. , a few days). The data of the three groups were, on the other hand, obtained at widely spaced time intervals (i. e. , on the order of weeks). Corrections have been applied for  $I_2$  loss in accordance with system conditions (see Table 20); in this case, 1.6% for distilled water and 2.9% for sea water. The overall agreement between theoretical and measured values is indicative of the accuracy of the method. The average deviation for distilled water samples was 1.7% or 0.8 ppb and for sea water samples, 1.9% or 0.7 ppb. Values obtained during the evaluation of the calibration module had an average deviation of 3.4% or 1.4 ppb. These data were obtained by an analyst who, initially at least, was less familiar with the manipulative aspects of the Aerojet-modified Winkler technique. It is especially significant that for all 30 values shown in Table 26, the average difference between measured and theoretical values was only 0.12 ppb or 0.15%. This suggests that the accuracy may be significantly better than the precision of the method.

## X. DESIGN OF THE CALIBRATION MODULE

The calibration module or Dissolved Oxygen Calibrator (DOC) was designed and fabricated following closely the configuration and arrangement of the laboratory apparatus. The DOC, packaged in a castor-mounted two-bay console, achieves deoxygenation of the water sample by passing purified  $N_2$  countercurrent to the flow of water through two stages of spinning-disc strippers. Appropriate liquid level controls are incorporated to maintain constant the optimum water level required for efficient stripping. Speed control and tachometer units serve to control and indicate the rotational speed of the discs. Oxygen is generated electrically in a third spinning-disc stripper by current provided from a constant current power supply; the  $O_2$  is introduced into the purified  $N_2$  which passes to the second stripping stage. The DOC also includes instruments for measuring the level of electrical current,  $N_2$  supply pressure,  $N_2$  flow rate, and water temperature. The DOC is shown photographically in Figure 11. Details covering its design and the components used in its fabrication are given below. An Operating and Maintenance Manual is provided under separate cover.

### A. NITROGEN-FLOW SYSTEM

A schematic diagram of the  $N_2$ -flow system is shown in Figure 12. Cylinder  $N_2$  or other nominally pure  $N_2$  is supplied at 30 to 50 psig. This flowing gas is purified in the combustion furnace and then cooled to room temperature in coils of stainless steel and copper tubing. The purified  $N_2$  is then divided into two streams for use in the two stripping stages.

The pressure of stream 1 is adjusted to 15 psig by means of pressure regulator, PCV-1; the pressure is indicated on pressure gage, P-1. The flow rate is adjusted by means of the needle valve, NV-1, located on the base of the rotameter, R-1. The metered  $N_2$  stream is then passed through the Stage-1 spinning-disc stripper and to a vent.

The pressure of stream 2 is adjusted to 15 psig by means of pressure regulator, PCV-2, and indicated on pressure gage, P-2. The flow rate is adjusted by means of flow control valve, FCV-2, located just below the rotameter. The flow control valve was selected to give a constant  $N_2$  flow rate where the downstream pressure is constant and the supply

pressure is variable. The needle valve, NV-2, on the base of the rotameter, is normally left open. It may be used to adjust the  $N_2$  flow in place of FCV-2. This  $N_2$  stream is then passed successively, through the  $O_2$ -generation stage, through the Stage-2 spinning-disc stripper, and to a vent.

## B. WATER-FLOW SYSTEM

A schematic diagram of the  $H_2O$ -flow system is shown in Figure 13. The sample water should be supplied at 5 to 30 psig. The inflow of water is controlled by the solenoid valve, SV-1, and needle valve NV-3. The solenoid valve (normally closed) is controlled by the level-control system, LC-1, which includes the control box and level sensing probes. When the level rises so as to contact all three probe tips, a signal from LC-1 closes SV-1; when the level drops so that the two upper electrodes, + (Hi) and - (Lo) no longer are in contact with water, a signal from LC-1 activates the solenoid opening SV-1. Water flows through SV-1, through needle valve, NV-3, and through rotameter R-3 into Stage 1. Water flows by gravity into Stage 2 and out through needle valve NV-4 to the point of use. The rate at which water flows into Stage 1 when SV-1 opens is determined largely by the setting of NV-3; this flow rate is indicated by rotameter R-3. The temperatures of feedwater and product water streams are indicated continuously by means of dial thermometers T-1 and T-2, respectively. Lines carrying the product water from Stage 2 to the point of use should be kept as short as possible; longer runs of tubing should be of Pyrex glass so as to avoid the intrusion of atmospheric  $O_2$  into the deoxygenated water stream.

As presently constructed, the DOC is capable of delivering product water at flow rates of up to about 100 ml/min. Flow between the two stages is limited. Flow rates of over 100 ml/min result in level-control problems because the flow is gravity dependent.

The rate at which SV-1 opens and closes is determined largely by the spacing of the Hi and Lo level-sensing probes. As delivered, the probes are set to control the level to within approximately 1/16-in., and as a consequence SV-1 opens and closes every 30 to 40 seconds. The cycle time can be

lengthened by allowing the water level to vary by 1/8-in. or 1/4-in.; this can be done simply by raising the Hi electrode the appropriate distance. The solenoid valve is suitable for continuous use, but after some 10,000 cycles the diaphragm tends to stick to the valve seat and must be replaced. Less frequent activation of SV-1 would allow the valve to be serviced less frequently.

### C. LEVEL CONTROL SYSTEM

Figure 14 gives a schematic diagram of the electrical wiring for the level control system. Strip 1 and Strip 2 are terminal strips located, respectively, inside the left and right doors as one faces the front of the DOC. The letters B, R, and G refer, respectively, to black, red, and green color-coded wires. The numbers refer to positions on Terminal Strip 1. Position 7 is a common ground for all electrical power. Electrical power (110 V, 60 cps) is supplied to positions 5, 6, 7. Power to the level controller LC-1 is controlled by means of a double-pole on-off switch SW-1, which is connected to 5 and 6, providing power to LC-1 through 3 and 4. An indicator light L-1 is also connected to 3 and 4. The level sensing probes are connected to Strip 2 at points designated R (Hi), B (Lo) and G (Ground), thence to Strip 1 and to LC-1. When LC-1 senses the need for more water, an actuation signal is sent to SV-1 via 1 and 2 on the two strips. An indicator light L-2 connected to 1 and 2 shows when SV-1 is activated. The switch SW-1 and lights L-1 and L-2 are located on the front panel of the DOC. The level controller is located inside the DOC cabinet; it contains its own power switch and indicator light.

### D. SPINNING DISC STRIPPERS

Details of the spinning-disc strippers are shown in Figure 15. Each is basically the same as those used in the research and development portions of the program, except that 40 mylar discs were used instead of 30. Some details of the end seals were changed to promote longer service life and better sealing effect; the changes may be noted by comparing Figure 15 with Figure 4. By lubricating the Teflon washers with a light grade

of silicone grease and adjusting the spring tension, it is possible to obtain a seal that will hold several psig pressure. This is more than adequate for a system that is being vented to atmospheric pressure.

The spinning-disc stripper used for O<sub>2</sub> generation is identical to the others in the major details. However, shorter spacers were used so that a smaller portion of the cylinder would be occupied by the discs. Twenty Mylar discs were positioned at each end of the tube and the generating electrodes were placed in the middle of the spinning-disc stripper, as indicated in Figures 12 and 13.

#### E. MECHANICAL DRIVE SYSTEM

The drive system for the spinning-disc strippers consists of a low-speed, fractional-horsepower motor with a speed controller, a chain-and-sprocket drive system, and a tachometer for continuous indication of the rotational speed of the discs. The motor is a 1/15 hp. shunt wound, reversible motor geared down to furnish low shaft speeds. The motor speed is controlled by means of an SCR speed controller. The speed controller has a Hi and Lo speed range and is supplied with a FORWARD-BRAKE-REVERSE switch so that the motor may be instantly started and stopped at any speed setting under full load. On the Hi range the motor speed may be varied from 11 to 500 rpm; on Lo, the speed range is 11 to 341 rpm. The torque supplied at the drive shaft is 5.5 and 10.2 in.-lb for the Hi and Lo speed ranges, respectively. The torque requirements for the system should not be greater than 4-in. lb under any circumstance, estimated from the starting torque of the system and the frictional (viscous) drag of water at low temperatures.

A chain-and-sprocket arrangement supported in case iron pillow blocks with bronze bearings forms the drive system. Each individual spinning-disc stripper is connected to its drive shaft by means of a flexible coupling. All components are driven at the same speed, as is the tachometer used to measure and indicate the rotational speed. However, the tachometer reading is one-half that of the actual speed and thus all tachometer readings must be multiplied by 2 to get the true rotational speed.

## F. OXYGEN-GENERATION SYSTEM

The O<sub>2</sub>-generation system is shown schematically in Figure 16. The system consists basically of a constant-current coulometric power supply, a current meter, and the spinning-disc stripper which serves as the O<sub>2</sub>-generation stage. The current level is adjusted at the power supply to any value from 0 to 1.00 amperes. The current is read on meter M-1. Current levels from 100 to 1000 ma are read on the Hi range; currents of 0 to 100 ma are read on the Lo range. The range switch SW-2 has three positions: Hi, Lo, and Off. The center off position allows the power supply to be turned on, warmed up, and adjusted to the desired current level, and then held on a standby (off) position in preparation for addition of O<sub>2</sub> to the sample stream.

The D. O. content of the product water theoretically can be varied by changing the N<sub>2</sub> flow rate and holding the O<sub>2</sub> generation rate constant. For example, generating oxygen at a current of 1000 ma into a N<sub>2</sub> stream flowing at 1000 ml/min would give a D. O. content of 109 ppb for sea water of salinity 34.0 ppt at 30°C. If the N<sub>2</sub> flow rate were reduced to 500 ml/min, the D. O. content of sea water at the same salinity and temperature would be 218 ppb. However, this approach is more tedious and subject to problems. For one, the response time of the system would be increased if the N<sub>2</sub> flow were decreased. Also, changes in the N<sub>2</sub> flow of this magnitude will cause the temperature of the combustion furnace to change (increase) by as much as 100°C. This higher temperature might cause the dissociation of any CO<sub>2</sub> in the N<sub>2</sub> to form CO and O<sub>2</sub>. This would be highly undesirable. A stepwise control of the composition of the O<sub>2</sub>-N<sub>2</sub> mixture is most easily achieved by changing the generating current.

## G. ELECTRICAL SERVICE

The DOC is designed to operate on 110V, 60 cps, 20 ampere electrical service. Electrical power is supplied to a 4-outlet box inside the instrument through a Hubbell-type connector. The combustion furnace is connected to one of the four outlets of this box; the furnace consumes a maximum of 800 watts of power (7 amperes) and has its own fuse. Other electrical needs

are supplied by way of a Pilot Strip located behind the combustion furnace and connected electrically to a second outlet of the 4-outlet box. The Pilot Strip has a built-in circuit breaker and pilot light; it is designed to carry up to 15 amperes. The Pilot Strip has 5 receptacles each with its own pilot light and switch. Electrical connections are made to the Pilot Strip to obtain power for the coulometric power supply (Coulometric P/S), Speed Control, and Level Control; the maximum power requirements for these components are, respectively, 0.75, 2.1, and 8.0 amperes.

#### H. ACCURACY OF COMPONENTS

All components were selected for 8-hrs/day operation. The temperature of the combustion furnace is constant and repeatable to within better than  $5^{\circ}\text{C}$  at a constant  $\text{N}_2$  flow rate. The motor driving the spinning disc strippers is overrated so that the speed will remain constant for any given setting to within 10 rpm under normal variations in water level in the system.

Component accuracy was primarily of concern where parameters were measured or controlled which directly influenced the D.O. content of the product water; namely, water temperature,  $\text{N}_2$ -flow rate, and  $\text{O}_2$ -generation rate. The dial thermometers provide temperature readings that are accurate to 0.5% of full scale reading ( $0.25^{\circ}\text{C}$  in this case). The  $\text{N}_2$ -flow rate in Stage 2, as determined by R-2, is accurate to within 1% of full scale (maximum calibrated accuracy) and reproducible to within 0.5% of the instantaneous reading. Through the use of the flow control valve, FCV-2, the flow rate is held constant to within a narrower limit than this so long as the downstream (vent) pressure remains constant. The rotameter in Stage 1 is capable of similar accuracy; however, flow rate here is not very critical. A flow controller was therefore omitted from this stage. The power supply included as the main component of the  $\text{O}_2$ -generation apparatus will hold the current constant to within  $\pm 0.002\%$  or 0.200 ma, whichever is greater, for line or load variations down to a short circuit across the output terminals. The accuracy of  $\text{O}_2$  generation is, therefore, determined by the accuracy with which the current can be set. The generating current is set and read

on the special DC ammeter which is accurate to  $\pm 1\%$ . Thus, the accuracy with which the D. O. output of the DOC (assuming equilibrium between gas and liquid and that the solubility data are accurate) is estimated to be:

$$\text{Accuracy} = \sqrt{a^2 + b^2 + c^2} \quad (36)$$

where a = accuracy of temperature-dependent parameter, approx. 0.4% as median value.

b = accuracy of  $N_2$ -flow parameters, 1%

c = accuracy of  $O_2$ -generation parameters, 1%

This means that from the standpoint of components the system accuracy should be within 1.45%.

## XI. CHARACTERIZATION OF THE DISSOLVED OXYGEN CALIBRATOR

The completed DOC was run through a series of tests to determine its operating characteristics. The accuracy and stability of the DOC output stream were measured and the D. O. concentration-time profile was determined at several D. O. levels and H<sub>2</sub>O-flow rates. The response to a step-wise change in salinity of the feedwater was also determined. The accuracy of the D. O. output was measured using the Aerojet-modified Winkler method. The stability and response characteristics were determined using the Magna Corporation Model 10755 Oxymeter with Recording Adapter and recorded using a Varian Model G-10 recorder.

### A. ACCURACY

The accuracy of the D. O. output at various levels was reported previously in Sections VIII, B, and IX, C. These data are shown in Tables 23 and 26. In summary, these data showed that the accuracy was comparable to that of values obtained throughout the laboratory tests. For deoxygenated water (Table 23) the measured values compare to calculated values in all tests to within 1.0 ppb with an average deviation of 1.1 ppb; for the DOC the measured value differed from the calculated value by 0.8 ppb with an average deviation (inexperienced analyst) of 4.46 ppb. During O<sub>2</sub>-generation at 25, 50, and the 100 ppb level (nominal) all tests (Table 26) gave measured values which were, on the average, lower than calculated values by 0.12 ppb  $\pm$  0.89 ppb and the DOC gave values which were low by 0.2 ppb  $\pm$  1.4 ppb. Thus, the DOC provides a calibration stream of unprecedented accuracy in the 0 to 100 ppb range.

### B. RESPONSE CHARACTERISTICS

#### 1. Changes in D. O. Level and H<sub>2</sub>O-Flow Rate

A series of tests were run in which the D. O. content of the product water was continuously monitored by means of an in-line D. O. analyzer (Magna Corporation Model 10755 Oxymeter); the signal from the sensor was fed to a Varian Model G-10 Recorder through a Recording Adaptor. The response time of the DOC was calculated from the record; it was assumed that the response time of the analyzer was negligible with respect to that of the DOC.

First, water was passed to the analyzer without O<sub>2</sub>-generation occurring in the DOC until the graphic recording indicated steady-state deoxygenation. Then O<sub>2</sub> generation was initiated at some level, such as 25, 50, or 100 ppb. The system was then operated in this mode until the new steady-state condition was attained, as indicated by the recorder plot. The rate of O<sub>2</sub> generation was next increased or decreased to some new level and the system again allowed to reach the new steady-state condition. It was found that the time required to achieve steady-state operation is the same for large or small increases in O<sub>2</sub>-generation rate so long as the H<sub>2</sub>O-flow rate is held constant. The response time is longer for decreases in the O<sub>2</sub>-generation rate. The observed response follows closely that of the logarithmic mixing equation ( $C/C_0 = e^{-kt}$ ). In the DOC the equation would be expressed in the form given below to incorporate the parameters of the N<sub>2</sub>- and H<sub>2</sub>O-flow system:

$$\log C = \log C_0 - \frac{Ft}{2.303V} \quad (37)$$

- where:
- C = D.O. content of the output stream at time, t, ppb
  - C<sub>0</sub> = D.O. content of the water delivered before a change in O<sub>2</sub>-generation rate (time, t<sub>0</sub>) ppb
  - F = flow rate of the output stream, ml/min.
  - t = elapsed time, min.
  - V = volume of H<sub>2</sub>O in Stage 2, ml.

Equation 37 shows that the response time is a function only of the volume of water (V) in Stage 2 and of the rate at which water flows (F) through Stage 2. Inasmuch as the volume of water in Stage 2 is fairly constant (≈ 500 ml), the response time is primarily a function (an inverse one) only of the flow rate, F. Table 27 shows values for C (C<sub>0</sub> = 100 ppb) at increment times from 0 to 104 min. and for selected flow rates. Note that the 90% response time at 50 and 100 ml/min. are, respectively, 23 and 11.5 minutes, and that the 99% response times are correspondingly, 46 and 23 minutes. A typical response curve for the DOC is shown in Figure 17 along with a theoretical curve calculated from equation 37, above. It will be seen that in general the two curves are quite similar. In the DOC response curve, however, a delay of approximately 2 minutes at the beginning occurs. This is due to the delay brought

about by the response-time characteristic of the  $O_2$ -generation cell. In this case the response time is a function of the  $N_2$ -flow rate, not of the  $H_2O$ -flow rate.

## 2. Changes in Salinity of the Feedwater

Changes in the salinity of the feedwater cause  $O_2$ -solubility differences and thus would affect the D. O. level in the output stream. The response time of this two-stage system may therefore be determined by monitoring the D. O. content of the output stream. One would predict that the response time for two stages in series would be approximately double that for a single stage. This was checked experimentally by monitoring the D. O. content of the product stream continuously while the salinity of the feedwater stream was changed from 33.6 ppt to 18.0 ppt. The  $H_2O$ -flow rate during this test averaged approximately 60 ml/min. Full recorder response was reached in 95 minutes. Based on the data of Table 27 the 99% and 99.9% response times should have been 77 and 115 minutes, respectively. Thus, there is adequate agreement between measured and theoretical response times. Here, too, the response time will depend on the volume of water in each of the two stages and upon the flow rate of the product water.

## C. STABILITY

There are several factors that will affect the stability of the D. O. level in the output stream. The first is the constancy of the parameters which determine the composition of the  $O_2$ - $N_2$  mixture, namely: the  $O_2$ -generation rate and the  $N_2$ -flow rate. These factors have been discussed in Section X, H, foregoing. A second set of factors is the constancy of the temperature, pressure, and salinity as they relate to the solubility of  $O_2$  in the sample stream. The solubility of  $O_2$  in sea water changes by approximately 1% per  $^{\circ}C$  at or near room temperature and for salinities around 34 ppt. Under the same conditions it changes about 0.7% per ppt salinity. The interrelationships of salinity, temperature, and  $O_2$  solubility are shown in Table 25. Solubility will also be directly related to the vent (atmospheric) pressure. For example, an increase in atmospheric pressure (or vent pressure) by 7.6 torr will increase the  $O_2$  solubility by 1%; the  $O_2$  solubility

is directly (linearly) related to the  $O_2$  pressure and thus to the total pressure on the system. Thus if the temperature is constant to  $\pm 0.5^\circ C$ , the salinity is constant to  $\pm 0.2$  ppt, and the pressure is constant to  $\pm 2$  torr, the D. O. content should not change by more than 0.90% (0.50% + 0.14% + 0.26%). Assuming these factors to vary randomly, and not so as to give errors in the same direction, the total of all the aforementioned factors should combine to give an error of not greater than 1.6%. If one is careful in the construction of delivery tubes so that no  $O_2$  can diffuse into the calibration stream, this then should represent the stability and accuracy of the output stream. Our experience during the evaluation of the DOC has been that once the D. O. level in the product stream has reached a steady state, the output of the D. O. analyzer as measured by the recorder will show no further change.

An additional important point should be made at this time. It has been noted previously in Section V, B, that the D. O. content of the output from Stage 1 depends upon the relative flow rates of  $N_2$  and water through that stage. Likewise it may be inferred from Section V, F, that there will be some minor dependence of the D. O. content upon flow rate ratios through Stage 2 during deoxygenation. This variation will, however, be minor in the DOC. For example, if a  $N_2$ -flow rate of 1000 ml/min is taken through the two stages, and if the  $H_2O$  flow rate is allowed to vary from 50 ml/min to 100 ml/min, the residual D. O. content will theoretically still remain below 0.1 ppb. When the generated  $O_2$  is transferred into the  $N_2$  stream,  $O_2$  is supplied at such a rate as to provide sufficient  $O_2$  for  $H_2O$  flows of up to 497 ml/min. Thus, even large relative changes in the  $H_2O$  flow rate will not bring about instability or inaccuracies so long as the instrument is operated as it was designed.

## XII. CONCLUSIONS AND RECOMMENDATIONS

### A. CONCLUSIONS

The experimental work performed during this program has demonstrated that the concept of a calibration device that will furnish fluids having accurate D. O. contents in the 0 to 100 ppb range is indeed realizable. The evaluation of methods of deoxygenation showed that the spinning-disc stripper is extremely efficient in effecting the transfer of gases between the vapor and liquid phase. This was pointed up by the fact that by the proper selection of liquid and gas flow rates and choosing appropriate disc parameters (number, size, and rotational speed), 99.999% of the D. O. can be removed from water in a single pass through a two-stage disc stripper. Extensive laboratory tests indicated it was possible to develop an improved Winkler method to give D. O. analyses that are precise and accurate to at least 2 ppb for measurements in the 0 to 100 ppb range. Oxygen addition by electrical generation was shown to be an accurate and convenient method for providing D. O. levels of calibration quality. The Dissolved Oxygen Calibrator designed and fabricated as a result of this research was evaluated and found to deliver a calibration stream having an accuracy equal to that demonstrated in the experimental laboratory model. Thus, it will now be possible to generate streams for the calibration of D. O. analyzers and/or for other applications requiring an accurately known D. O. content.

### B. RECOMMENDATIONS

It is believed that the achievements under the present program have pointed the way to several important areas which require further development work. The two main areas have to do with the Winkler Method and with improvements in the calibrator itself.

#### 1. Further Improvement of the Winkler Method

The research conducted under the present program resulted in an improved Winkler method whose accuracy could be demonstrated. The Winkler method is widely accepted as the method of choice for D. O. analysis, and will probably be used more and more extensively in the years to come,

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OPERATING TIME		PRODUCTION (INCLUDING CONDENSATE)				RAW MATERIALS					CHEMICALS			PROCESS CONDITIONS												AMBIENT CONDITIONS						CALCULATED QUANTITIES AND RATIOS												
DATE	HOURS	M GALLONS			POUNDS TOTAL	STEAM (DOW)		POWER TOTAL kWhr.	SEA WATER FEED		ACID POUNDS	SC. INH. POUNDS	CAUSTIC POUNDS	CONC. FACTOR		TEMPERATURES						PRESSURES				pH	DRY BULB TEMP.		WIND		PRECIPITATION		EXTRACTION RATIO	H <sub>2</sub> O SEP. M LBS.	CONDENSATE IN PRODUCT M LBS.	H <sub>2</sub> O/LB. DOW STEAM FED WITH COND.	M LBS. H <sub>2</sub> O PER kWhr	kwhr PER M LBS. SW						
		DOW	FREE-PORT	PLANT		TOTAL	TOTAL LBS. M		MAXIMUM RATE M LBS./HR.	TOTAL LBS. M				MAXIMUM RATE M LBS./HR.	IN	OUT	SWF TO P-1	SWF TO NO. 1	DISCH. BRINE FROM 17	STEAM TO NO. 1	DOW STEAM	FREEPORT PRODUCT	VAPOR FROM 17	VAPOR FROM 1	TO NO. 1 psig		DOW STEAM psig	318 CONDENSER		VAPOR HEAD psia		MINIMUM							AVERAGE	STR.	DIR.	FORM	INT.	DURAT. HOURS
4-17	24	626	432	55	1,114	9,297	615	27	12,990	11,520	480	951	0	0	0.50	1.65	71	263	95	276	472	87	97	266	31.1	166	0.6	39.18	0.86	8.0	70	72	Light	S	None			.697	8,029	1,217	14.1	.719	1.12	
4-18	24	617	426	53	1,097	9,159	609	26	12,800	11,520	480	988	32.7	0	0.52	1.64	71	263	96	276	472	87	98	266	31.1	161	0.6	39.18	0.89	8.0	63	68	Light	NW	None			.683	7,868	1,292	14.0	.716	1.11	
4-19	24	630	411	51	1,095	9,144	570	26	12,600	11,200	480	1,061	23.7	0	0.72	2.09	68	263	93	275	468	86	97	266	31.1	163	0.6	39.18	0.86	8.1	66	70	Light	SW	None			.647	7,246	1,899	15.0	.726	1.13	
4-20	24	624	408	55	1,088	9,079	583	25	12,820	11,520	480	894	0	0	0.78	2.25	67	263	91	275	464	84	94	266	31.0	164	0.5	39.18	0.79	8.1	65	68	Light	NE	Rain	light	2		.653	7,523	1,557	14.6	.708	1.11
4-21	24	614	415	52	1,082	9,033	572	25	12,589	11,520	480	1,280	25.2	0	0.65	1.95	69	263	94	275	470	86	97	266	31.0	165	0.6	39.18	0.86	8.2	64	70	Light	NE	None			.667	7,684	1,350	14.8	.718	1.09	
4-22	13	345	229	33	608	5,070	319	25	6,950	6,240	480	792	13.3	0	0.63	1.86	70	264	94	275	472	87	98	266	31.1	165	0.6	39.18	0.89	8.1	68	72	Light	SW	None			.661	4,125	954	14.9	.730	1.11	
4-23							0				0	0	0																															
4-24							0				0	0	0																															
4-25	5.7	138	500	68	257	2,148	179				485	554	21.2	0	0.65	2.10	72	263	95	274	440	88	98	265	31.0	139	0.7	38.53	0.89	8.0	75	77	Light	S	None			.690	4,896	970	11.5	1.33	4.28	
4-26	14.66	369	294	36	702	5,866	470	27	3,040	7,095	485	1,024	28.5	0	0.56	1.93	72	264	96	275	442	88	98	266	31.1	138	0.6	39.18	0.89	7.9	70	72	Light	SE	Rain	lard	2		.710	8,179	535	13.0	.685	1.10
4-27	24	558	436	49	1,044	8,713	623	27	12,720	11,520	480	951	0	0	0.53	1.80	73	264	96	276	448	89	99	266	31.0	139	0.7	39.18	0.91	8.2	65	72	Light	NE	Rain	light	1		.706	8,133	917	12.9	.698	1.13
4-28	24	590	441	52	1,084	9,050	652	28	12,960	11,520	480	973	32.7	0	0.57	1.90	75	264	95	275	472	88	97	266	31.2	150	0.6	39.18	0.86	9.0	57	70	Light	NE	None			.700	7,997	1,240	14.0	.740	1.09	
4-29	24	620	436	50	1,106	9,236	617	27	12,480	11,424	476	1,006	6.5	0	0.57	1.95	74	264	94	275	446	87	97	266	31.2	154	0.6	39.18	0.86	9.1	63	70	Brisk	E	Rain	light	1		.708	8,071	1,149	14.2	.731	1.11
4-30	24	624	434	45	1,104	9,219	604	26	12,620	11,400	475	512	14.1	0	0.54	1.84	73	264	95	274	444	88	97	266	31.2	155	0.6	39.18	0.86	9.0	66	70	Light	E	None			.707	8,060	1,210	14.4	.730	1.11	
5-1	24	624	442	43	1,110	9,270	601	26	12,700	11,400	475	512	14.1	0	0.54	1.84	73	264	95	274	444	88	97	266	31.2	155	0.6	39.18	0.86	9.0	66	70	Light	SE	Rain	light	2		.684	7,748	1,296	14.4	.718	1.11
5-2	24	617	422	44	1,083	9,044	586	26	12,600	11,328	472	512	24.4	0	0.67	2.12	73	263	95	275	446	90	97	266	31.2	155	0.6	39.18	0.86	9.0	68	71	Light	NE	None			.651	7,421	1,606	14.3	.685	1.12	
5-3	24	589	408	46	1,044	8,716	570	25	12,720	11,400	475	512	23.6	0	0.94	2.69	73	263	94	274	444	91	97	265	31.0	156	0.6	38.53	0.86	9.0	68	71	Light	NE	None			.651	7,421	1,606	14.3	.685	1.12	
5-4	24	589	403	43	1,036	8,650	564	25	12,700	11,400	475	512	23.9	0	0.96	2.70	73	263	98	274	445	92	100	265	31.0	156	0.7	38.53	0.95	9.1	72	74	Light	E	Rain	light	2		.644	7,342	1,308	14.3	.681	1.11
5-5	24	592	376	44	1,013	8,458	551	24	12,720	11,376	475	206	21.9	0	0.98	2.61	73	263	102	274	444	94	104	265	31.0	156	0.8	38.53	0.95	8.9	72	75	Light	E	Rain	light	2		.625	7,110	1,348	14.4	.665	1.12
5-6	24	592	376	44	1,013	8,458	551	24	12,720	11,376	475	194	18.9	0	0.99	2.70	76	263	101	274	442	93	103	265	30.8	154	0.8	38.53	1.03	8.8	74	75	Light	SE	Rain	light	24		.633	7,168	1,278	14.0	.653	1.14
5-7	24	585	380	45	1,012	8,445	561	24	12,940	11,324	475	193	0.9	0	1.00	2.76	74	263	95	274	440	93	98	265	30.8	154	0.6	38.53	0.89	8.8	70	74	Light	E	Rain	light	24		.638	7,168	1,403	14.3	.664	1.15
5-8	24	582	398	46	1,027	8,571	559	25	12,900	11,256	469	193	3.2	0	0.99	2.77	75	263	95	274	446	93	99	265	30.8	156	0.6	38.53	0.91	8.9	70	75	Light	NE	None			.643	7,222	1,398	14.5	.673	1.14	
5-8	14	583	401	47	1,032	8,619	557	25	12,800	11,232	469	193	3.2	0	0.99	2.77	75	263	95	274	446	93	99	265	30.8	156	0.6	38.53	0.91	8.9	70	75	Light	NE	None			.643	7,222	1,398	14.5	.673	1.14	
5-9	15	390	280	38	710	5,926	381	25	7,950	7,020	469	192	2.1	0	0.98	2.76	76	263	96	274	471	94	99	265	30.4	156	0.6	38.53	0.91	9.1	65	70	Light	N	None			.645	4,528	1,398	14.6	.745	1.13	

REMARKS

RUN TOTALS (WHERE APPLICABLE)  
 24 HOUR DAILY AVERAGE (WHERE APPLICABLE)

U.S. Department of the Interior  
OFFICE OF SALINE WATER  
FREEPORT DEMONSTRATION PLANT

Operator Data Sheet Development Run No. 16

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Prepared By

OPERATING TIME		PRODUCTION (INCLUDING CONDENSATE)					RAW MATERIALS					CHEMICALS			PROCESS CONDITIONS												AMBIENT CONDITIONS						CALCULATED QUANTITIES AND RATIOS										
DATE	HOURS	M GALLONS			POUNDS		STEAM (DOW)		POWER	SEA WATER FEED		ACID	SC. INH.	CAUSTIC	CONC. FACTOR		TEMPERATURES						PRESSURES		pH		DRY BULB TEMP.		WIND		PRECIPITATION		EXTRACTION RATIO	H <sub>2</sub> O SEP. M LBS.	CONDENSATE IN PRODUCT M LBS.	H <sub>2</sub> O/LB. DOW STEAM FED WITH COND.	M LBS. H <sub>2</sub> O PER kWh	kwhr PER M LBS. SWF					
		FREE-PORT	PLANT	TOTAL	TOTAL	TOTAL LBS. M	MAXIMUM RATE M LBS./HR.	TOTAL kWhr.	TOTAL LBS. M	MAXIMUM RATE M LBS./HR.	POUNDS	POUNDS	POUNDS	IN	OUT	SWF TO P-1	SWF TO NO. 1	DISCH. BRINE FROM 17	STEAM TO NO. 1	DOW STEAM	FREEPORT PRODUCT	VAPOR FROM 17	VAPOR FROM 1	TO NO. 1 psig	DOW STEAM psig	313 CONDENSER		VAPOR HEAD psia	NO. 1	NO. 17	FREEPORT PRODUCT	°C MINIMUM							°C AVERAGE	STR.	DIR.	FORM	INT.
3-8	24	705	386	24	1,115	9,312	652	28	12,560	11,760	490	530	19.3	0.63	2.08	56	262	86	274	472	76	88	262	31.3	158	0.4	36.65	0.66	9.2	50	56	Mod	E	None			.697	8,197	1,115	13.3	.741	1.07	
3-9	24	689	403	23	1,116	9,315	658	28	12,740	11,760	490	530	13.1	0.63	2.12	56	262	86	274	472	76	89	263	31.4	163	0.4	37.27	0.68	9.2	39	49	Brisk	E	None			.703	8,267	1,048	12.5	.731	1.08	
3-10	24	680	409	25	1,114	9,301	653	28	12,760	11,760	490	523	9.3	0.68	2.23	57	262	85	274	470	75	86	262	31.2	162	0.4	36.65	0.62	9.2	40	46	Brisk	N	None			.695	8,173	1,128	13.2	.729	1.09	
3-11	24	672	426	25	1,134	9,464	658	28	13,062	11,736	490	550	18.8	0.65	2.21	60	262	80	274	469	73	80	262	31.3	158	0.3	36.65	0.58	9.3	43	45	Light	NE	Rain	Light	6		.706	8,286	1,179	13.4	.724	1.11
3-12	24	677	428	24	1,130	9,430	650	28	13,000	11,712	489	530	29.0	0.64	2.18	58	262	80	271	470	73	84	262	31.3	163	0.3	36.65	0.58	9.2	49	53	Light	SE	Rain	Mod	16		.706	8,269	1,162	13.5	.725	1.11
3-13	24	679	482	22	1,184	9,885	637	27	12,940	11,736	490	550	37.3	0.65	2.19	58	262	80	274	472	75	84	262	31.5	163	0.3	36.65	0.58	9.2	45	59	Light	E	None			.703	8,250	1,636	14.5	.764	1.10	
3-14	24	676	423	20	1,120	9,348	634	27	12,940	11,712	490	563	6.4	0.66	2.18	60	262	81	274	467	75	85	262	31.4	162	0.3	36.65	0.60	9.2	57	58	Light	SE	None			.697	8,163	1,186	13.7	.722	1.10	
3-15	24	678	428	21	1,129	9,425	655	28	12,720	11,760	490	550	15.5	0.63	2.15	60	262	81	274	460	75	85	262	31.2	161	0.3	36.65	0.60	9.3	46	49	Hard	NE	Rain	Hard	24		.707	8,314	1,111	13.4	.741	1.08
3-16	24	672	441	21	1,135	9,473	657	28	12,860	11,736	490	523	11.7	0.53	2.00	60	262	81	274	473	75	85	262	31.6	161	0.3	36.65	0.60	9.3	46	58	Mod	NE	Rain	Mod	24		.735	8,626	848	13.4	.737	1.10
3-17	24	676	434	22	1,133	9,458	642	27	12,940	11,736	489	523	2.6	0.58	2.03	57	262	79	275	475	74	84	262	31.5	161	0.3	36.65	0.58	9.3	45	49	Light	N	Rain	Light	20		.714	8,380	1,079	13.7	.731	1.10
3-18	24	684	414	22	1,122	9,364	633	27	12,720	11,736	489	585	5.5	0.66	2.25	55	262	81	275	471	75	85	262	31.4	161	0.3	36.65	0.60	9.0	52	63	Light	SW	None			.707	8,297	1,068	13.8	.736	1.08	
3-19	24	711	373	22	1,116	9,318	625	27	13,080	11,736	489	644	11.7	0.75	2.56	56	262	82	274	467	77	86	262	31.5	156	0.3	36.65	0.62	8.0	50	61	Light	S	None			.707	8,297	1,021	13.9	.712	1.11	
3-20	11	207	126	16	350	2,923	327	26	12,960	5,379	489	295		0.83	2.67	56	262	81	274	465	76	86	262	31.6	162	0.3	36.65	0.62	8.0	55	61	Mod	SE	None			.689	3,706	(782)	8.9	.226	2.41	
3-21	24	669	393	28	1,092	9,113	665	28	12,980	11,760	490	644	23.5	0.83	2.62	57	262	83	287	503	76	87	263	31.4	161	0.4	37.27	0.64	8.3	60	62	Light	NE	None			.683	8,032	1,082	12.7	.702	1.10	
3-22	24	633	410	30	1,074	8,970	640	27	12,720	11,760	490	651	17.3	0.82	2.49	60	262	85	274	459	78	88	262	31.4	147	0.4	36.65	0.66	9.4	58	60	Light	SE	None			.671	7,891	1,079	13.0	.705	1.08	
3-23	24	636	416	30	1,083	9,044	612	26	12,840	11,760	490	651	14.5	0.78	2.36	61	261	86	274	466	78	89	262	31.5	165	0.4	36.65	0.68	9.4	58	58	Mod	SW	Rain	Light	4		.669	7,867	1,177	13.8	.704	1.09
3-24	24	629	415	30	1,075	8,978	623	27	12,960	11,760	490	651	0	0.74	2.31	61	262	87	274	482	79	89	262	31.5	162	0.4	36.65	0.68	9.4	60	64	Light	NW	None			.680	7,997	982	13.4	.693	1.10	
3-25	24	633	420	30	1,084	8,969	631	27	12,960	11,760	490	669	19.2	0.80	2.46	63	262	83	274	476	77	87	263	31.5	162	0.4	37.27	0.64	9.3	49	52	Brisk	NW	None			.675	7,938	1,031	13.2	.692	1.10	
3-26	24	620	398	30	1,049	8,757	601	27	12,960	11,760	490	695	17.0	0.86	2.32	62	262	83	275	475	76	87	263	31.3	169	0.3	37.27	0.64	9.3	46	53	Light	NE	None			.629	7,397	1,360	13.6	.676	1.10	
3-27	24	629	398	31	1,060	8,848	604	26	13,200	11,760	490	644	12.6	0.88	2.53	61	262	83	274	473	76	87	262	31.1	161	0.3	36.65	0.64	9.2	57	64	Light	NW	None			.652	7,668	1,181	13.6	.670	1.12	
3-28	24	628	405	29	1,063	8,872	609	26	13,200	11,760	490	1,170	0	0.89	2.66	61	263	84	275	477	77	88	263	31.2	162	0.4	37.27	0.66	9.3	62	66	Light	NW	None			.665	7,820	1,052	13.6	.672	1.12	
3-29	24	630	406	32	1,069	8,925	616	26	12,960	11,712	490	1,181	16.4	0.88	2.67	61	263	84	275	472	80	88	263	31.2	161	0.4	37.27	0.66	9.0	59	65	Light	SE	None			.670	7,847	1,078	13.5	.689	1.11	
3-30	24	627	398	36	1,062	8,868	606	26	12,960	11,712	488	1,170	13.8	0.89	2.60	62	263	85	275	473	78	88	263	30.7	162	0.4	37.27	0.66	9.3	61	66	Light	SE	None			.658	7,706	1,163	13.6	.684	1.11	
3-31	24	618	385	36	1,040	8,686	597	26	13,200	11,592	488	1,170	19.0	0.85	2.50	68	262	88	275	471	80	91	265	31.2	163	0.4	38.53	0.71	9.4	57	61	Light	NE	None			.660	7,651	1,036	13.5	.658	1.14	
4-1	24	632	383	36	1,052	8,785	604	26	13,200	11,472	478	1,185	13.6	0.82	2.47	64	263	88	275	472	81	91	265	31.2	162	0.4	38.53	0.71	9.4	59	62	Light	SE	None			.668	7,663	1,123	13.5	.666	1.15	
4-2	8.58	216	118	15	352	2,940	199	26	4,100		478	418	2.2	0.83	2.42	65	263	88	275	471	82	92	265	31.2	162	0.4	38.53	0.74	9.4	62	62	Light	SE	None			.657			13.7	.717		
4-3	3.75	766	95	17	186	1,557	159						3.2																74	74	Light	SE	None				9.7						
4-4	24	615	404	52	1,072	8,954	574	26	12,720	11,472	478	1,061	0	0.75	2.20	67	263	90	274	472	83	93	266	31.0	158	0.5	39.18	0.76	7.7	65	67	Light	S	Rain	Light	1		.659	7,560	1,394	14.6	.704	1.11
4-5	24	614	394	59	1,067	8,912	593	26	12,960	11,496	480	1,042	15.2	0.70	2.12	67	263	91	273	463	84	93	265	31.0	154	0.5	38.53	0.76	8.0	55	67	Light	S	Rain	Light	1		.670	7,702	1,210	14.0	.688	1.13
4-6	24																																										

U.S. Department of the Interior  
OFFICE OF SALINE WATER  
FREEPORT DEMONSTRATION PLANT

Operator Data Sheet Development Run No. 16  
2 of 4  
From 12-18-68 To 5-9-69  
Prepared By

OPERATING TIME		PRODUCTION (INCLUDING CONDENSATE)				RAW MATERIALS				CHEMICALS			PROCESS CONDITIONS										AMBIENT CONDITIONS						CALCULATED QUANTITIES AND RATIOS																
DATE	HOURS	M GALLONS			TOTAL	TOTAL	STEAM (DOW)		TOTAL	SEA WATER FEED	ACID	SC. INH.	CAUSTIC	CONC. FACTOR		TEMPERATURES						PRESSURES				pH	DRY BULB TEMP.		WIND		PRECIPITATION		EXTRACTION RATIO	H <sub>2</sub> O SEP. M LBS.	CONDENSATE IN PRODUCT M LBS.	H <sub>2</sub> O/LB. DOW STEAM FED WITH COND.	M LBS. H <sub>2</sub> O PER kWh?	kwhr PER M LBS. SWF							
		DOW	FREE-PORT	PLANT			MAXIMUM RATE M LBS./HR.	MAXIMUM RATE M LBS./HR.						IN	OUT	SWF TO P-1	SWF TO NO. 1	DISCH. BRINE FROM I7	STEAM TO NO. 1	DOW STEAM	FREEPORT PRODUCT	VAPOR FROM I7	VAPOR FROM I	TO NO. 1 psig	DOW STEAM psig		318 CONDENSER		VAPOR HEAD psia	FREEPORT PRODUCT	MINIMUM	AVERAGE							STR.	DIR.	FORM	INT.	DURAT. HOURS		
1-27	18.3	405	459	29	894	7,462	472	25	8,692	480	552	4.0	46.7	0.98	2.66	56	262	83	314	463	77	86	262	31.0	163			0.4	36.65	0.62	8.8	60	64	Light	S	None			.632	5,494	1,968	14.8			
1-28	19.5	351	248	27	627	5,238	319	25	12,480	8,638	449	4.1	9	0.82	2.80	58	264	86	311	456	77	89	263	31.3	164			0.5	37.27	0.68	8.2	60	64	Light	S	None			.707	6,107	(868)	15.4	.419	1.44	
1-29																																													
1-30																																													
1-31	9.2	187	140	9	337	2,814	238	22	12,000	3,680	122	0.7		0.64	2.74	58	255	85	264	471	76	89	254	24.0	158			0.5	31.97	0.68	8.1	65	65	Calm	S	None			.766	2,819	(4,000)	10.8	.234	3.26	
2-1	24	548	403	31	983	8,203	499	22	12,000	9,600	312	4.7	9.2	0.64	2.65	59	254	85	264	466	78	89	254	24.0	165			0.5	31.97	0.68	8.3	60	64	Light	E	None			.758	7,277	927	15.4	.684	1.25	
2-2	24	549	402	31	983	8,210	499	22	12,000	9,600	312	3.9	9.2	0.64	2.64	58	254	85	264	468	77	90	254	24.0	165			0.4	31.97	0.70	8.3	62	63	Light	SW	Rain	Light	10		.758	7,277	933	15.5	.684	1.25
2-3	24	561	444	30	1,036	8,648	559	26	12,000	10,488	408	3.8	9.5	0.74	2.68	59	258	85	269	467	77	89	258	27.6	166			0.4	34.25	0.68	8.4	46	48	Brisk	N	None			.724	7,593	1,056	14.5	.721	1.14	
2-4	24	553	439	31	1,096	8,987	598	26	12,960	11,808	552	6.4	14.1	0.74	2.30	58	264	85	275	465	75	88	263	31.4	166			0.4	37.27	0.66	8.2	40	51	Brisk	N	None			.678	8,006	981	14.0	.693	1.10	
2-5	24	596	424	30	1,065	8,888	568	25	12,960	11,760	552	6.5	14.0	0.74	2.14	61	263	84	274	465	74	87	263	31.2	165			0.4	37.27	0.64	8.2	52	57	Brisk	SE	Rain	Light	6		.654	7,691	1,197	14.7	.686	1.10
2-6	24	616	417	29	1,064	8,880	578	25	13,200	11,760	600	9.0	18.8	0.74	2.23	61	263	83	274	476	75	88	263	31.2	170			0.4	37.27	0.66	8.4	59	60	Light	SW	None			.668	7,856	1,024	14.3	.673	1.12	
2-7	24	600	433	30	1,063	8,877	566	25	12,960	11,808	624	9.0	9.4	0.78	2.42	62	263	85	274	482	77	89	263	31.1	174			0.4	37.27	0.68	8.6	56	61	Light	SW	None			.678	8,006	872	14.7	.685	1.10	
2-8	24	599	419	28	1,047	8,737	573	25	12,720	11,808	624	5.2	18.7	0.87	2.58	63	263	85	274	481	77	89	263	31.1	174			0.4	37.27	0.68	8.4	51.5	55	Brisk	SW	None			.663	7,829	909	15.8	.687	1.08	
2-9	24	594	427	28	1,050	8,768	568	25	12,720	11,808	624	8.0	18.5	0.87	2.62	65	263	86	275	483	77	89	263	31.1	174			0.4	37.27	0.68	8.4	40	54	Mod	SW	None			.668	7,888	860	14.4	.689	1.08	
2-10	24	592	432	28	1,053	8,793	566	24	12,720	11,808	792	7.4	28.2	0.83	2.55	63	263	86	275	496	77	89	263	31.1	176			0.4	37.27	0.68	8.3	60	60	Light	SW	None			.675	7,970	824	14.5	.691	1.08	
2-11	24	589	425	31	1,045	8,727	566	25	12,720	11,808	1,032	4.6	27.5	0.83	2.51	63	263	86	274	475	78	89	263	30.8	169			0.4	37.27	0.68	8.2	59	68	Light	SW	None			.669	7,900	827	14.4	.686	1.08	
2-12	24	593	428	29	1,051	8,776	573	25	12,960	11,808	1,080	3.8	53.7	0.81	2.45	60	262	86	274	473	77	89	262	30.8	167			0.4	36.65	0.68	8.4	58	64	Light	NE	None			.669	7,900	877	14.3	.677	1.10	
2-13	24	618	412	30	1,061	8,859	594	26	12,960	11,808	936	12.0	50.3	0.81	2.45	60	262	86	274	463	78	88	262	30.6	167			0.4	36.65	0.66	9.3	55	58	Brisk	E	Rain	Mod	6		.669	7,900	959	13.9	.684	1.10
2-14	24	601	410	29	1,041	8,690	604	26	12,960	11,832	950	12.3	72.4	0.71	2.24	67	262	90	273	463	79	91	261	30.4	163			0.4	36.04	0.72	9.1	51	53	Hard	N	Rain	Hard	18		.683	8,081	610	13.4	.671	1.10
2-15	24	670	416	29	1,116	9,315	611	26	12,720	11,808	950	19.3	12.7	0.71	2.29	58	263	85	274	460	76	88	263	30.7	159			0.4	37.27	0.66	9.2	47	51	Light	N	Rain	Light	6		.690	8,148	1,167	14.2	.732	1.08
2-16	24	647	414	29	1,092	9,114	607	26	12,480	11,808	950	21.3	26.6	0.78	2.27	56	262	84	274	458	75	87	263	30.5	159			0.3	37.27	0.64	9.2	44	47	Light	E	None			.656	7,746	1,368	14.0	.730	1.06	
2-17	24	646	400	31	1,078	9,001	608	26	12,960	11,808	604	18.7	79.1	0.74	2.38	58	262	83	274	468	75	87	263	30.7	159			0.3	37.27	0.64	9.1	43	44	Brisk	N	Rain	Light	4		.689	8,136	866	13.8	.695	1.10
2-18	24	649	406	29	1,085	9,057	604	26	12,720	11,808	604	8.2	8.5	0.73	2.39	61	263	82	274	470	74	86	263	30.8	159			0.3	37.27	0.62	9.1	40	44	Light	NE	None			.695	8,207	850	14.0	.712	1.08	
2-19	24	638	403	30	1,073	8,954	591	26	12,720	11,808	604	21.4	8.5	0.76	2.46	60	262	82	274	463	74	84	262	31.3	154			0.3	36.65	0.58	9.2	45	51	Light	NE	None			.691	8,159	796	14.1	.704	1.08	
2-20	24	643	417	31	1,092	9,115	613	27	12,720	11,808	622	14.8	4.3	0.70	2.32	59	262	81	274	460	74	85	262	31.6	163			0.3	36.65	0.60	9.1	53	57	Brisk	NE	Rain	Hard	20		.698	8,242	873	13.9	.717	1.08
2-21	24	645	435	33	1,115	9,306	627	27	12,720	11,808	622	15.6	4.2	0.64	2.19	59	262	83	274	460	75	87	263	31.7	161			0.3	37.27	0.64	9.3	50	57	Mod	NE	Rain	Hard	24		.708	8,360	946	13.8	.732	1.08
2-22	24	643	415	34	1,092	9,120	598	26	12,480	11,808	622	12.6	17.3	0.71	2.32	60	262	85	274	469	75	88	262	31.5	164			0.4	36.65	0.66	9.2	49	54	Light	N	Rain	Light	4		.694	8,195	925	14.3	.731	1.06
2-23	24	647	404	36	1,087	9,078	591	25	12,480	11,808	640	11.9	8.7	0.75	2.41	60	262	85	274	462	76	88	262	31.4	165			0.4	36.65	0.66	9.2	55	56	Light	NE	None			.689	8,136	942	14.3	.727	1.06	
2-24	24	649	399	36	1,085	9,059	583	25	12,720	11,808	622	16.3	8.8	0.73	2.35	60	262	85	274	473	76	89	263	31.3	165			0.4	37.27	0.68	9.3	55	57	Light	NE	None			.689	8,136	924	14.5	.712	1.08	
2-25	24	627	417	36	1,080	9,																																							



especially for measurements at the low ppb level. Therefore, it is recommended that further studies of the Winkler method be initiated in the immediate future. The goal of this research should be several-fold. Reagent parameters should be explored in detail, interferences should be investigated, and a handling routine should be developed; these three should all be oriented to the generation of a standardized procedure that is as simple, routine, and accurate as possible. Although the D. O. range of primary interest should be 0 to 100 ppb, the procedure should also be evaluated for wide-range applicability. The end product of this work should be an optimized Winkler method published as in ASTM style.

## 2. Improvements in the Dissolved Oxygen Calibrator

The performance of the DOC is well within proposed objectives and within the expectations of the instrument design. As it is presently designed there are two limitations on the instrument, or more specifically on the rate and pressure at which the calibration stream is delivered for use. The DOC is capable of delivering up to about 100 ml/min of product water at atmospheric pressure. It would be highly advantageous to be able to have a flow of up to 500 or 1000 ml/min at pressures of up to 20 or 25 psig; this would allow product water to be provided at greater pressures and flow rates for test setups or sensors requiring this increased capacity. It is believed that these improvements could be effected by making changes in the sizes of the spinning-disc strippers and associated tubing and by incorporating commercial mechanical seals designed to maintain the required pressures. The delivery pressure could be established by adjusting and controlling the vent pressure from each stripping stage. An improved version should include the capability for set-point calibrations; i. e., by dialing in solubility-determining factors such as salinity, temperature, and  $N_2$  flow it would then be possible to dial in and get the desired D. O. content in the product water. This might be essentially a manual process wherein a dial or dials are set based on nomograph values. Or, it might be a completely automatic operation wherein in-line transducers continuously monitor the solubility-determining parameters and provide compensating signals to modify the  $O_2$ -generation

current so as to give a specified D. O. level in the output stream. The goal of such a program should be to develop a versatile calibration model of prototype quality that might be made available for a variety of applications such as calibration of D. O. analyzers, investigation of corrosion phenomena, verification of  $O_2$ -solubility data at various salinities, temperatures, pressures, and  $O_2$  levels, research on new D. O. analyzers, production of media for biological studies, and other scientific endeavors.

## REFERENCES

1. D. D. Williams and R. R. Miller, "An Instrument for 'On Stream' Stripping and Analysis of Dissolved Gases in Water," NRL Report 5678, U. S. Naval Research Laboratory, Washington, D. C., 12 September 1961.
2. "Heart-lung Machines Equipped with Thin Silicone Membranes for Oxygenating Blood," Chemical and Engineering News, p. 37, 9 September 1968.
3. A. H. White, C. H. Leland, and D. W. Button, "Determination of Dissolved Oxygen in Boiler Feed Water," Proceedings, Am. Soc. Testing Materials, Vol. 36, Part II, 697 (1936).
4. G. A. Truesdale, A. L. Downing, and G. F. Lowden, "The Solubility of Oxygen in Pure Water and Sea Water," J. Appl. Chem., 5, 53 (1955).
5. H. A. C. Montgomery, N. S. Thom, and A. Cockburn, "Determination of Dissolved Oxygen by the Winkler Method and the Solubility of Oxygen in Pure Water and Sea Water," J. Appl. Chem., 14, 280 (1964).
6. D. E. Carritt and J. H. Carpenter, J. Marine Res., 24 (3), 286 (1966).
7. J. P. Riley and G. Skirrow, Chemical Oceanography, Vol. I, Academic Press, New York, 1965.

TABLE 1

## DEOXYGENATION BY VACUUM DEGASSING

<u>Treatment</u>		<u>D. O. Content, ppb</u>	<u>% O<sub>2</sub> Removed</u>
None	Run 1	7680	
	2	7790	
	3	7800	
	4	7850	
	Avg		7780
<hr/>			
Vacuum, 5 min.	Run 1	590	
	2	640	
	Avg		615
<hr/>			
Vacuum, 10 min.	Run 1	490	
	2	410	
	Avg		450
<hr/>			
Vacuum, 20 min.	Run 1	350	
	2	440	

TABLE 2

DEOXYGENATION WITH EVAPORATING DRY ICE

<u>Weight of Dry Ice, g</u>	<u>Sample Temperature After Treatment, °C</u>	<u>D. O. Content, ppb</u>	<u>% Removed</u>
None	24	8160	0
50	22	2530	69
100	20	780	90
200	17.5	170	98

TABLE 3

## DEOXYGENATION IN A PACKED COLUMN

<u>Flow Rate, ml/min</u> <u>(N<sub>2</sub>/Feedwater)</u>		<u>D. O. Content, ppb</u>	<u>% O<sub>2</sub> Removed</u>
Initial	Run 1	7690	
	2	7740	
	Avg	7715	0
100/100	Run 1	2130	
	2	2050	
	3	2050	
	4	1980	
	Avg	2052	73
100/50	Run 1	1500	
	2	1570	
	Avg	1535	80
200/50	Run 1	1570	
	2	1600	
	Avg	1585	79
200/50*	Run 1	1090	
	2	1250	
	Avg	1170	85

-----  
\*Nitrogen gas vented through 2-inch head of mercury.

APPARATUS FOR PERMEATION TESTS

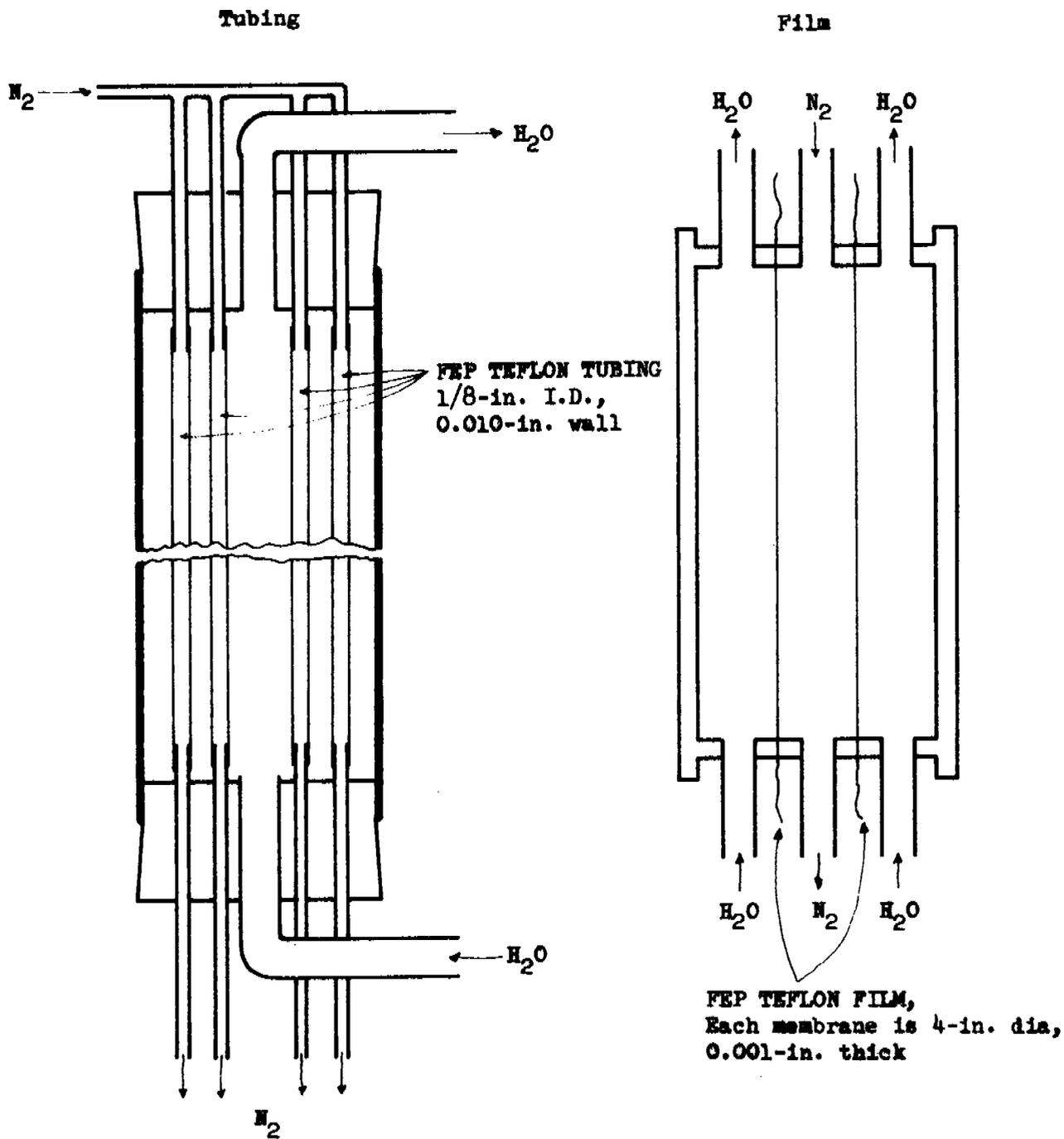
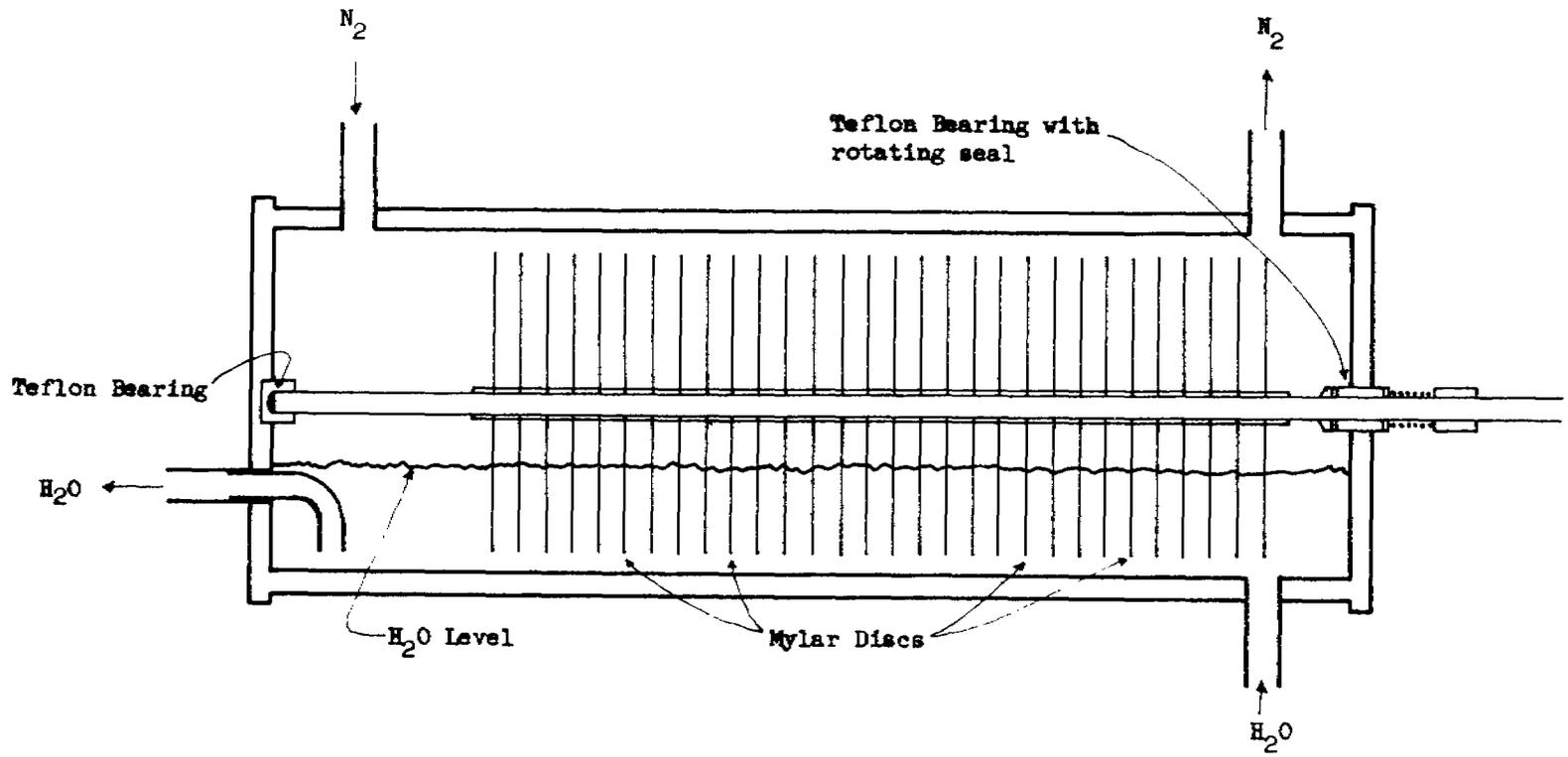


Figure 3

DISC STRIPPER FOR OXYGEN REMOVAL



110

Figure 4

CONTAINER FOR SAMPLING IN AN INERT ATMOSPHERE

Acrylic Sample Container  
4-in. I.D. by 7-in. long

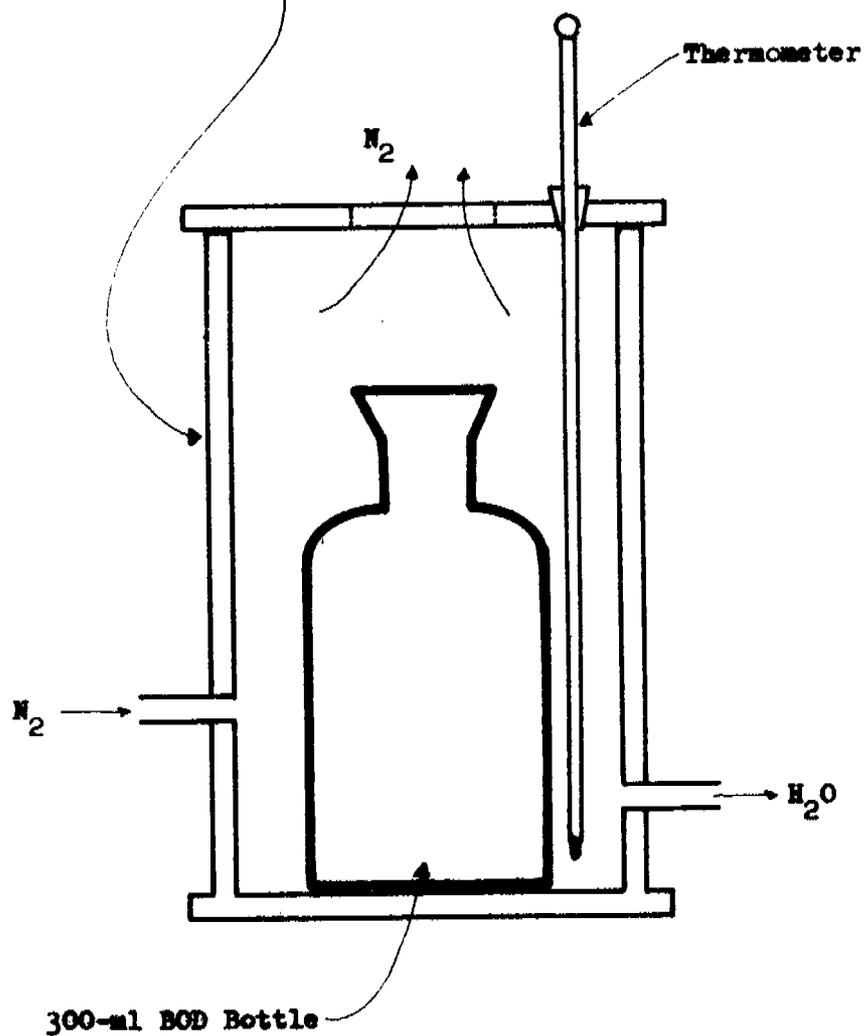


Figure 5



FIGURE 6

APPARATUS FOR TITRATION IN A NITROGEN ATMOSPHERE

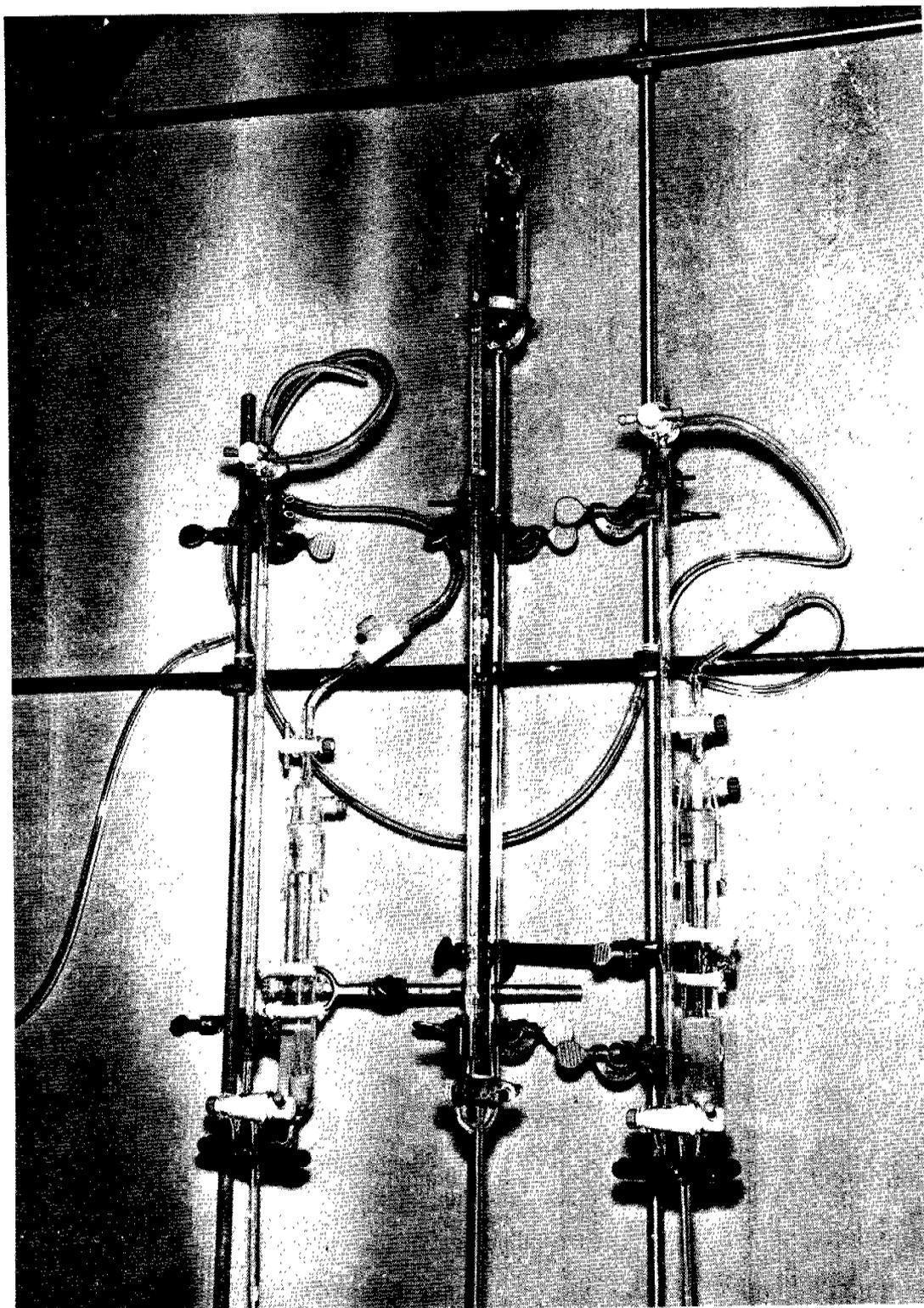
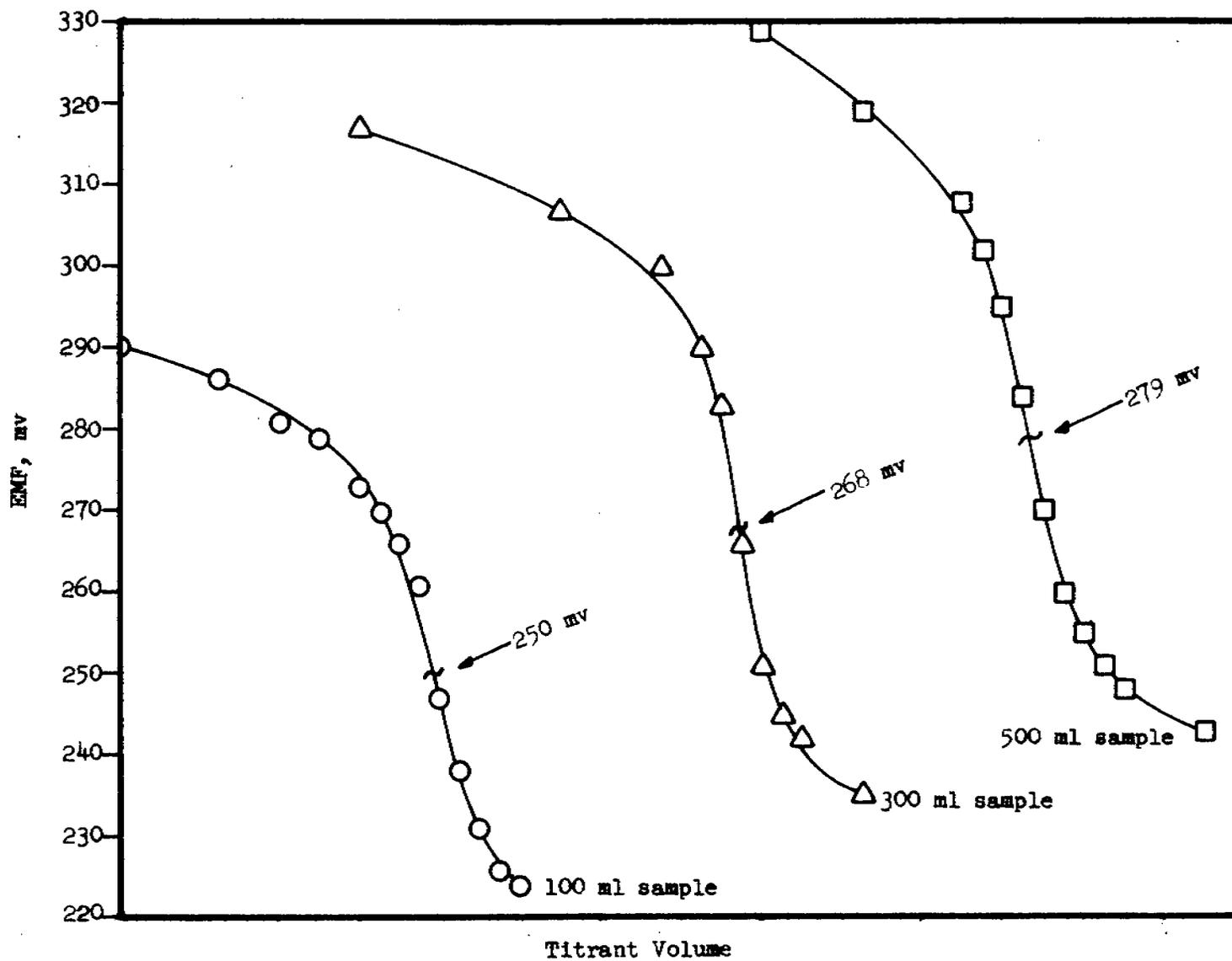


FIGURE 7

APPARATUS FOR PURGING AND HANDLING  
WINKLER REAGENTS UNDER NITROGEN

EFFECT OF KI CONCENTRATION ON THE END-POINT POTENTIAL



EFFECT OF STARCH ON THE POTENTIOMETRIC END-POINT CURVE

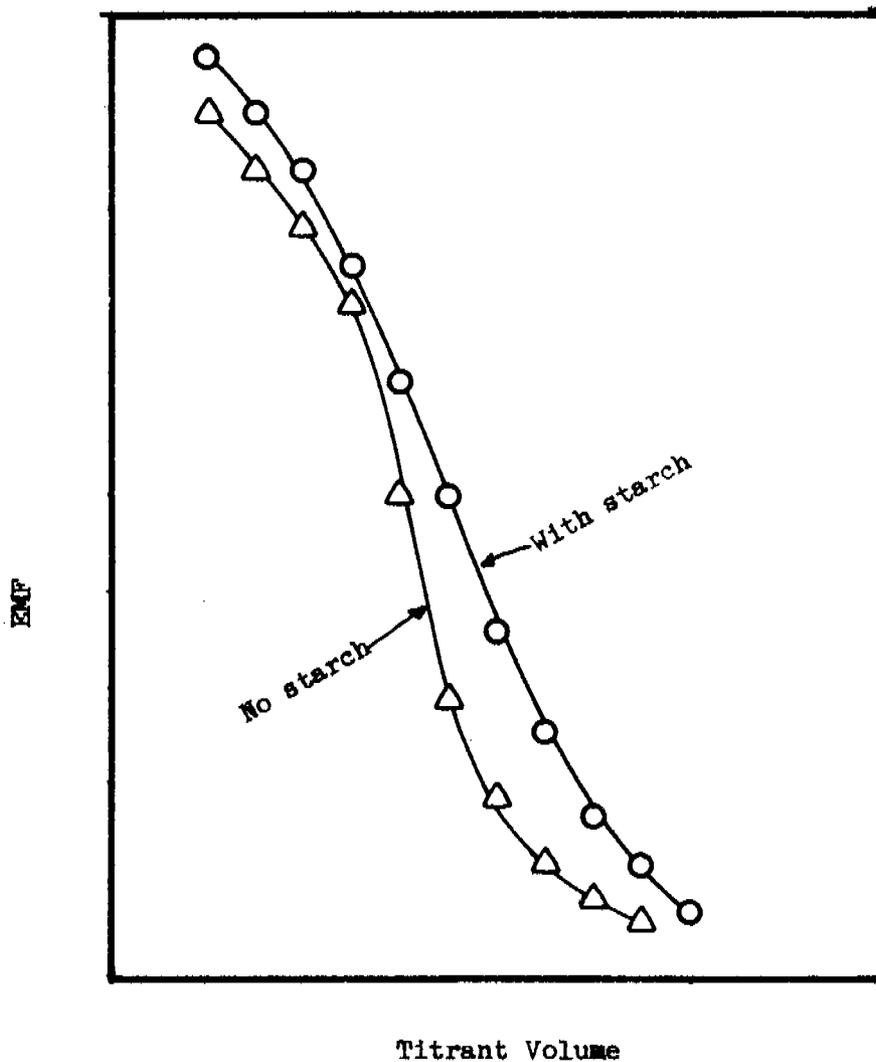


Figure 9

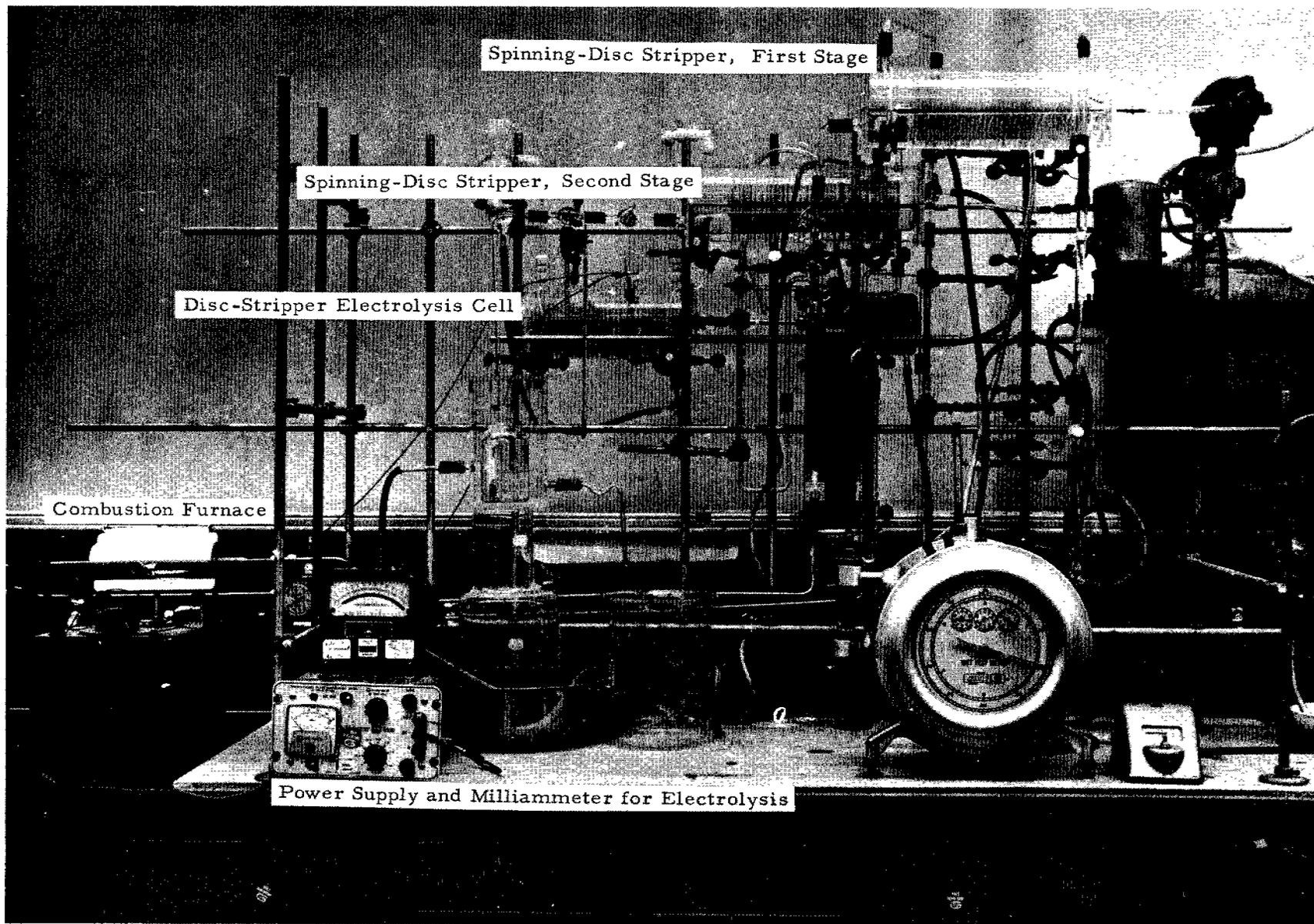


FIGURE 10

LABORATORY SETUP FOR DEOXYGENATION AND OXYGEN ADDITION

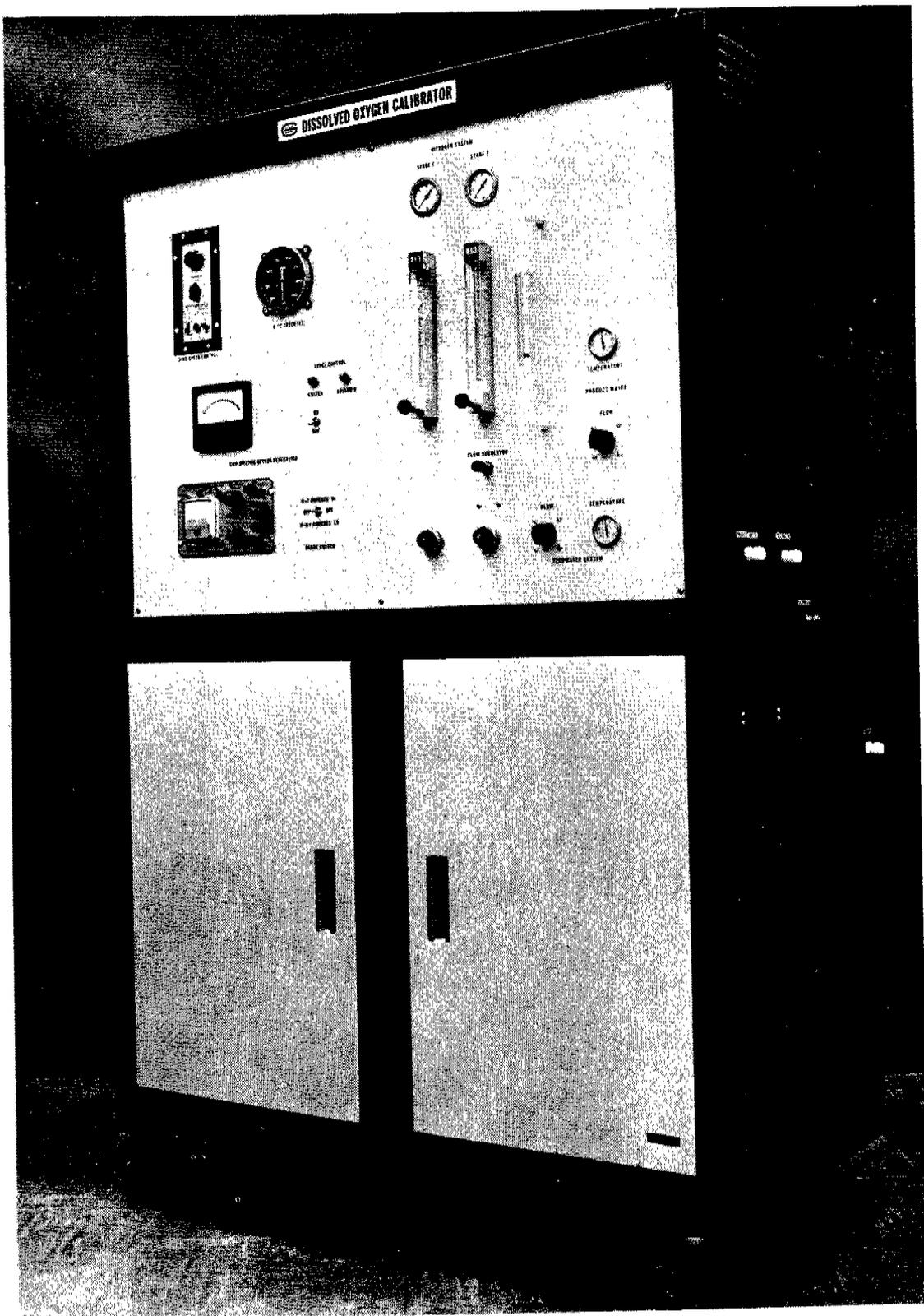


FIGURE 11

PHOTOGRAPHIC VIEW OF THE DISSOLVED OXYGEN CALIBRATOR

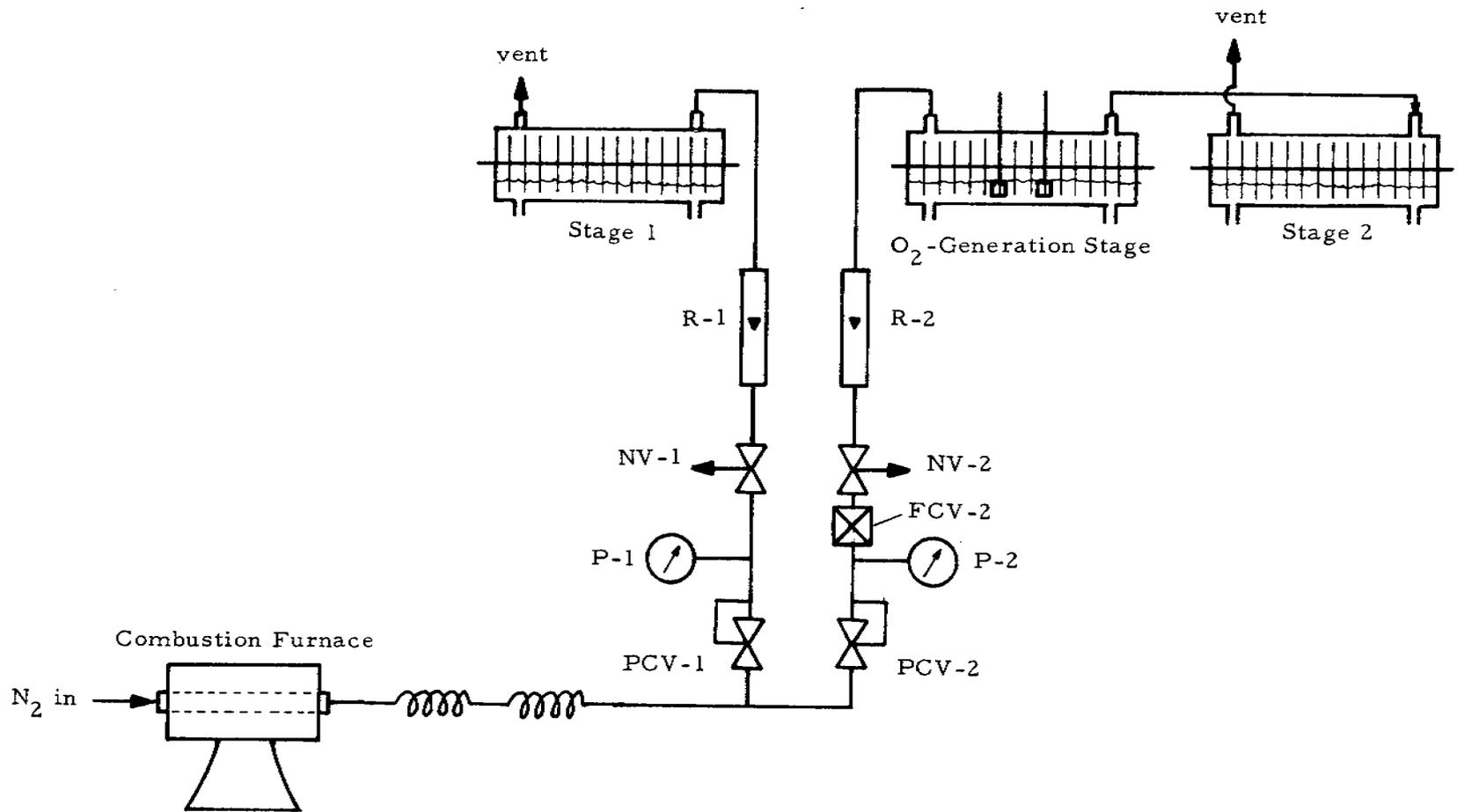
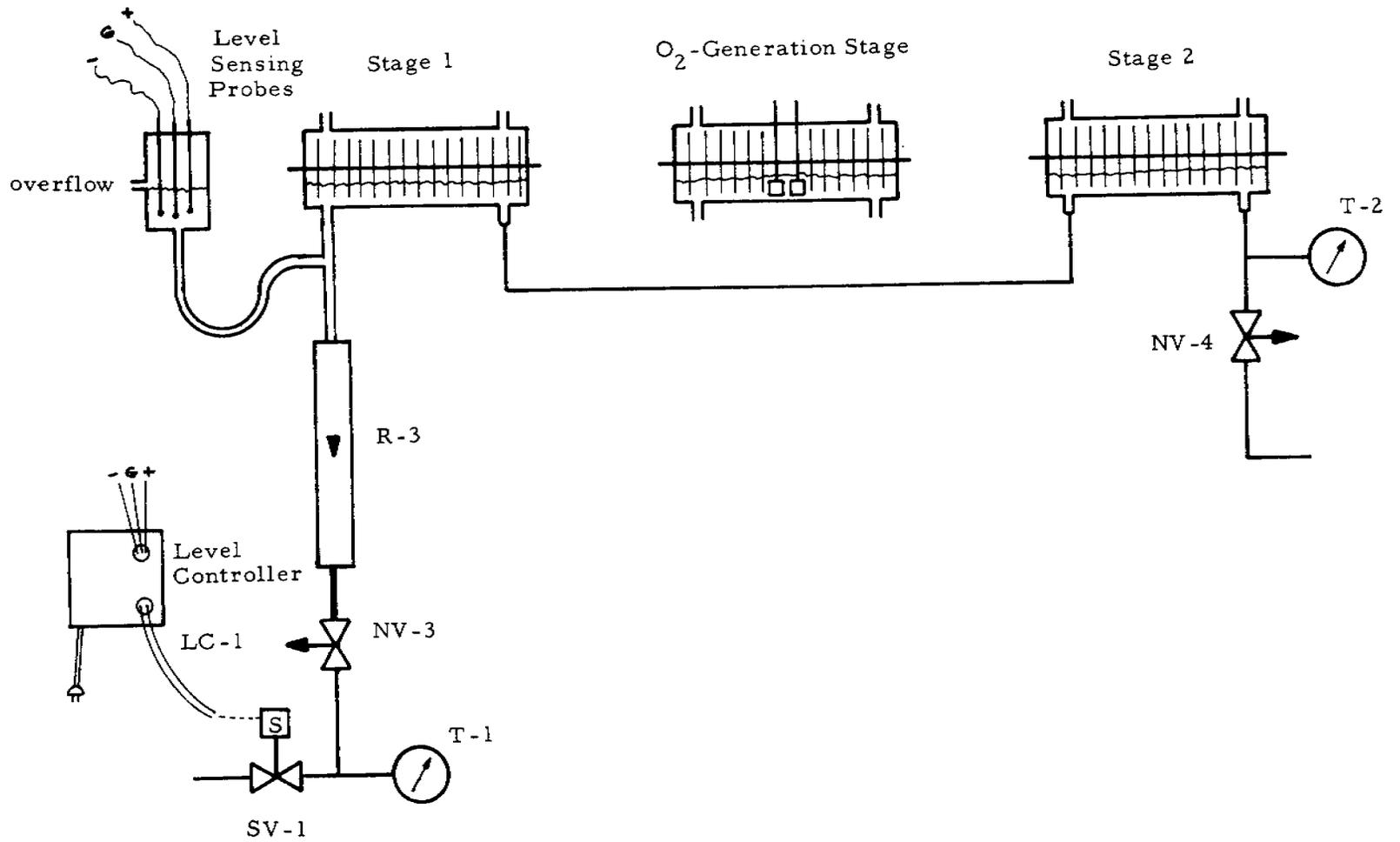
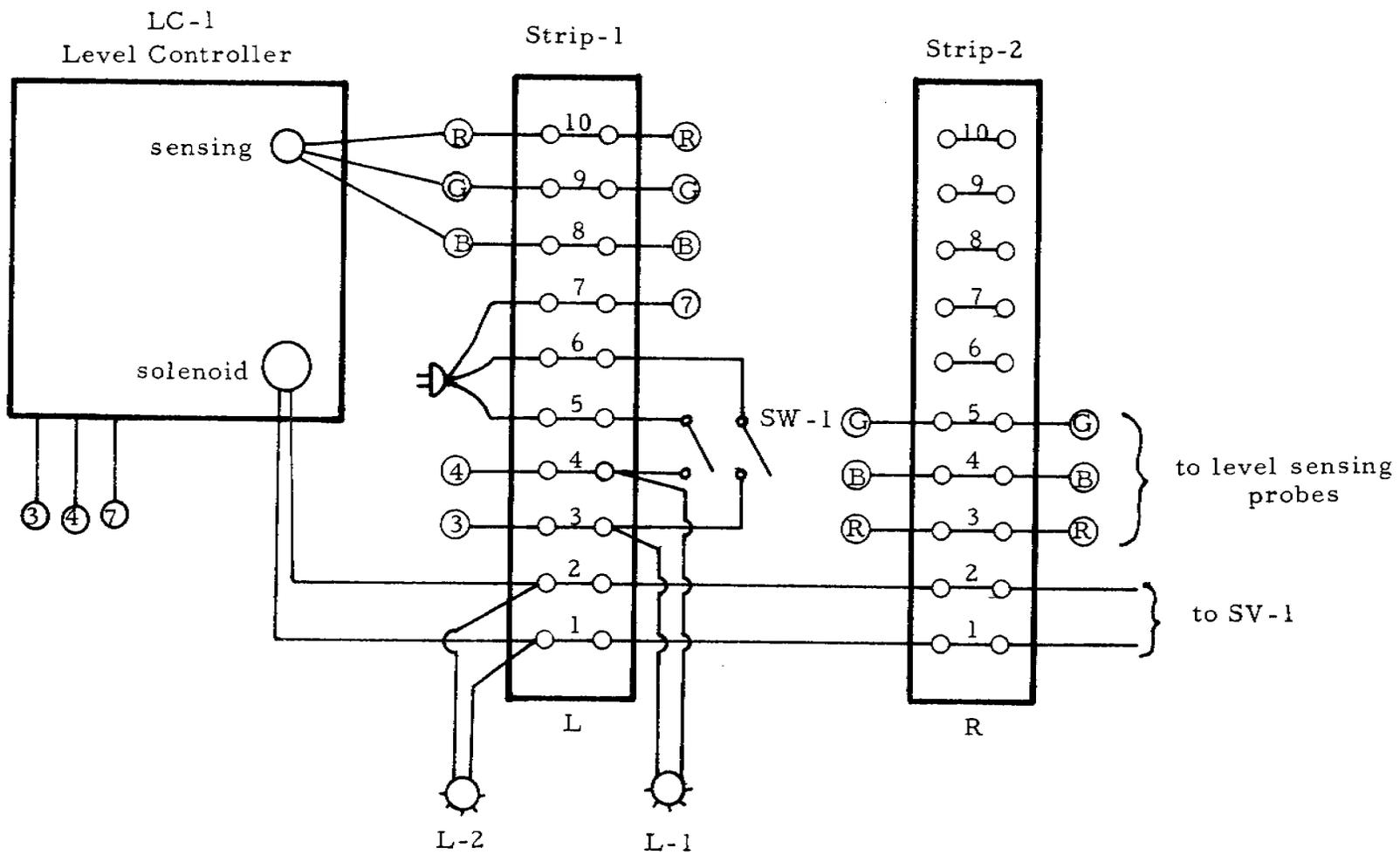
Schematic Diagram of the N<sub>2</sub>-Flow System

Figure 12



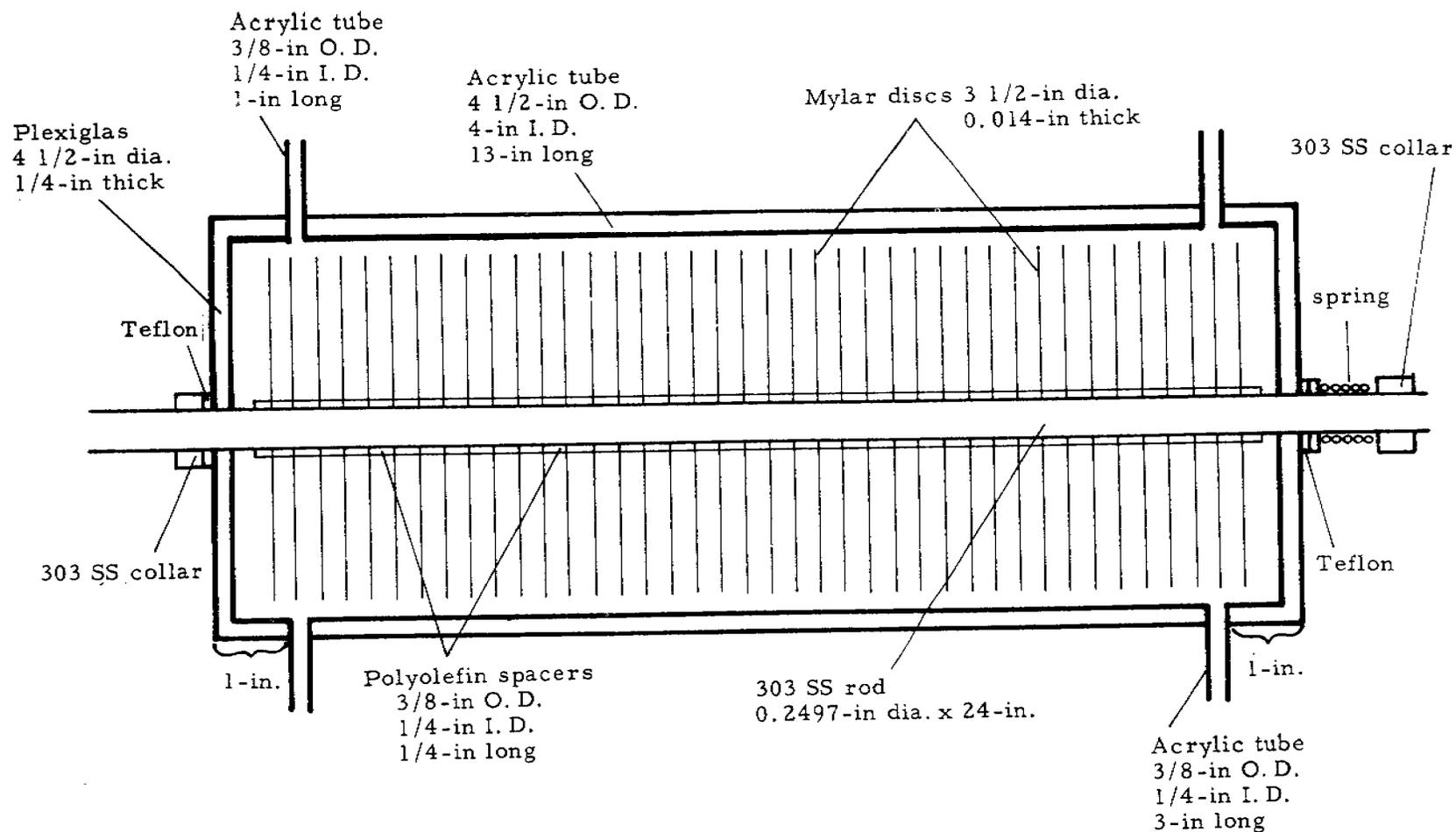
Schematic Diagram of H<sub>2</sub>O-Flow System

Figure 13



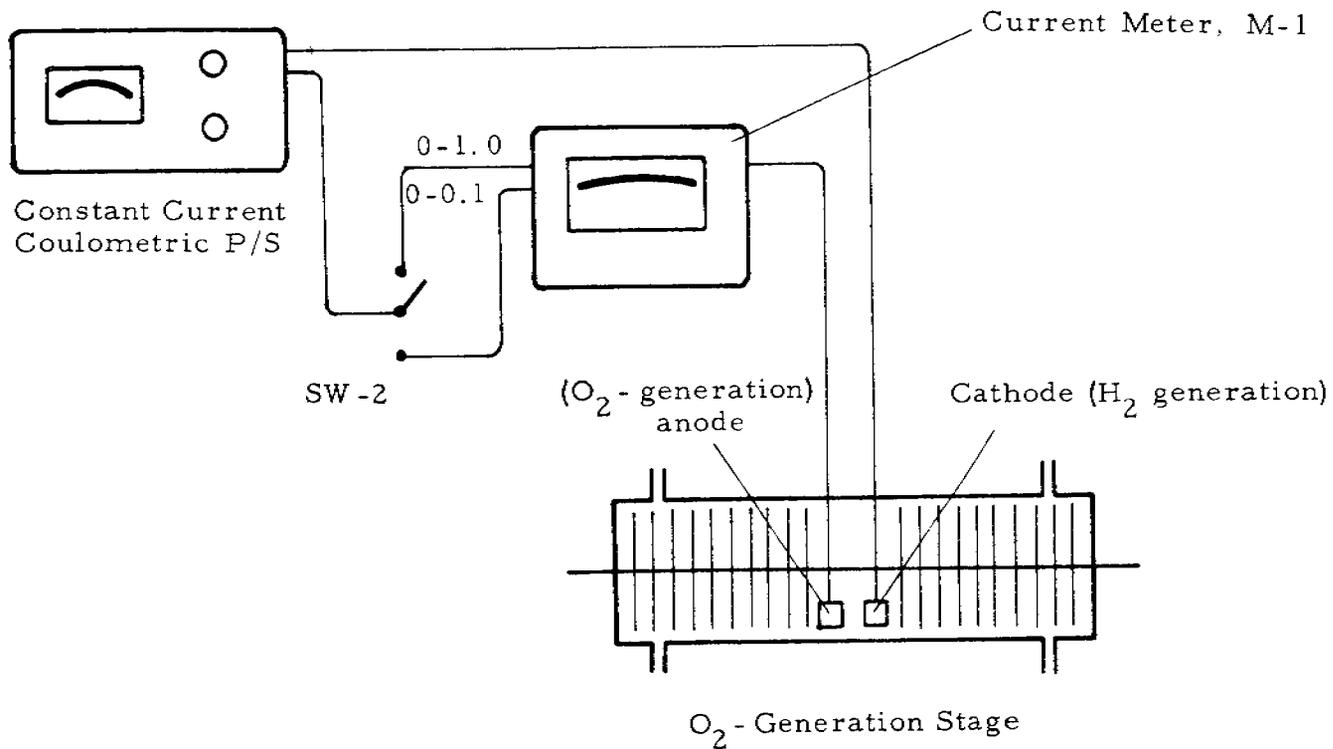
Schematic Diagram of the Electrical Wiring for the Level-Control System

Figure 14



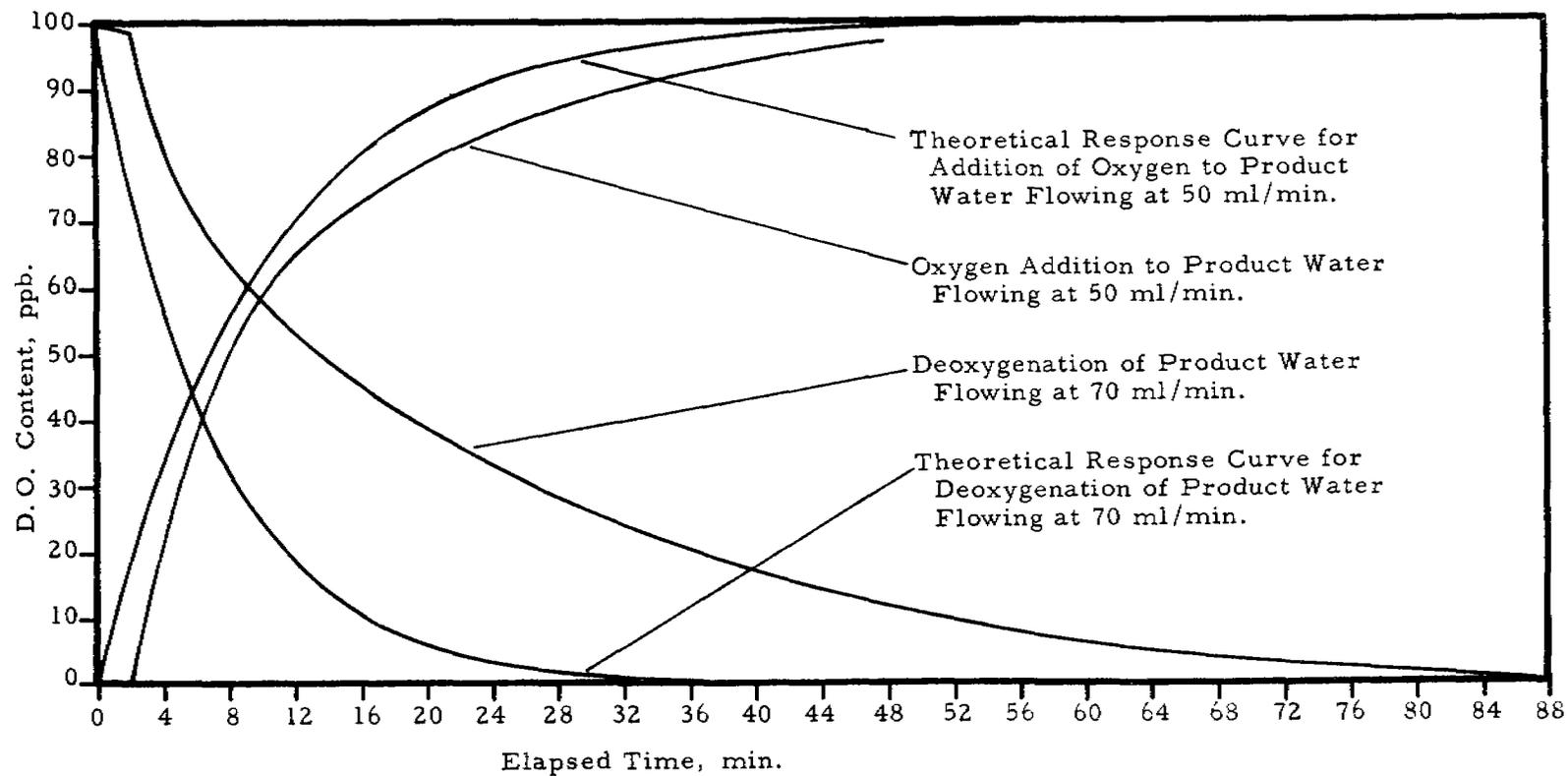
Details of the Spinning-Disc Stripper

Figure 15



Schematic Diagram for the Oxygen-Generation System

Figure 16



Theoretical and Measured Response-Time Curves for Step Changes in  $O_2$  Levels.  
(Addition and Deoxygenation)

Figure 17

APPENDIX I  
CHEMICALS AND EQUIPMENT

I. CHEMICALS

A. REAGENTS

The chemicals used to make up reagent solutions for the Winkler analysis (KOH, KI,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{I}_2$ ), titrants ( $\text{AgNO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ ,  $\text{KIO}_3$ ), indicators ( $\text{K}_2\text{CrO}_4$ , starch), reagent solutions of interfering ions ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ ), and solutions and reagents for the colorimetric indigo carmine procedure ( $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , HCl, dextrose, glycerine, KOH) were all Baker Analyzed Reagents. Exceptions to this were  $\text{NaN}_3$  and indigo carmine, which were practical grade, and  $\text{H}_2\text{SO}_4$  which was duPont reagent grade chemical. The sodium thiosulfate solution was standardized against weighed quantities of primary standard  $\text{K}_2\text{Cr}_2\text{O}_7$  (99.97% assay) or against weighed quantities of Baker Analyzed Reagent  $\text{KIO}_3$  (100.0% assay).

B. PURGE GASES

The purge gases employed throughout this program were  $\text{CO}_2$ ,  $\text{N}_2$ , and purified  $\text{N}_2$ . The  $\text{CO}_2$  was obtained from subliming dry ice; although the purity was not specifically determined during this research, past experience has shown it to assay over 99.99%. For purging BOD bottles, purging the vessel in which the BOD bottle was handled, and in purging and maintaining an inert blanket in the titration vessel, the  $\text{N}_2$  was used as received from the  $\text{N}_2$  outlet in the laboratory. The  $\text{N}_2$  plumbed to our laboratory is pressurized  $\text{N}_2$  generated from a liquid  $\text{N}_2$  storage vessel. The oxygen content of this gas typically is less than 100 ppm and maybe as low as 10 ppm level (0.001 vol. %). The laboratory  $\text{N}_2$  was passed through a combustion tube containing a mixture of Cu and CuO maintained at  $525 \pm 25^\circ\text{C}$  to obtain a supply of purified  $\text{N}_2$  of constant purity. The Cu removes  $\text{O}_2$  by forming CuO; organic impurities are oxidized to  $\text{H}_2\text{O}$  and  $\text{CO}_2$  by the CuO. In some initial runs  $\text{H}_2\text{O}$  and  $\text{CO}_2$  were removed on an Ascarite/Anhydrone column, but this purification step was removed shortly inasmuch as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were not considered detrimental. There was some question as to whether the residual  $\text{O}_2$  content of this purified  $\text{N}_2$  might be

significant. If, for example, the residual  $O_2$  amounted to 0.011 vol-% distilled water in equilibrium with it at  $20^\circ C$  would contain a D. O. content of 5 ppb. Consequently, several tests were made to determine the  $O_2$  content of the purified  $N_2$ . In one test indigo carmine reagent (ASTM D888A) was introduced directly into deoxygenated water in the disc stripper. The color was observed initially and after deoxygenated  $N_2$  had purged through the system for measured periods of time. The  $O_2$  content of the stripping gas was estimated from the flow rates and the sensible color change to be less than 0.001 vol. %.

In another test the Winkler method was used to estimate the residual  $O_2$  content. The apparatus employed here consisted of two identical gas-washing columns in series, as shown in Figure 1. Each column consisted of a test tube 1.5-in. I. D. and 24-in. long, fitted with a rubber stopper and a fritted-disc gas bubbler which extended to the bottom of the tube. Gas exiting from the train was passed to a wet-test meter to measure the gas flow rate. With 500 ml of distilled water added to each scrubber, the gas was forced to pass through approximately 20 in. of liquid in each column. A carefully ordered and timed procedure was adapted for adding reagents and allowing the reaction of  $O_2$  in the scrubber. The apparatus was cleaned and set up and then the procedure below was followed:

1. Add 500 ml distilled water to each scrubber.
2. Add 2.0 ml  $MnSO_4$  solution to each scrubber.
3. Assemble apparatus for purging with sample  $N_2$ .
4. Begin flow of gas through the two columns and simultaneously start stopwatch.
5. Allow 15-minute purge of the two columns. As the end of the 15-min purge (900 seconds) approaches, draw iodized alkaline iodide into the pipet and prepare to add 2.0 ml of reagent to column No. 1.
6. At precisely 900 seconds, begin adding the 2.0 ml of iodized alkaline iodide to column No. 1.

7. As soon as Step 6 is complete, add 2.0 ml of iodized alkaline iodide to column No. 2.
8. Allow  $N_2$  to continue purging through the 2 columns. As 1200 seconds approach, prepare to add 2.0 ml  $H_2SO_4$  to each.
9. At precisely 1200 seconds begin adding 2.0 ml of  $H_2SO_4$  to column No. 2. When reagent addition is complete, stop the flow of  $N_2$  to column No. 2 by lifting the stopper from column No. 1.
10. Quickly pipet and add 2.0 ml of  $H_2SO_4$  to column No. 1. When reagent addition is complete, stop the flow of  $N_2$  through column No. 1.
11. Pipet 200 ml of fixed solution from column No. 1 into 250 ml beaker and titrate as in Aerojet-modified Winkler procedure. (See Appendix II for procedure.)
12. Repeat Step 11 for fixed solution No. 2.

The procedure outlined in these 12 steps furnishes the blank. The  $O_2$  analysis of the  $N_2$  stream is obtained in a similar process by allowing  $N_2$  to flow 30 minutes (1800 seconds) beyond the 1200 second stop point in Step 8. The actual  $N_2$  flow rate is measured during the 15-minute purge in Step 5.

The  $O_2$  content of the  $N_2$  stream was first estimated from the difference between sample and blank run as described above. The net difference measured corresponded to 0.000174 vol-%  $O_2$  in  $N_2$ . Of this amount 0.000056 vol-% was in column No. 1 and 0.000118 vol-% was in column No. 2. Thus, column No. 1 did not collect all the  $O_2$ . This means, then, that the  $O_2$  content is not less than the sum, or 0.000174 vol-%.

Further tests were made to determine the per cent of  $O_2$  abstracted using this setup. An electrolysis cell was inserted in the  $N_2$  stream just ahead of column No. 1. The procedure followed was as for the sample gas described above, except that additional  $O_2$  (generated at a current of 100 ma) was added to the purified  $N_2$  for five minutes duration at the 5-minute timing point in the 30-min sampling period. The increased  $O_2$  content was

measured by titration, in the same manner as the sample and blank. The  $O_2$  produced during the steady-state 5-min generation time corresponds to an  $O_2-N_2$  mixture that is 0.080 vol-%  $O_2$ . Altogether 2.486 mg of  $O_2$  were formed, but only 0.2174 mg, or 8.7% of the total, was absorbed according to the measurement. This confirms that the scrubber is not 100% efficient in removing the  $O_2$  in the gas stream, at least not at the 0.080 vol-% level.

It is realized that any estimate of recovery efficiency at 0.0002 vol-% based on a value derived for a level some 400 times higher is subject to uncertainties. The absorption efficiency in a given column and at a given sample flow rate would be expected to be greater at 0.0002 vol-% than at 0.080 vol-%. The  $O_2$  content measured for the purified gas stream was 0.000174 vol-%; this must be regarded as a minimum  $O_2$  value. If the absorption efficiency were 8.7% this would correspond to a true  $O_2$  concentration of 0.002 vol-%. If the absorption efficiency is greater than 8.7% at  $O_2$  concentrations lower than 0.080 vol-%, the true  $O_2$  concentration would be less than 0.002 vol-%. Thus, the series of tests demonstrated that the  $O_2$  content of the purified  $N_2$  stream lies within the range of 0.000174 to 0.002 vol-%. These gas concentrations would be in equilibrium with distilled water at 20°C having a D. O. content of 0.07 and 0.9 ppb, respectively. The two tests, taken together, indicate that the  $O_2$  content of the purified  $N_2$  is on the order of 0.001 vol-%.

### C. WATER SAMPLES

The water samples used throughout the program were either bottled distilled water or sea water. The sea water was collected in a 55-gal stainless steel drum several miles offshore in the Santa Catalina channel and brought to this laboratory. After it was received here, it was transferred to 5-gal glass bottles and retained for use. The chlorinity of this sea water was determined by the procedure of Strickland and Parsons;\* the sea water was compared with standard sea water (chlorinity: 19.374 ppt) by titration with 0.21 N  $AgNO_3$  solution. The analysis showed the sea water to have a chlorinity of 18.604 ppt which is equivalent to a salinity of 33.610 ppt.

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\*J. D. H. Strickland and T. R. Parsons, "A Manual of Sea Water Analysis", Bulletin, Fisheries Research Board of Canada, 125, 185 (1960).

## II. EQUIPMENT

### A. SPECIAL RESEARCH APPARATUS

Although no attempt will be made in this section to describe here in detail the specific design of special research apparatus, some generalized comments are in order. Laboratory models for the various investigations were generally fabricated from Pyrex glass or Plexiglas. To the extent that it was possible, contact of metal parts with the water sample was avoided so that corrosion would not contaminate the water or limit the life of the part. Pyrex glass tubing was found to be especially beneficial in transferring the deoxygenated water to the receiving vessel or to the D. O. Analyzer. In one instance completely deoxygenated distilled water passed through a 2-foot section of polyethylene tubing (3/8-in. O. D., 1/4-in. I. D.) to the sample container (300 ml BOD bottle) consistently gave an analysis corresponding to a D. O. content of approximately 20 ppb. Based on the permeation characteristics of the tubing, the diffusion of O<sub>2</sub> into the water was calculated to correspond to approximately 10 ppb/ft. When the 2-foot section of polyolefin tubing was replaced with Pyrex glass tubing, the D. O. analysis immediately dropped to approximately 0 ppb. Thus, the need for care in the selection of tubing materials for transporting the deoxygenated water is clear.

### B. SAMPLE CONTAINERS

Samples of water for analysis by the Winkler method or by the Aerojet-modified Winkler procedure were collected in 300 ml BOD bottles or in 500 ml McLean sampling tubes, as recommended in ASTM D 1589 and ASTM D 888C, respectively. Samples for analysis by the colorimetric indigo carmine method were collected in 300 ml BOD bottles, as allowed in ASTM D 888A. The McLean tubes were calibrated with respect to one another as recommended in ASTM D 888 C. The BOD bottles were all assumed to have volumes of exactly 300.0 ml; relative volumes obtained by measuring the volume delivered to a graduated cylinder indicated that the volumes are, on the average, all within 0.3%. This is well within the precision aimed for in this research.

### C. ROTAMETERS

The flow of  $N_2$  stripping gas utilized in the deoxygenation studies and in all subsequent tests during the development of the spinning-disc stripper, research of  $O_2$  addition techniques, and refinement of the analysis procedure was monitored continuously by means of appropriately sized rotameters. These rotameters were calibrated periodically in the various systems and under various conditions of use by the wet-test-meter or bubble-in-buret method.

### D. LIQUID FLOW

The flow rate of sample water was measured either by collecting the discharge for 1 minute or by collecting the total discharge during sampling and measuring the time of sampling.

### E. TITRATION APPARATUS

Throughout the entire program the end points in the potentiometric titrations were derived from the inflection in the emf vs titrant volume curve. The emf values were measured by means of a Pt-saturated calomel electrode (sleeve type) in conjunction with a Beckman model H2 pH meter.

### F. OXYGEN-GENERATION APPARATUS

Oxygen was generated in a spinning-disc stripper which had been fitted with electrodes to serve as an electrolysis cell. An 0.5 M sodium sulfate solution was used as the electrolyte because it is known to give 100%  $O_2$ -generation efficiency. The solution was electrolyzed between platinum electrodes. Oxygen was generated at an anode having a surface area of approximately  $2.6 \text{ cm}^2$ . Hydrogen was generated at a wire electrode located within a compartment separating it from the bulk of the electrolyte by a fritted disc; the  $H_2$  was vented to the atmosphere. A constant DC current in the range from 0 to 1000 ma was passed between the electrodes to generate the required volume of  $O_2$ . The current was provided by means of a constant-current power supply and read from a multirange DC ammeter that was accurate to 1%. The formed  $O_2$  was then transferred to the gas phase by the spinning-disc stripper, the gas phase being the purified  $N_2$  carrier gas flowing to the second stage disc stripper at a rate of 1 liter per minute.

APPARATUS FOR ABSORPTION OF O<sub>2</sub> FROM N<sub>2</sub> PURGE GAS

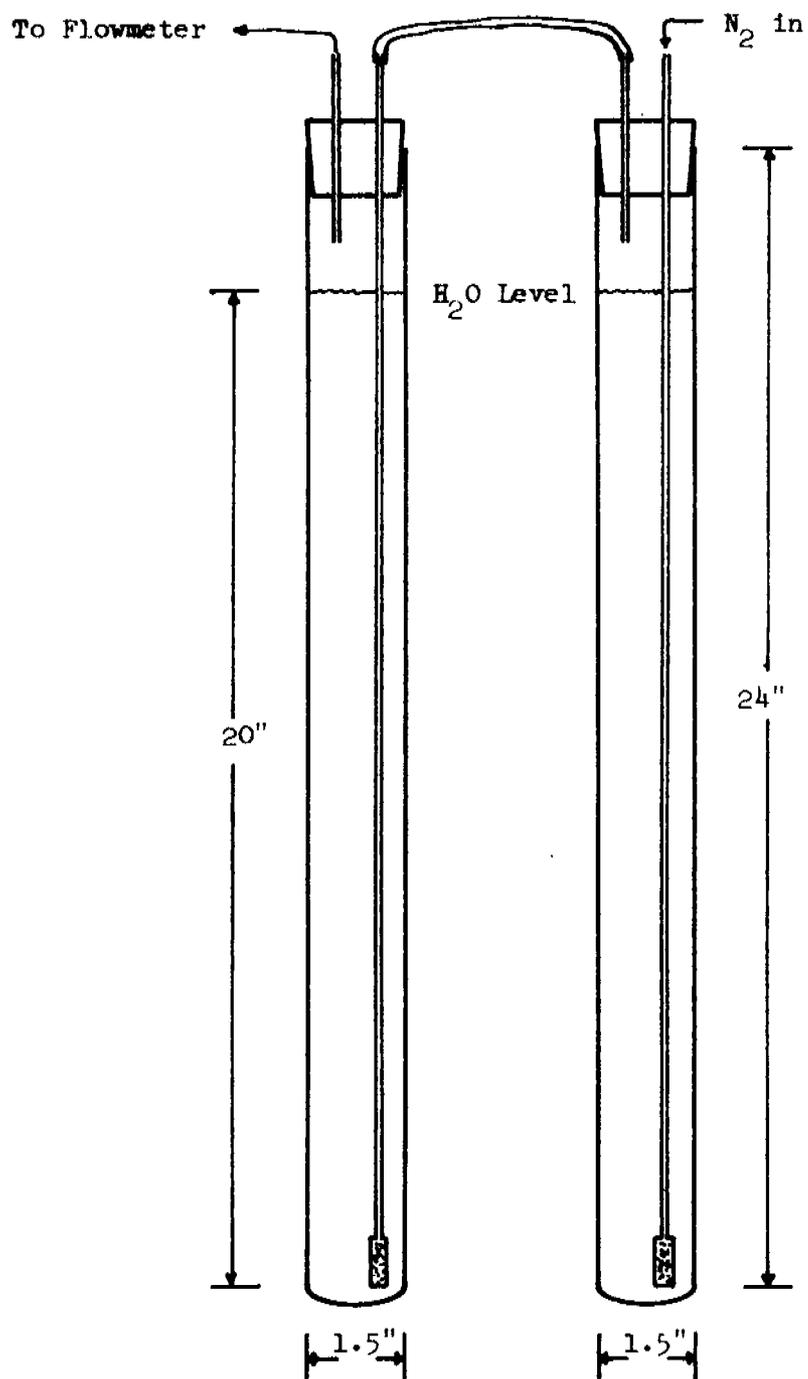


Figure I-1

## APPENDIX II

### PROCEDURE FOR AEROJET-MODIFIED WINKLER METHOD (July 1969)

#### I. SCOPE

This method covers the determination of D. O. content of distilled water or natural sea water in the range of 0 to 100 ppb.

#### II. APPARATUS

##### A. BEAKER

One 250 ml Pyrex beaker.

##### B. BURET

One 1-ml Koch-type buret with Teflon stopcock and 0.01-ml subdivisions. This buret is used to deliver the sodium thiosulfate solution during sample titration.

##### C. BURETS

Three 5-ml Koch-type burets with Teflon stopcocks and 0.01-ml subdivisions. These burets are used to deliver the Winkler reagents during fixing.

##### D. BOD BOTTLES

Several 300-ml BOD bottles having a raised lip around the neck and glass stoppers ground to a conical lower tip.

##### E. GRADUATED CYLINDER

One 100-ml graduated cylinder with 1-ml subdivisions. This is used to check sample flow rate, if necessary.

##### F. BOTTLE CONTAINER

The sample container should be as shown in Figure 5. The thermometer may be deleted if another means of temperature measurement is available.

### G. TITRATION CONTAINER

The titration container should be as described in Section VII, C, 2 and shown photographically in Figure 6.

### H. POTENTIOMETRIC END POINT APPARATUS

The apparatus consists of (1) a pH meter with a total range of  $\pm 1400$  mv and a limit of error of not greater than 3 mv, (2) a platinum sensing electrode, and (3) a saturated calomel reference electrode of either the glass sleeve or asbestos wick type.

### I. STIRRING BARS

Two Pyrex-coated stirring bars approximately 1-1/8-in. long by 1/4-in. diameter.

### J. MAGNETIC STIRRER

Two variable-speed motor-driven magnetic stirrers are required.

### K. PIPET

One 100-ml or 200-ml pipet.

### L. PURGE TUBES

Two purge tubes, each consisting of a 1-ft. section of 9-mm O. D. Pyrex tubing connected via rubber or Tygon tubing to a source of  $N_2$  for purging.

## III. REAGENTS

Reagent grade chemicals shall be used in all tests.

### A. IODINE SOLUTION

Dissolve 6.346 g of resublimed iodine in a solution of 75 g of KI in 60 ml of distilled water and dilute with distilled water to 500 ml in a volumetric flask. Store in a dark, stoppered bottle.

B. SULFURIC ACID

Concentrated sulfuric acid is used for acidification.

C. MANGANOUS SULFATE SOLUTION

Dissolve 364 g of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  in water, dilute to 1 liter, and filter.

D. IODIZED ALKALINE IODIDE SOLUTION

Dissolve 700 g KOH in enough distilled water to make approximately 700 ml of solution. Cool to room temperature. Dissolve 150 g of iodate-free KI in 200 ml of distilled water. Add the KI solution and 10 ml of the iodine solution to the KOH solution. Mix. Dilute to 1 liter with distilled water, mix, and store in a stoppered flask.

E. SODIUM THIOSULFATE SOLUTION

Dissolve 24.82 g of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in 800 ml of distilled water that has just been boiled and cooled. Dissolve 1 g  $\text{Na}_2\text{CO}_3$  in the solution to stabilize it. Dilute to 1 liter with boiled distilled water.

Standardize the sodium thiosulfate solution against primary standard or known purity  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{KIO}_3$  as follows: Dissolve 2 g of iodate-free KI and 2 g of  $\text{NaHCO}_3$  in 300 ml of distilled water in a 500-ml iodine flask containing a stirring bar. Add 12 ml conc. HCl (sp. g. 1.19) slowly. Swirl the flask and stopper lightly. Place a small quantity of distilled water around the stopper to effect a seal. Weigh out 100 mg  $\text{KIO}_3$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ . Add the weighed salt to the flask. Calculate the normality of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution as follows:

$$N = \frac{1000 A}{M B}$$

where: N = normality of  $\text{Na}_2\text{S}_2\text{O}_3$  solution

A = grams of standard salt used

M = equivalent weight of standard salt

B = ml of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration.

It has been our experience that either  $\text{KIO}_3$  or  $\text{K}_2\text{Cr}_2\text{O}_7$  may be used. The same normalities are obtained for each. The preferred standard is  $\text{KIO}_3$  because of the more distinctive color change at the end point. Wash down the inside of the flask with a small amount of distilled water. Restopper. Swirl to dissolve the salt. Place a small quantity of distilled water around the stopper to effect a seal. Allow to stand for 10 min. Titrate with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution using starch solution as the indicator. If  $\text{KIO}_3$  is used as the standard the solution color will change from blue to colorless; if  $\text{K}_2\text{Cr}_2\text{O}_7$  is used the change will be from blue to green.

#### F. SODIUM THIOSULFATE, TITRANT SOLUTION

With a calibrated pipet transfer 10.00 ml of the standardized 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution to a 200-ml volumetric flask. Dilute to the mark with distilled water and mix completely. This solution should be prepared fresh daily just before use.

#### G. POTASSIUM IODATE OR POTASSIUM DICHROMATE

These should be primary standard or known-purity salts.

### IV. PROCEDURE

#### A. PREPARATION

##### 1. Winkler Reagents

These solutions should be made up several days or more before the time of use and set aside to equilibrate with  $\text{O}_2$  in the atmosphere. At the time of use the three 5-ml burets should be set up and filled with the three solutions in preparation for the fixing step. The reagents may be stored in these Koch-type burets provided that the reservoir is covered to prevent changes in concentration or contamination.

##### 2. Sodium Thiosulfate Titrant Solution

This solution should be made up daily in the morning in preparation for the day's analyses. The 1-ml Koch-type buret should be rinsed several times with the titrant and then filled in preparation for the titrations. Normally a single filling of the buret and reservoir will be adequate for a day's work.

### 3. Purging of Sampling Vessels

Prior to sampling a BOD bottle containing a Pyrex-coated magnetic stirring bar is placed in the bottle container. Turn on the  $N_2$  to give a flow of approximately 2 liters per minute through the purge tube. Remove the stopper of the BOD bottle and insert the purge tube. Allow the BOD bottle to be swept with  $N_2$  for 5 minutes. Remove the purge tube and restopper the BOD bottle. Disconnect the Pyrex glass tube and connect the rubber or Tygon tubing to the side arm of the bottle container. After 5 minutes or more the sampling vessels are ready for collecting a water sample.

### 4. Titration Container

Place a 250 ml beaker containing a Pyrex-coated stirring bar in the titration container. Position the cover. Turn on the  $N_2$  to give a flow of approximately 2 liters per minute through the purge tube. Insert purge tube into the 250-ml beaker.

### 5. pH Meter

Prepare pH meter for potentiometric measurements. Connect platinum and calomel electrodes. Fill the calomel electrode with a saturated KCl solution, if necessary.

### 6. Pipet Purging

Connect the 100-ml or 200-ml pipet to a stream of  $N_2$  flowing at approximately 1 liter per minute. Allow  $N_2$  to flow until the pipet is used. This purging dries the pipet and sweeps out the air.

## B. SAMPLING

Note: The flow of  $N_2$  through the bottle container is to continue throughout this step. Remove the stopper of the BOD bottle and position the bottle container and BOD bottle under the tube delivering the sample stream so that the tube is approximately 1/4-in. from the bottom of the BOD bottle. Allow the sample water to flow through and sweep out the BOD bottle for 25 to 30 minutes. As a general guide the volume of water passed should be at

least 5 times the volume of the BOD bottle. Samples flowing at flow rates greater than 100 ml/min may be sampled for a shorter time and at rates less than 50 ml/min for correspondingly longer periods of time. Just before the conclusion of sampling, read and record the temperature of the water sample. At the conclusion of sampling, lower the bottle container quickly away from the sample tube and restopper the BOD bottle. The stopper of the BOD bottle should be dry or should be wiped dry with a clean, dry, lint-free cloth or absorbent paper. Wipe the cover of the bottle container inside and outside (without removing from the vessel) to blot up droplets of water. Once these droplets have come into contact with air they must not be allowed to fall back into the water in the BOD bottle. Measure the flow rate of the sample by collecting water from the tube delivering the sample stream for 1 min.; collect the water in a 100-ml graduated cylinder.

### C. FIXING

Fill each of the three burets from the reservoir to just slightly above the zero mark. Wipe the tip of each buret with a clean, dry, lint-free disposable paper. NOTE: The flow of  $N_2$  through the bottle container is to continue throughout the fixing step.

#### 1. Sample (NR)

Add 2.0 ml of the iodized alkaline iodide solution to the sample. This is done in the following manner: Remove the stopper of the BOD bottle and lay it on a clean, dry paper. Insert the tip of the buret inside the bottle container but outside the BOD bottle. Allow the solution to flow out of the buret until the upper liquid level (meniscus) is at the zero mark. Then insert the buret tip to the bottom of the BOD bottle. Allow 2.0 ml of the solution to flow slowly into the BOD bottle. Stop the flow and quickly lower the bottle container and BOD bottle down and away from the tip of the buret. Do not allow liquid running down the tip of the buret to drop into the BOD bottle. Set the bottle container and BOD bottle on the magnetic stirrer. Wipe the stopper of the BOD bottle dry with a clean, dry, lint-free paper and place it lightly into the BOD bottle with a slight

turn. Wipe the tip of the just-used buret and discard the paper. Turn on the magnetic stirrer at a slow speed that is adequate to give complete mixing of the contents of the BOD bottle. Allow the contents to stir 30 seconds. Turn off the stirrer. Add 2.0 ml of the  $\text{MnSO}_4$  solution in exactly the same manner as described above for iodized alkaline iodide solution. After the 30-second stirring allow the precipitate to settle 5 minutes. Then add 2.0 ml of  $\text{H}_2\text{SO}_4$  in exactly the same manner as for the above two solutions, except that the  $\text{H}_2\text{SO}_4$  is delivered near the top of the solution instead of at the bottom. This sample is now ready for titration.

2. Blank (RR)

The blank is fixed by exactly the same procedure except that the reagents are added in the order:  $\text{H}_2\text{SO}_4$ , iodized alkaline iodide solution,  $\text{MnSO}_4$  solution. There need be no waiting after any of these additions inasmuch as the chemical reactions are all rapid. In distilled water it makes no difference whether the  $\text{H}_2\text{SO}_4$  or the iodized alkaline iodide is added first, but in sea water a precipitate is formed in basic solution. Certain metal ions might be present in sea water, especially in sea water which has been in contact with metal parts, and these metal ions might undergo some reaction with D. O. This potential problem is largely avoided by the order of addition suggested above.

3. Sample (DNR)

The fixing procedure is identical to that for Sample (NR) except that 4.0 ml of each reagent is added instead of 2.0 ml.

4. Blank (DRR)

The fixing procedure is identical to that for Blank (RR) except that 4.0 ml of each reagent is added instead of 2.0 ml.

5. Volume of Reagents

The delivered volume of  $\text{MnSO}_4$  and of iodized alkaline iodide solutions are read at least 15 minutes after the fixing step to allow adequate time for wall drainage. Read to the nearest 0.001 ml and record as  $V_M$  and  $V_I$ , respectively.

## D. TITRATION

NOTE: The flow of  $N_2$  through the bottle container is to continue until the sample is pipetted out for titration.

### 1. Sample (NR)

Remove the purge tube from the titration container. Position the platinum-calomel electrode pair through the cover and in the 250-ml beaker. Fill the buret to above the zero mark and then drain out titrant solution to bring the liquid level (meniscus) down to zero. Wipe the tip of the buret with a clean, dry, lint-free paper wiper. Position the buret so that the tip extends through the cover of the titration container and into the 250-ml beaker.

Remove the stopper from the BOD bottle and pipet 200 ml of the sample into the 250-ml beaker in the titration container. Be sure that the electrodes are positioned properly and that the buret tip touches the surface of the sample. Turn the pH meter dial to read. Start the stirrer. Read and record emf and ml (0). Add titrant in 0.10-ml increments, reading and recording ml and emf in vertical columns at each increment. When the end point is approached, as indicated by a disappearance of any trace of brown or yellow from the solution being titrated and by the lowering of the emf to 300 to 310 mv, reduce the size of increments added to 0.01 ml. Titrate in 0.01-ml increments through and approximately 0.05 ml beyond the end point, recording emf and ml at each increment. In a third column parallel to those in which ml of thiosulfate and emf were recorded, write the  $\Delta$  emf values for the 0.01-ml increments. Estimate the end point to  $\pm 0.001$  ml from a plot of ml vs emf or by interpolation of  $\Delta$  emf values.

### 2. Blank (RR)

This procedure is identical to that for Sample (NR).

### 3. Sample (DNR)

This procedure is identical to that for Sample (NR) except that the potential just before the end point break will be some 20 mv lower.

#### 4. Blank (DRR)

This procedure is identical to that for Sample (DNR).

### V. CALCULATION

#### A. UNCORRECTED VALUES

The volume of thiosulfate titrant required to reach the end point is converted to an uncorrected equivalent D. O. content, as follows:

$$D_u = 40,000 NV$$

where:  $D_u$  = equivalent D. O. content, ppb

$N$  = normality of thiosulfate titrant (nominally, 0.005)

$V$  = ml of thiosulfate solution required for titration of the sample.

$D_u$  corresponds to values for  $NR_u$ ,  $RR_u$ ,  $DNR_u$ , and  $DRR_u$ , depending on whether the volumes were for Sample (NR), Blank (RR), Sample (DNR), or Blank (DRR), respectively.

#### B. CORRECTED VALUES

Uncorrected values for R and  $R_{O_2}$  ( $R_u$  and  $R_{O_{2u}}$ ) are calculated from the preceding uncorrected values ( $NR_u$ ,  $RR_u$ ,  $DNR_u$ , and  $DRR_u$ ) as follows:

$$R_u = DRR_u - RR_u$$

$$R_{O_{2u}} = DNR_u - NR_u - R_u$$

Corrected values for NR, RR, DNR, and DRR are then calculated from uncorrected values ( $NR_u$ ,  $RR_u$ ,  $DNR_u$ , and  $DRR_u$ , respectively) as follows:

$$NR = 1.0506 [NR_u + R_{O_2u} (2.000 - V_M) + R_u (2.000 - V_I)]$$

$$RR = 1.0506 [RR_u + R_u (2.000 - V_I)]$$

$$DNR = 1.040 [DNR_u + R_{O_2u} (4.000 - V_M) + R_u (4.000 - V_I)]$$

$$DRR = 1.040 [DRR_u + R_u (4.000 - V_I)]$$

where:  $V_M$  is in each case the ml of  $MnSO_4$  solution delivered for that specific sample

$V_I$  is in each case the ml of iodized alkaline iodide solution delivered for that specific sample.

These corrected values are then used to calculate R, H,  $R_{O_2}$ , and  $H_{O_2}$ , as follows:

$$R = DRR - RR$$

$$H = 2RR - DRR$$

$$R_{O_2} = DNR - NR - R$$

$$H_{O_2} = 2NR - DNR - H$$

where: R = net redox of the Winkler reagents, ppb (calculated as D.O. equivalent)

H = net redox of the water sample, ppb (calculated as D.O. equivalent)

$R_{O_2}$  = D.O. content of the Winkler reagents, ppb

$H_{O_2}$  = D.O. content of the water sample, ppb.

## VI. PRECISION AND ACCURACY

This method is capable of giving values for R, H,  $R_{O_2}$ , and  $H_{O_2}$  which are precise and accurate to  $\pm 2$  ppb or better.

APPARATUS FOR PERMEATION TESTS

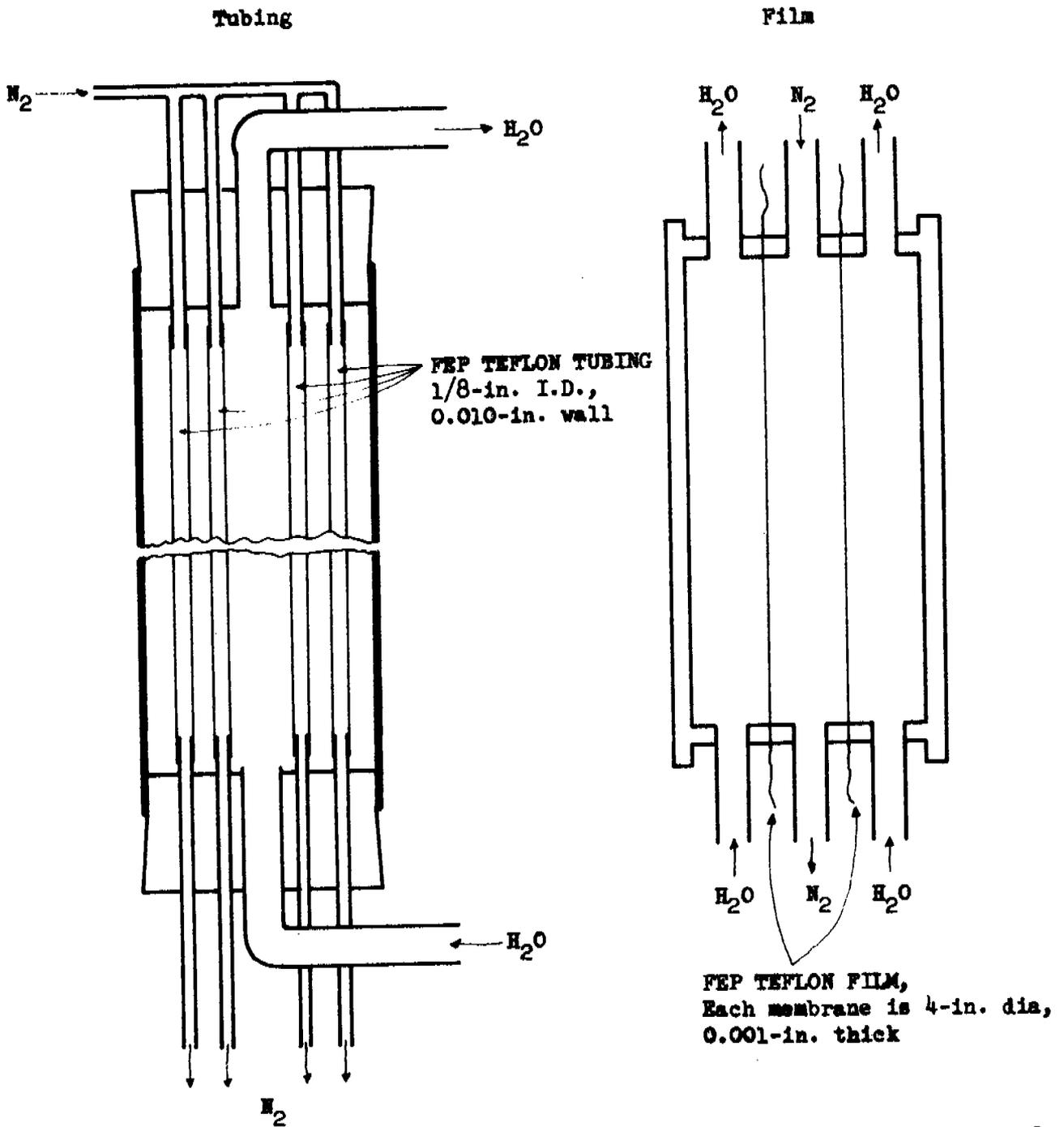
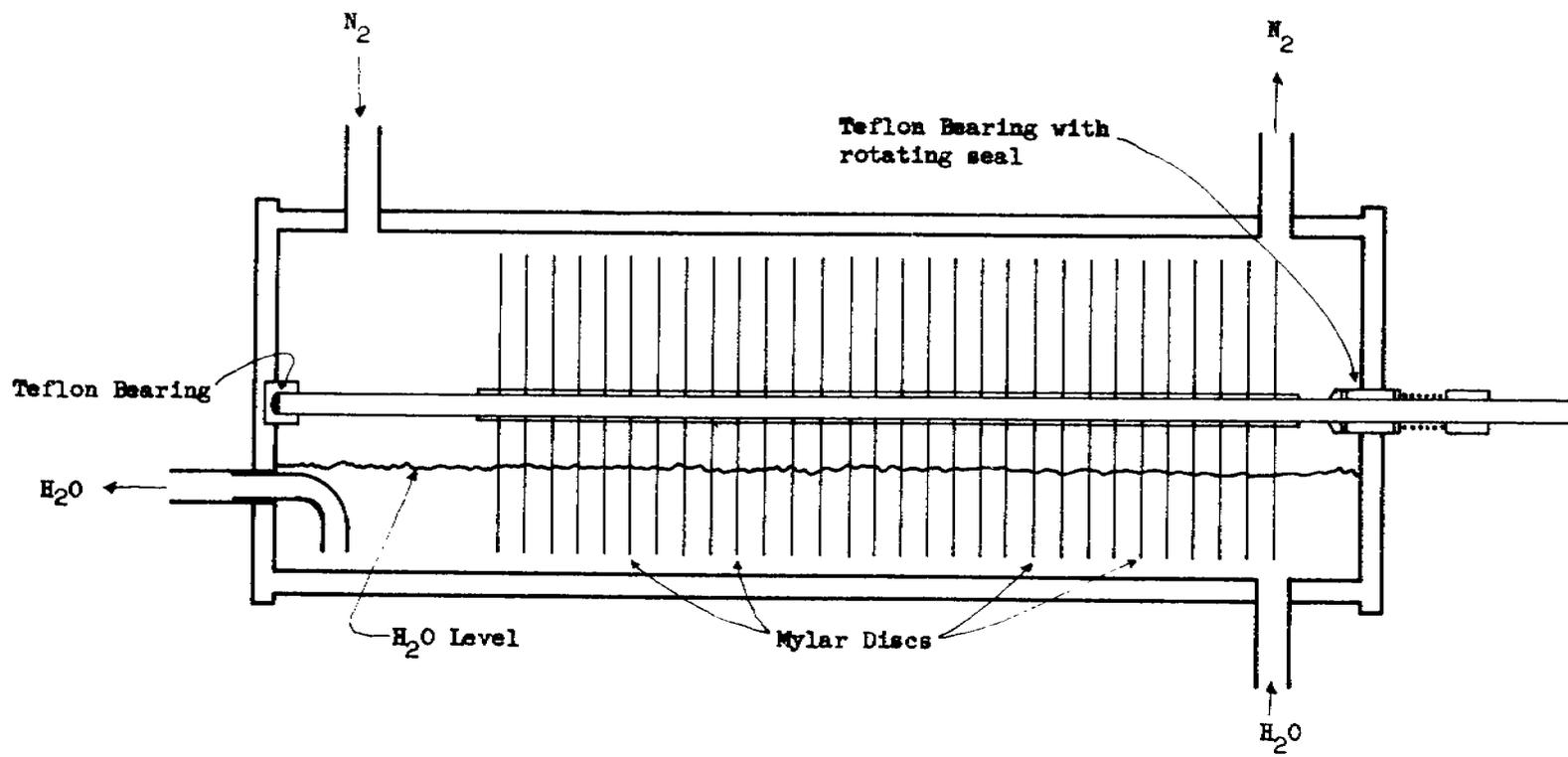


Figure 3

DISC STRIPPER FOR OXYGEN REMOVAL



110

Figure 4

CONTAINER FOR SAMPLING IN AN INERT ATMOSPHERE

Acrylic Sample Container  
4-in. I.D. by 7-in. long

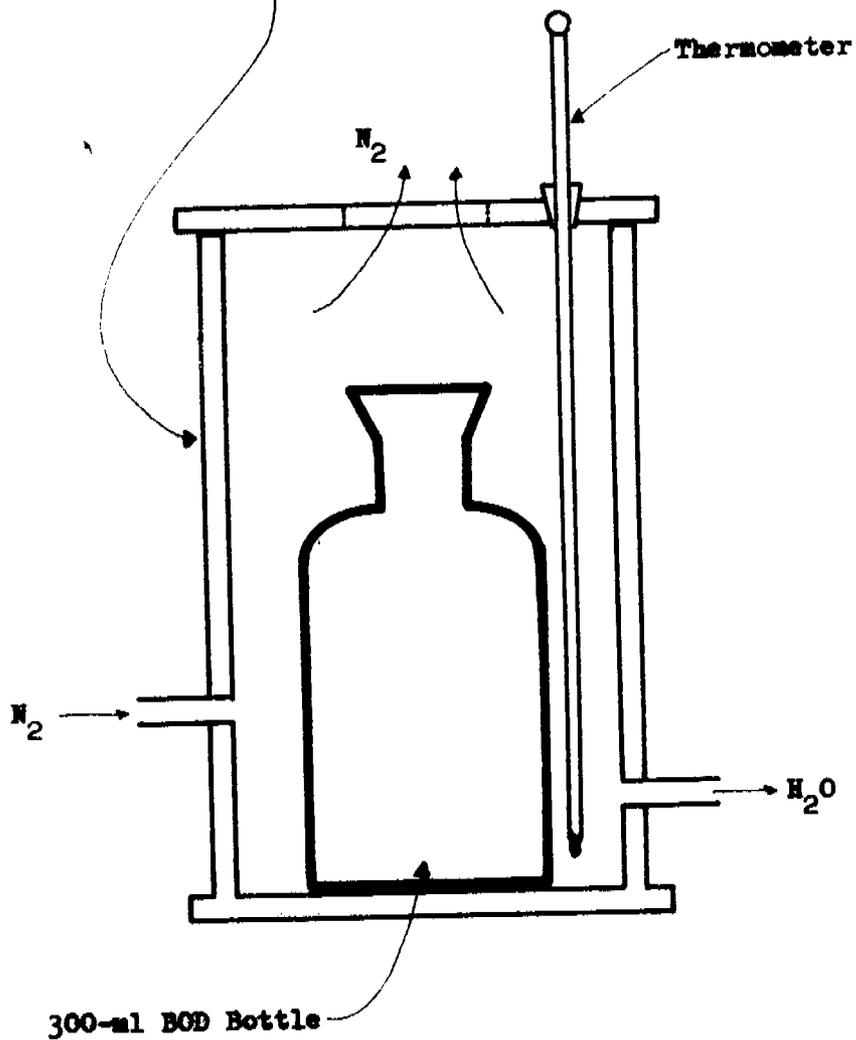


Figure 5



FIGURE 6

APPARATUS FOR TITRATION IN A NITROGEN ATMOSPHERE

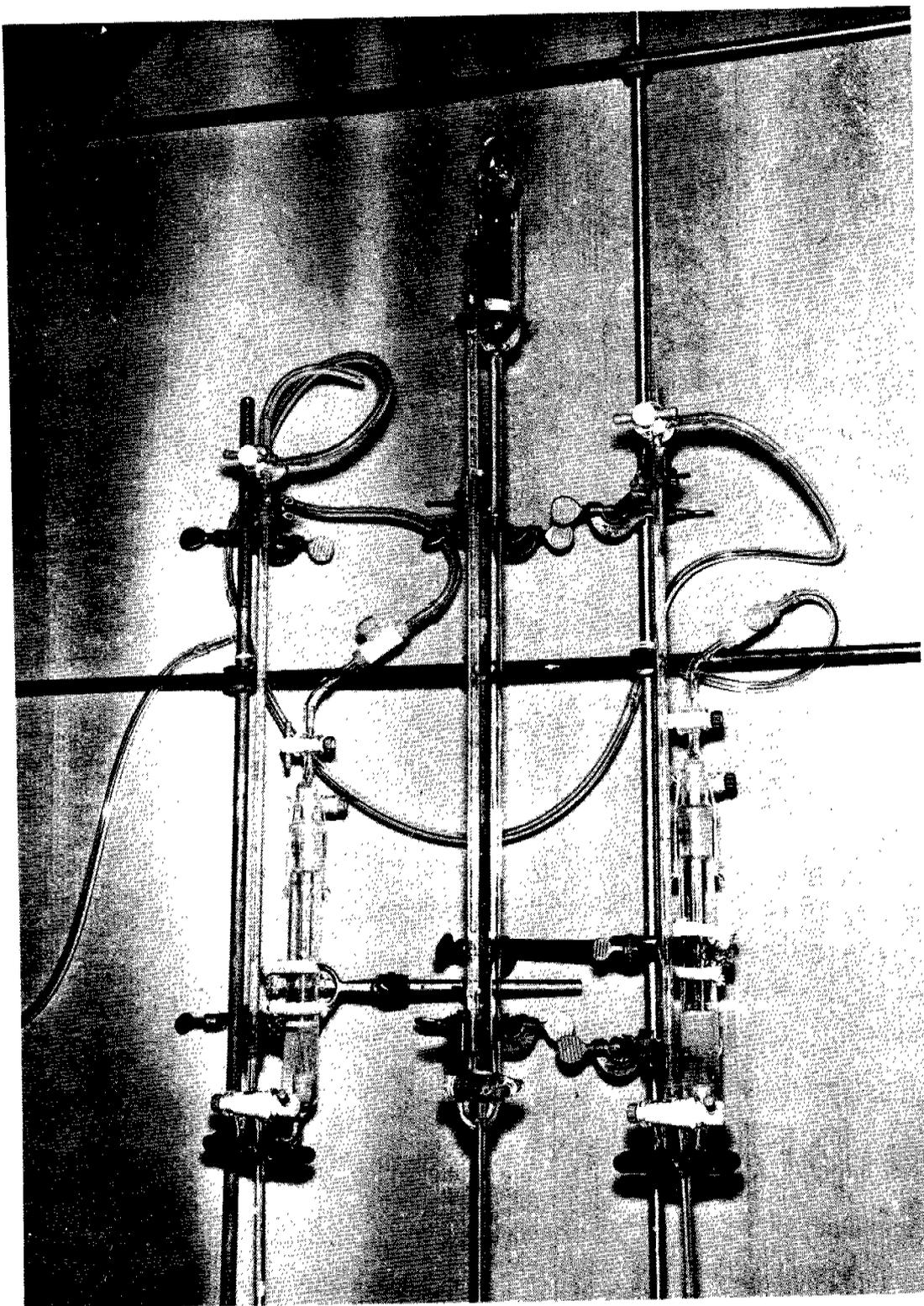
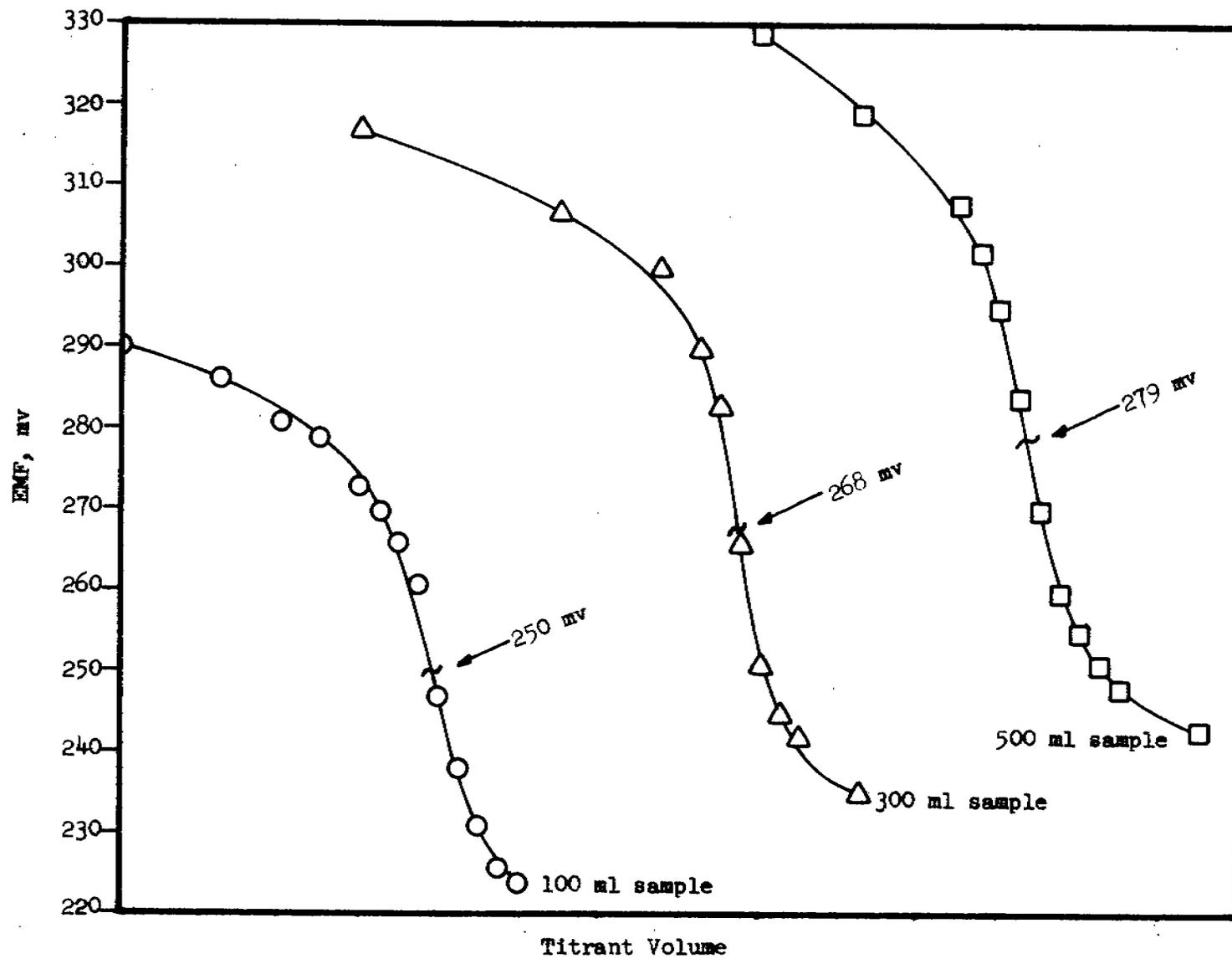


FIGURE 7

APPARATUS FOR PURGING AND HANDLING  
WINKLER REAGENTS UNDER NITROGEN

EFFECT OF KI CONCENTRATION ON THE END-POINT POTENTIAL



EFFECT OF STARCH ON THE POTENTIOMETRIC END-POINT CURVE

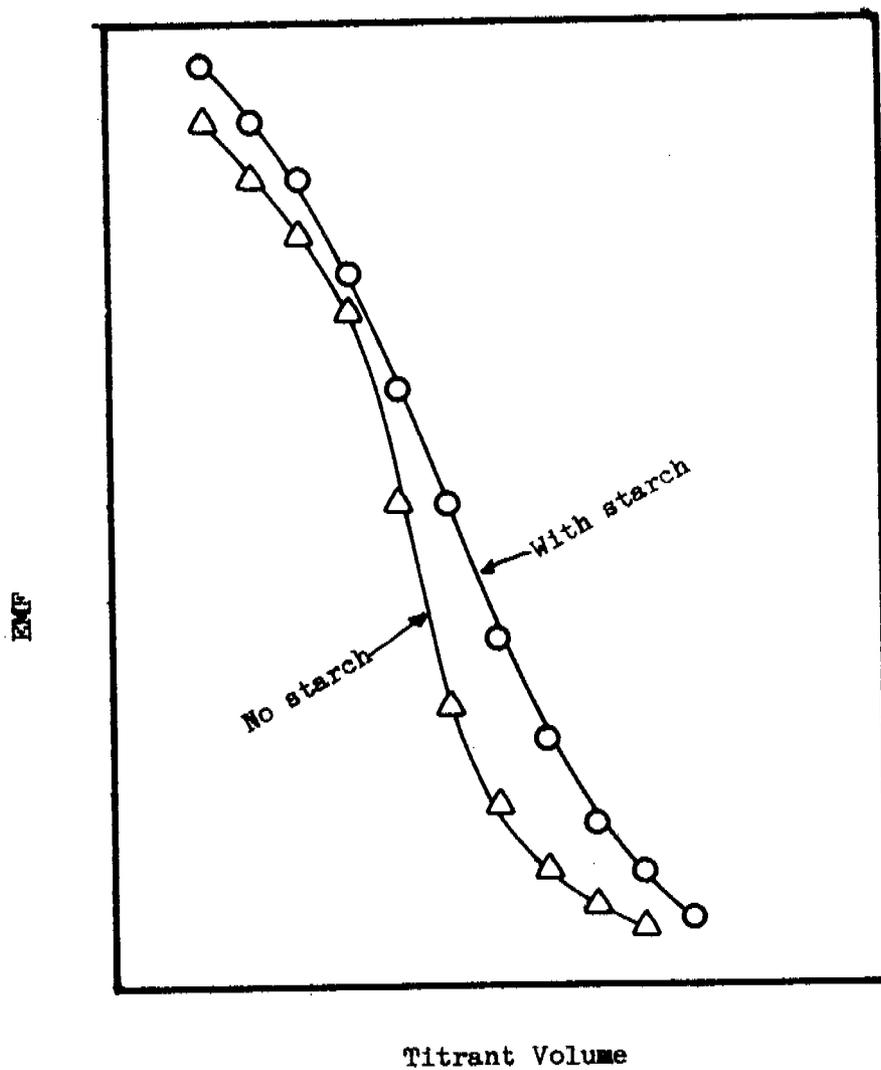


Figure 9

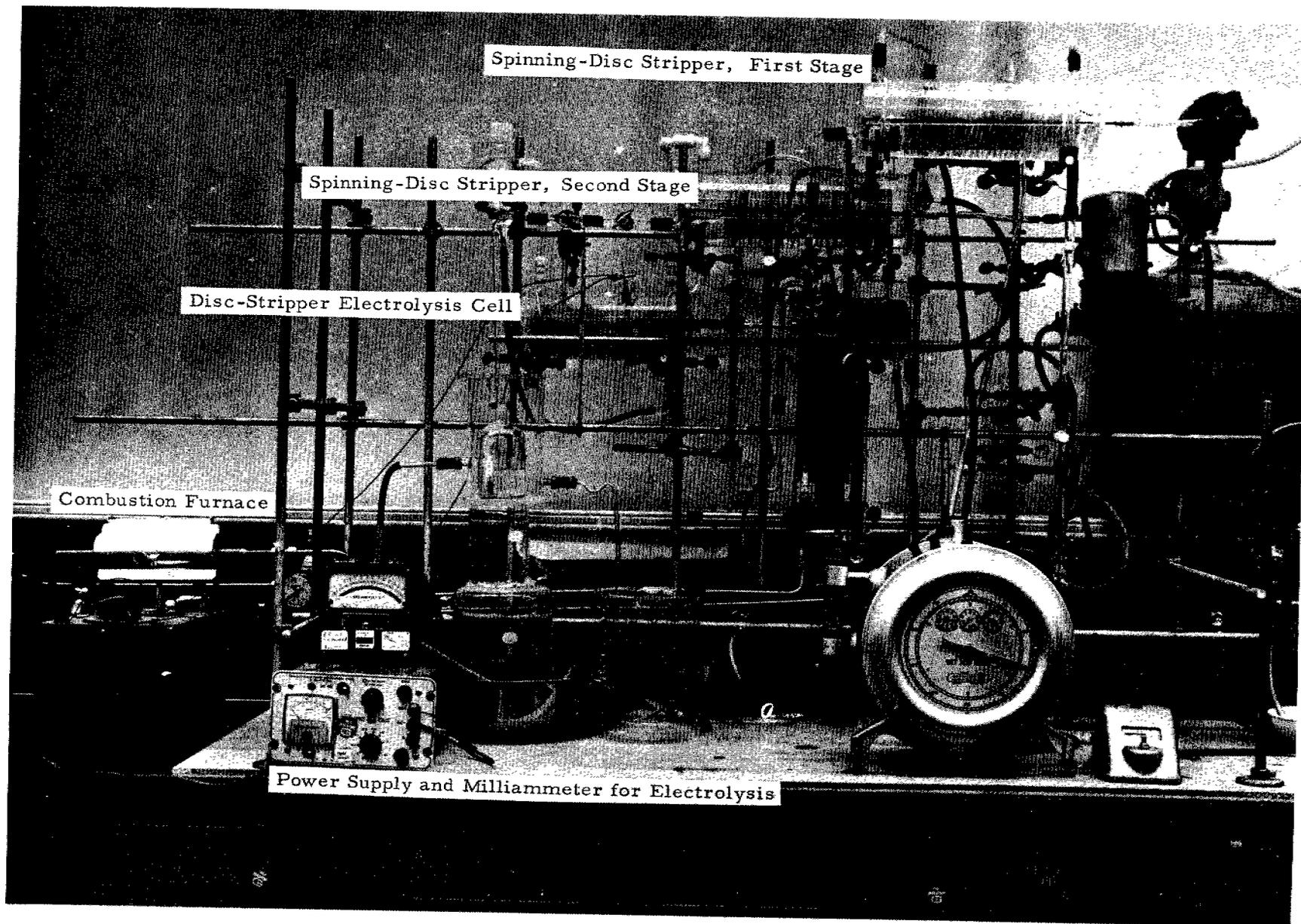


FIGURE 10

LABORATORY SETUP FOR DEOXYGENATION AND OXYGEN ADDITION

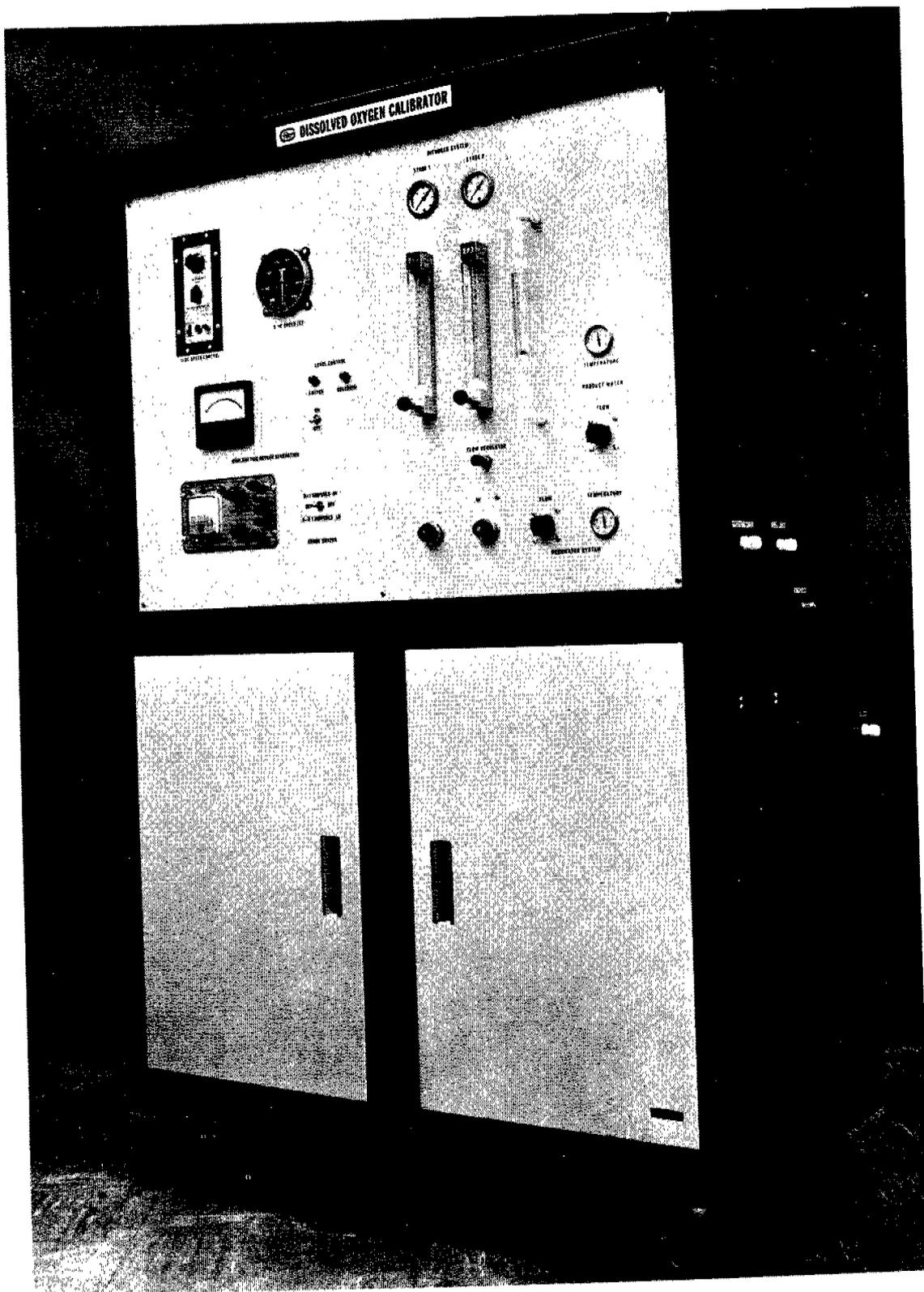


FIGURE 11

PHOTOGRAPHIC VIEW OF THE DISSOLVED OXYGEN CALIBRATOR

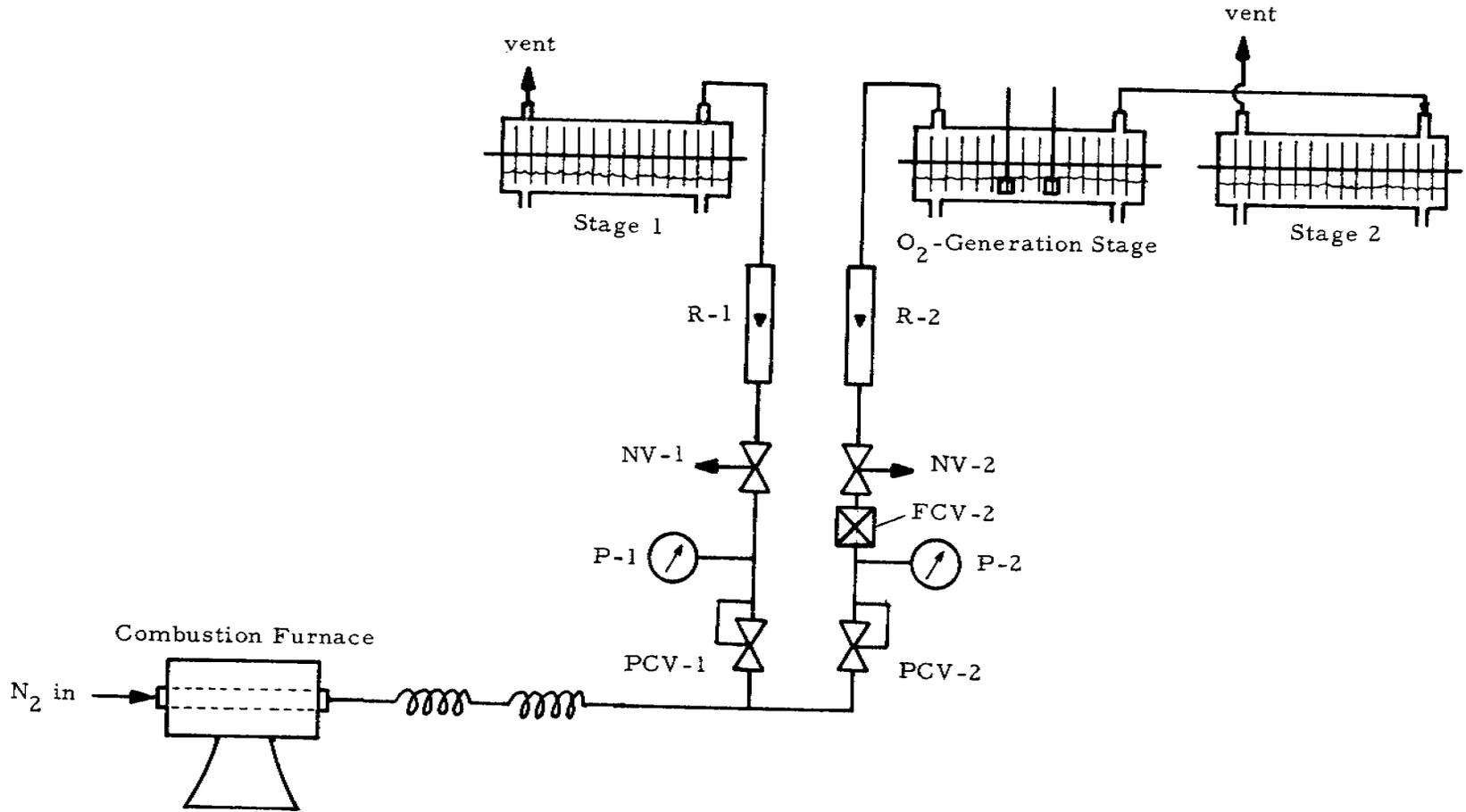
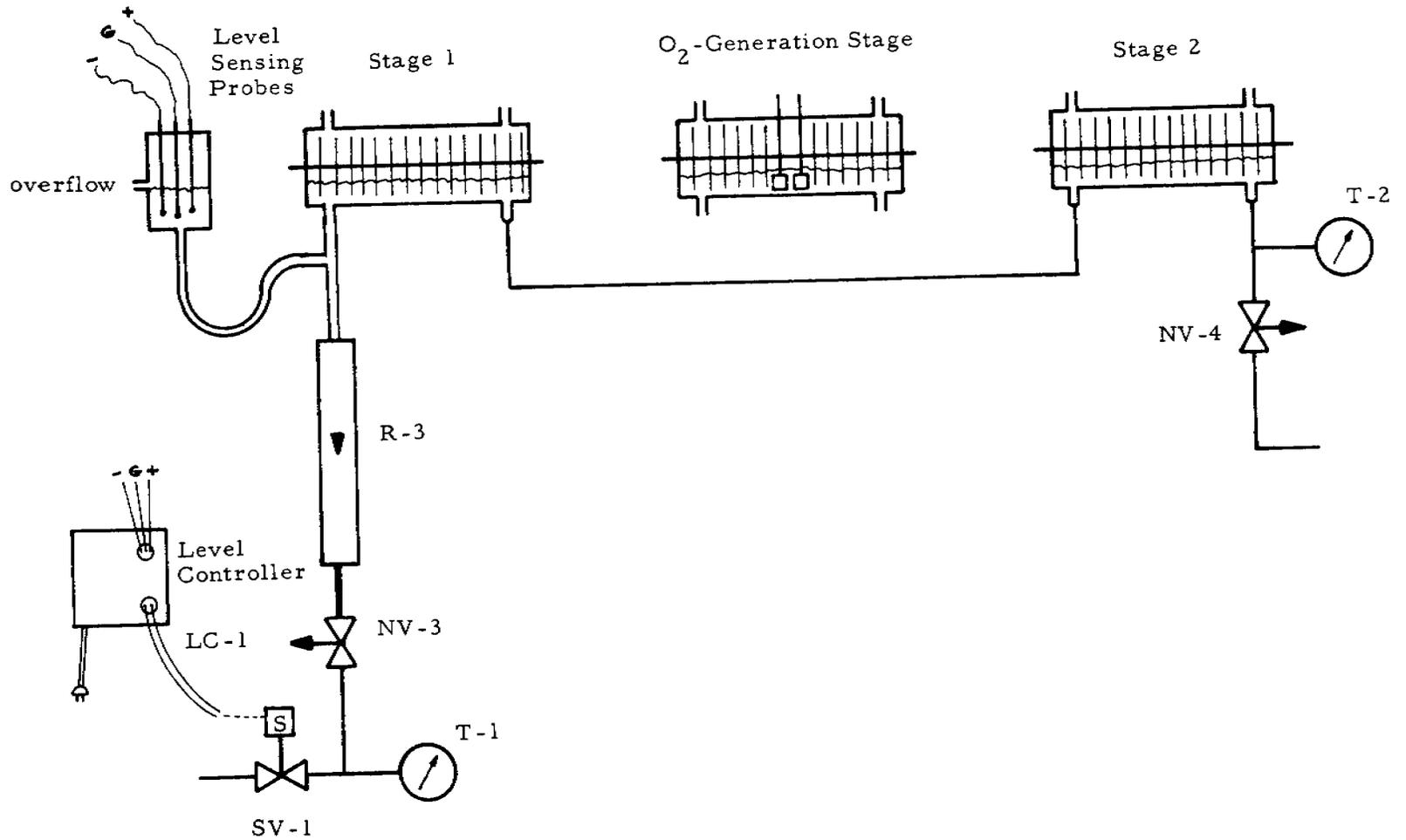
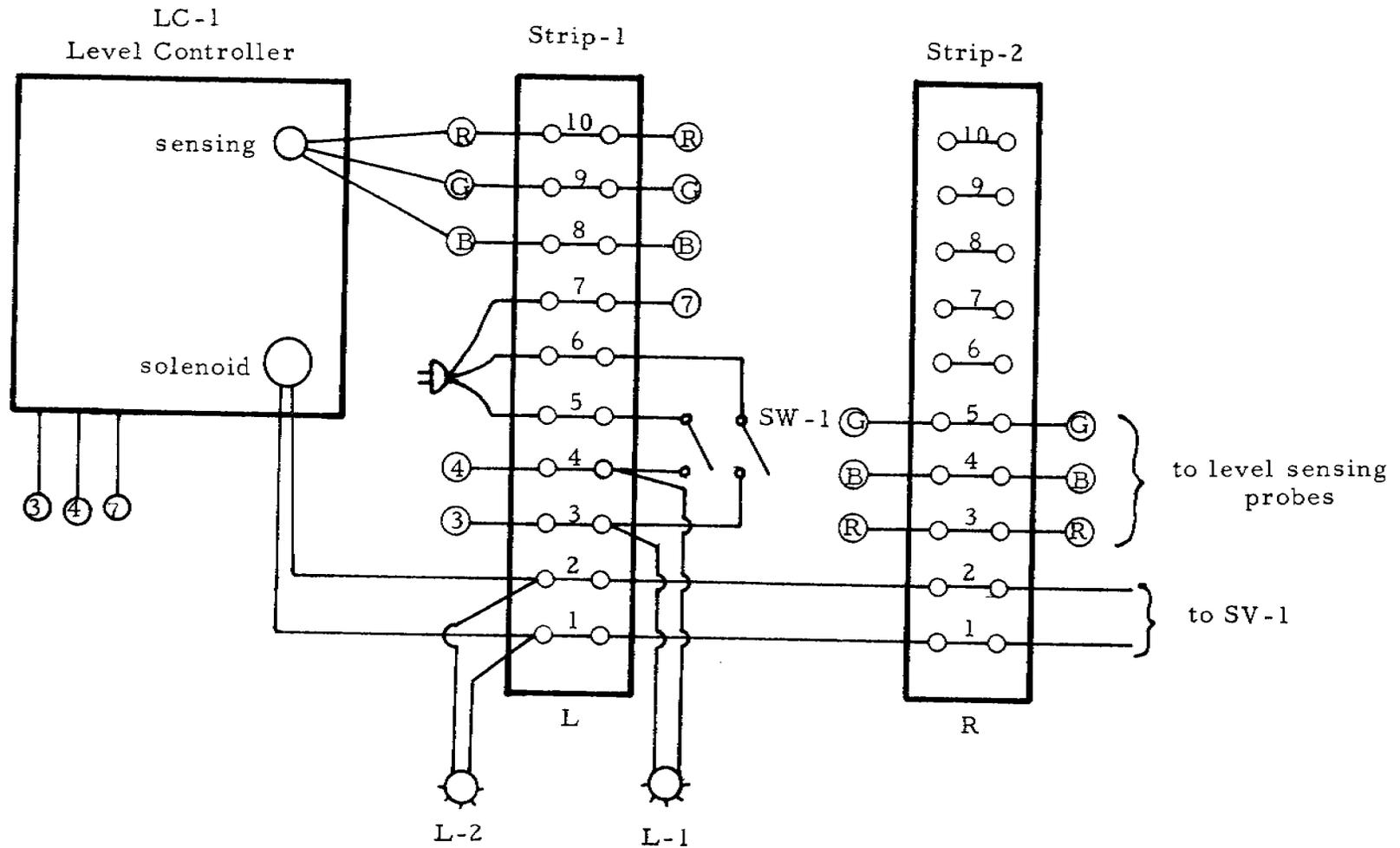
Schematic Diagram of the N<sub>2</sub>-Flow System

Figure 12



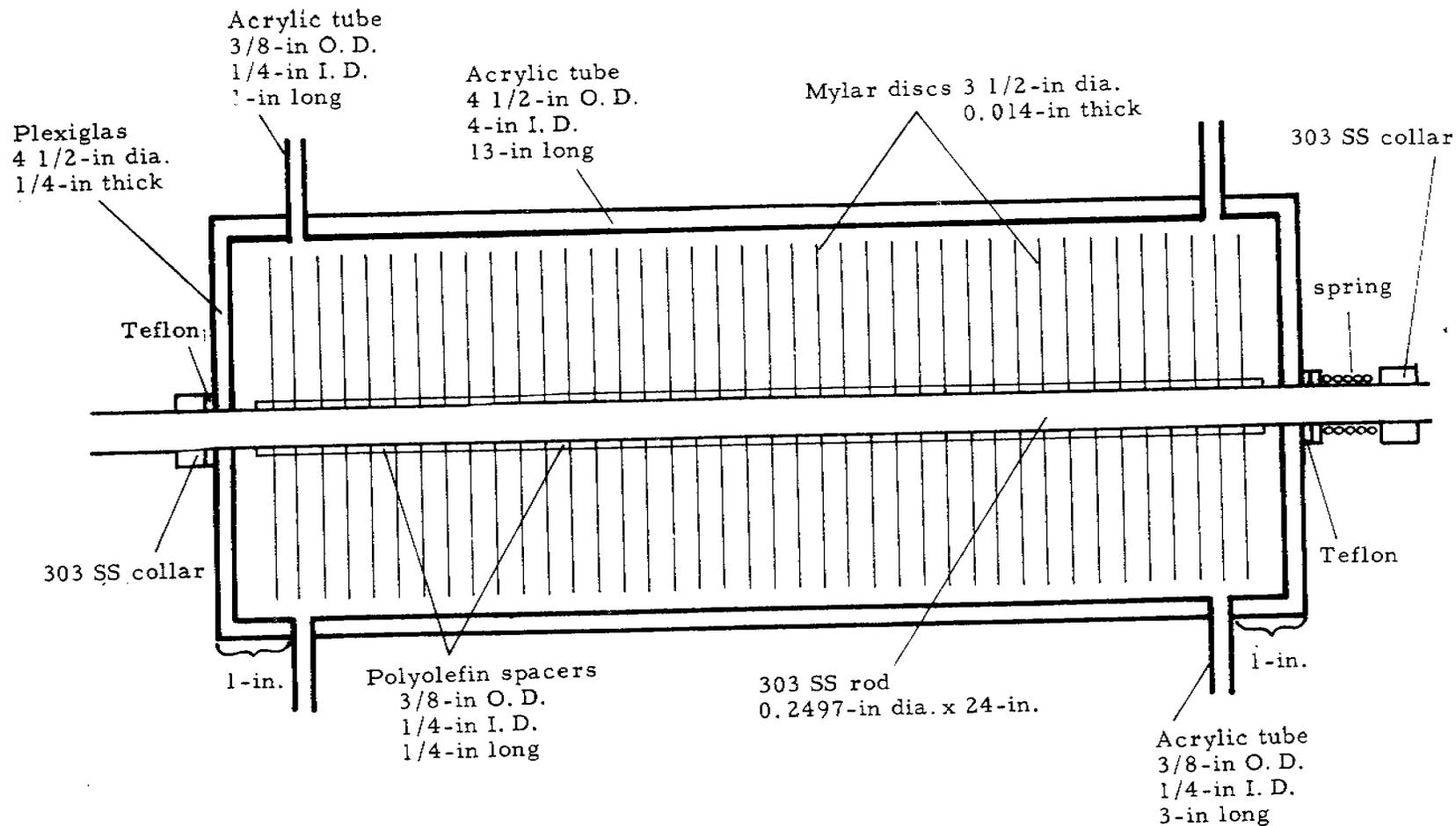
Schematic Diagram of H<sub>2</sub>O-Flow System

Figure 13



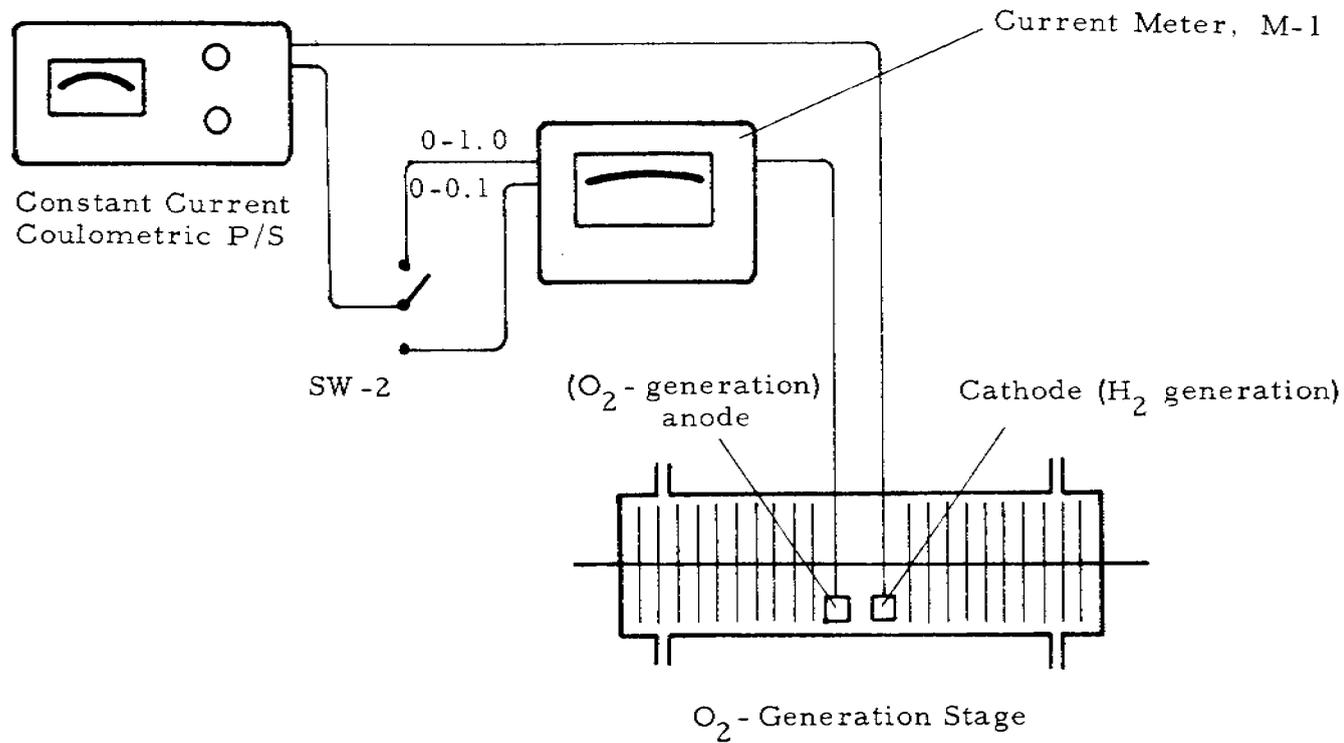
Schematic Diagram of the Electrical Wiring for the Level-Control System

Figure 14



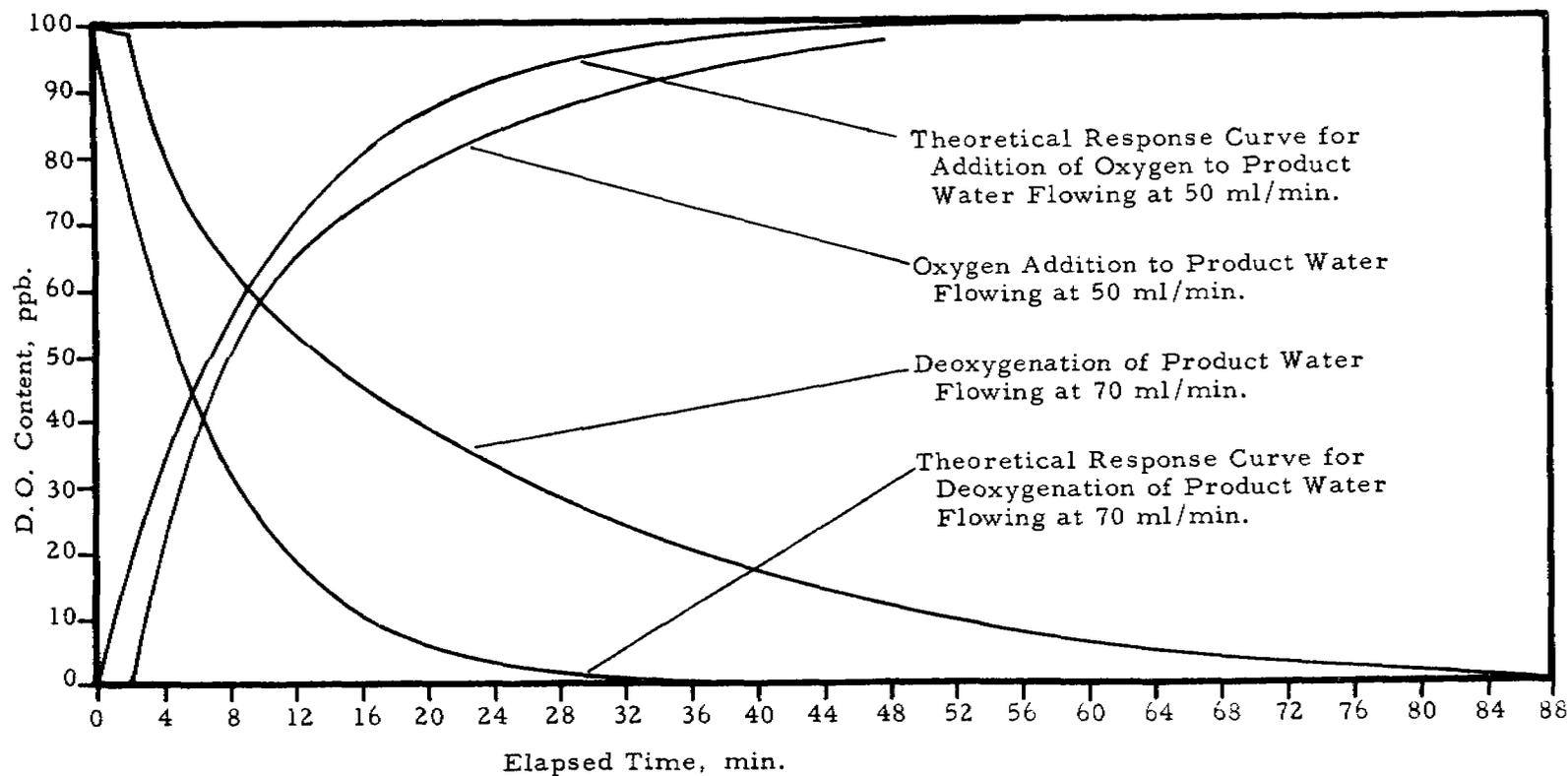
Details of the Spinning-Disc Stripper

Figure 15



Schematic Diagram for the Oxygen-Generation System

Figure 16



Theoretical and Measured Response-Time Curves for Step Changes in  $O_2$  Levels.  
(Addition and Deoxygenation)

Figure 17

APPENDIX I  
CHEMICALS AND EQUIPMENT

I. CHEMICALS

A. REAGENTS

The chemicals used to make up reagent solutions for the Winkler analysis (KOH, KI,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{I}_2$ ), titrants ( $\text{AgNO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ ,  $\text{KIO}_3$ ), indicators ( $\text{K}_2\text{CrO}_4$ , starch), reagent solutions of interfering ions ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ ), and solutions and reagents for the colorimetric indigo carmine procedure ( $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , HCl, dextrose, glycerine, KOH) were all Baker Analyzed Reagents. Exceptions to this were  $\text{NaN}_3$  and indigo carmine, which were practical grade, and  $\text{H}_2\text{SO}_4$  which was duPont reagent grade chemical. The sodium thiosulfate solution was standardized against weighed quantities of primary standard  $\text{K}_2\text{Cr}_2\text{O}_7$  (99.97% assay) or against weighed quantities of Baker Analyzed Reagent  $\text{KIO}_3$  (100.0% assay).

B. PURGE GASES

The purge gases employed throughout this program were  $\text{CO}_2$ ,  $\text{N}_2$ , and purified  $\text{N}_2$ . The  $\text{CO}_2$  was obtained from subliming dry ice; although the purity was not specifically determined during this research, past experience has shown it to assay over 99.99%. For purging BOD bottles, purging the vessel in which the BOD bottle was handled, and in purging and maintaining an inert blanket in the titration vessel, the  $\text{N}_2$  was used as received from the  $\text{N}_2$  outlet in the laboratory. The  $\text{N}_2$  plumbed to our laboratory is pressurized  $\text{N}_2$  generated from a liquid  $\text{N}_2$  storage vessel. The oxygen content of this gas typically is less than 100 ppm and maybe as low as 10 ppm level (0.001 vol. %). The laboratory  $\text{N}_2$  was passed through a combustion tube containing a mixture of Cu and CuO maintained at  $525 \pm 25^\circ\text{C}$  to obtain a supply of purified  $\text{N}_2$  of constant purity. The Cu removes  $\text{O}_2$  by forming CuO; organic impurities are oxidized to  $\text{H}_2\text{O}$  and  $\text{CO}_2$  by the CuO. In some initial runs  $\text{H}_2\text{O}$  and  $\text{CO}_2$  were removed on an Ascarite/Anhydrone column, but this purification step was removed shortly inasmuch as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were not considered detrimental. There was some question as to whether the residual  $\text{O}_2$  content of this purified  $\text{N}_2$  might be

significant. If, for example, the residual  $O_2$  amounted to 0.011 vol-% distilled water in equilibrium with it at  $20^\circ C$  would contain a D. O. content of 5 ppb. Consequently, several tests were made to determine the  $O_2$  content of the purified  $N_2$ . In one test indigo carmine reagent (ASTM D888A) was introduced directly into deoxygenated water in the disc stripper. The color was observed initially and after deoxygenated  $N_2$  had purged through the system for measured periods of time. The  $O_2$  content of the stripping gas was estimated from the flow rates and the sensible color change to be less than 0.001 vol. %.

In another test the Winkler method was used to estimate the residual  $O_2$  content. The apparatus employed here consisted of two identical gas-washing columns in series, as shown in Figure 1. Each column consisted of a test tube 1.5-in. I. D. and 24-in. long, fitted with a rubber stopper and a fritted-disc gas bubbler which extended to the bottom of the tube. Gas exiting from the train was passed to a wet-test meter to measure the gas flow rate. With 500 ml of distilled water added to each scrubber, the gas was forced to pass through approximately 20 in. of liquid in each column. A carefully ordered and timed procedure was adapted for adding reagents and allowing the reaction of  $O_2$  in the scrubber. The apparatus was cleaned and set up and then the procedure below was followed:

1. Add 500 ml distilled water to each scrubber.
2. Add 2.0 ml  $MnSO_4$  solution to each scrubber.
3. Assemble apparatus for purging with sample  $N_2$ .
4. Begin flow of gas through the two columns and simultaneously start stopwatch.
5. Allow 15-minute purge of the two columns. As the end of the 15-min purge (900 seconds) approaches, draw iodized alkaline iodide into the pipet and prepare to add 2.0 ml of reagent to column No. 1.
6. At precisely 900 seconds, begin adding the 2.0 ml of iodized alkaline iodide to column No. 1.

7. As soon as Step 6 is complete, add 2.0 ml of iodized alkaline iodide to column No. 2.

8. Allow  $N_2$  to continue purging through the 2 columns. As 1200 seconds approach, prepare to add 2.0 ml  $H_2SO_4$  to each.

9. At precisely 1200 seconds begin adding 2.0 ml of  $H_2SO_4$  to column No. 2. When reagent addition is complete, stop the flow of  $N_2$  to column No. 2 by lifting the stopper from column No. 1.

10. Quickly pipet and add 2.0 ml of  $H_2SO_4$  to column No. 1. When reagent addition is complete, stop the flow of  $N_2$  through column No. 1.

11. Pipet 200 ml of fixed solution from column No. 1 into 250 ml beaker and titrate as in Aerojet-modified Winkler procedure. (See Appendix II for procedure.)

12. Repeat Step 11 for fixed solution No. 2.

The procedure outlined in these 12 steps furnishes the blank. The  $O_2$  analysis of the  $N_2$  stream is obtained in a similar process by allowing  $N_2$  to flow 30 minutes (1800 seconds) beyond the 1200 second stop point in Step 8. The actual  $N_2$  flow rate is measured during the 15-minute purge in Step 5.

The  $O_2$  content of the  $N_2$  stream was first estimated from the difference between sample and blank run as described above. The net difference measured corresponded to 0.000174 vol-%  $O_2$  in  $N_2$ . Of this amount 0.000056 vol-% was in column No. 1 and 0.000118 vol-% was in column No. 2. Thus, column No. 1 did not collect all the  $O_2$ . This means, then, that the  $O_2$  content is not less than the sum, or 0.000174 vol-%.

Further tests were made to determine the per cent of  $O_2$  abstracted using this setup. An electrolysis cell was inserted in the  $N_2$  stream just ahead of column No. 1. The procedure followed was as for the sample gas described above, except that additional  $O_2$  (generated at a current of 100 ma) was added to the purified  $N_2$  for five minutes duration at the 5-minute timing point in the 30-min sampling period. The increased  $O_2$  content was

measured by titration, in the same manner as the sample and blank. The  $O_2$  produced during the steady-state 5-min generation time corresponds to an  $O_2-N_2$  mixture that is 0.080 vol-%  $O_2$ . Altogether 2.486 mg of  $O_2$  were formed, but only 0.2174 mg, or 8.7% of the total, was absorbed according to the measurement. This confirms that the scrubber is not 100% efficient in removing the  $O_2$  in the gas stream, at least not at the 0.080 vol-% level.

It is realized that any estimate of recovery efficiency at 0.0002 vol-% based on a value derived for a level some 400 times higher is subject to uncertainties. The absorption efficiency in a given column and at a given sample flow rate would be expected to be greater at 0.0002 vol-% than at 0.080 vol-%. The  $O_2$  content measured for the purified gas stream was 0.000174 vol-%; this must be regarded as a minimum  $O_2$  value. If the absorption efficiency were 8.7% this would correspond to a true  $O_2$  concentration of 0.002 vol-%. If the absorption efficiency is greater than 8.7% at  $O_2$  concentrations lower than 0.080 vol-%, the true  $O_2$  concentration would be less than 0.002 vol-%. Thus, the series of tests demonstrated that the  $O_2$  content of the purified  $N_2$  stream lies within the range of 0.000174 to 0.002 vol-%. These gas concentrations would be in equilibrium with distilled water at 20°C having a D.O. content of 0.07 and 0.9 ppb, respectively. The two tests, taken together, indicate that the  $O_2$  content of the purified  $N_2$  is on the order of 0.001 vol-%.

### C. WATER SAMPLES

The water samples used throughout the program were either bottled distilled water or sea water. The sea water was collected in a 55-gal stainless steel drum several miles offshore in the Santa Catalina channel and brought to this laboratory. After it was received here, it was transferred to 5-gal glass bottles and retained for use. The chlorinity of this sea water was determined by the procedure of Strickland and Parsons;\* the sea water was compared with standard sea water (chlorinity: 19.374 ppt) by titration with 0.21 N  $AgNO_3$  solution. The analysis showed the sea water to have a chlorinity of 18.604 ppt which is equivalent to a salinity of 33.610 ppt.

\*J. D. H. Strickland and T. R. Parsons, "A Manual of Sea Water Analysis", Bulletin, Fisheries Research Board of Canada, 125, 185 (1960).

## II. EQUIPMENT

### A. SPECIAL RESEARCH APPARATUS

Although no attempt will be made in this section to describe here in detail the specific design of special research apparatus, some generalized comments are in order. Laboratory models for the various investigations were generally fabricated from Pyrex glass or Plexiglas. To the extent that it was possible, contact of metal parts with the water sample was avoided so that corrosion would not contaminate the water or limit the life of the part. Pyrex glass tubing was found to be especially beneficial in transferring the deoxygenated water to the receiving vessel or to the D.O. Analyzer. In one instance completely deoxygenated distilled water passed through a 2-foot section of polyethylene tubing (3/8-in. O.D., 1/4-in. I.D.) to the sample container (300 ml BOD bottle) consistently gave an analysis corresponding to a D.O. content of approximately 20 ppb. Based on the permeation characteristics of the tubing, the diffusion of  $O_2$  into the water was calculated to correspond to approximately 10 ppb/ft. When the 2-foot section of polyolefin tubing was replaced with Pyrex glass tubing, the D.O. analysis immediately dropped to approximately 0 ppb. Thus, the need for care in the selection of tubing materials for transporting the deoxygenated water is clear.

### B. SAMPLE CONTAINERS

Samples of water for analysis by the Winkler method or by the Aerojet-modified Winkler procedure were collected in 300 ml BOD bottles or in 500 ml McLean sampling tubes, as recommended in ASTM D 1589 and ASTM D 888C, respectively. Samples for analysis by the colorimetric indigo carmine method were collected in 300 ml BOD bottles, as allowed in ASTM D 888A. The McLean tubes were calibrated with respect to one another as recommended in ASTM D 888 C. The BOD bottles were all assumed to have volumes of exactly 300.0 ml; relative volumes obtained by measuring the volume delivered to a graduated cylinder indicated that the volumes are, on the average, all within 0.3%. This is well within the precision aimed for in this research.

### C. ROTAMETERS

The flow of  $N_2$  stripping gas utilized in the deoxygenation studies and in all subsequent tests during the development of the spinning-disc stripper, research of  $O_2$  addition techniques, and refinement of the analysis procedure was monitored continuously by means of appropriately sized rotameters. These rotameters were calibrated periodically in the various systems and under various conditions of use by the wet-test-meter or bubble-in-buret method.

### D. LIQUID FLOW

The flow rate of sample water was measured either by collecting the discharge for 1 minute or by collecting the total discharge during sampling and measuring the time of sampling.

### E. TITRATION APPARATUS

Throughout the entire program the end points in the potentiometric titrations were derived from the inflection in the emf vs titrant volume curve. The emf values were measured by means of a Pt-saturated calomel electrode (sleeve type) in conjunction with a Beckman model H2 pH meter.

### F. OXYGEN-GENERATION APPARATUS

Oxygen was generated in a spinning-disc stripper which had been fitted with electrodes to serve as an electrolysis cell. An 0.5 M sodium sulfate solution was used as the electrolyte because it is known to give 100%  $O_2$ -generation efficiency. The solution was electrolyzed between platinum electrodes. Oxygen was generated at an anode having a surface area of approximately  $2.6 \text{ cm}^2$ . Hydrogen was generated at a wire electrode located within a compartment separating it from the bulk of the electrolyte by a fritted disc; the  $H_2$  was vented to the atmosphere. A constant DC current in the range from 0 to 1000 ma was passed between the electrodes to generate the required volume of  $O_2$ . The current was provided by means of a constant-current power supply and read from a multirange DC ammeter that was accurate to 1%. The formed  $O_2$  was then transferred to the gas phase by the spinning-disc stripper, the gas phase being the purified  $N_2$  carrier gas flowing to the second stage disc stripper at a rate of 1 liter per minute.

APPARATUS FOR ABSORPTION OF O<sub>2</sub> FROM N<sub>2</sub> PURGE GAS

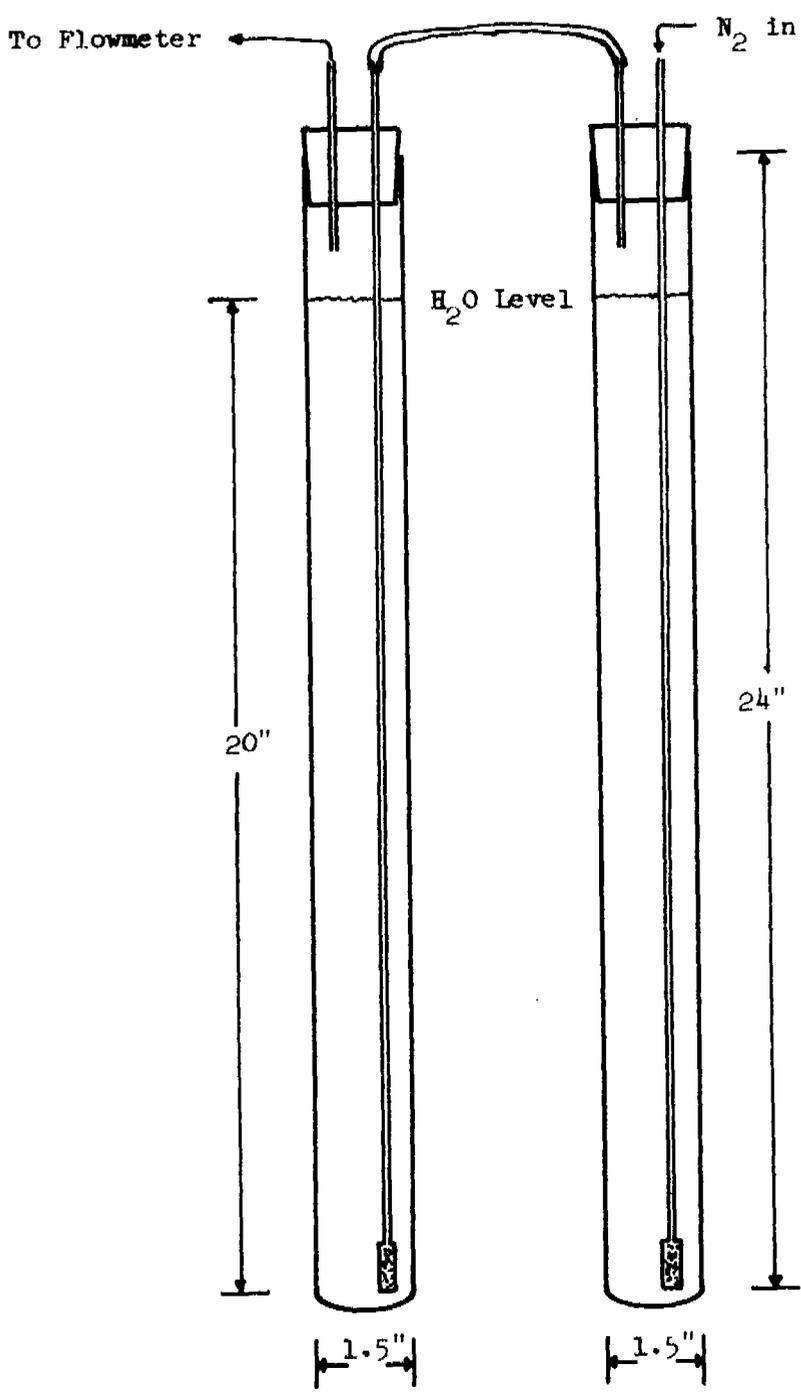


Figure I-1

## APPENDIX II

### PROCEDURE FOR AEROJET-MODIFIED WINKLER METHOD (July 1969)

#### I. SCOPE

This method covers the determination of D. O. content of distilled water or natural sea water in the range of 0 to 100 ppb.

#### II. APPARATUS

##### A. BEAKER

One 250 ml Pyrex beaker.

##### B. BURET

One 1-ml Koch-type buret with Teflon stopcock and 0.01-ml subdivisions. This buret is used to deliver the sodium thiosulfate solution during sample titration.

##### C. BURETS

Three 5-ml Koch-type burets with Teflon stopcocks and 0.01-ml subdivisions. These burets are used to deliver the Winkler reagents during fixing.

##### D. BOD BOTTLES

Several 300-ml BOD bottles having a raised lip around the neck and glass stoppers ground to a conical lower tip.

##### E. GRADUATED CYLINDER

One 100-ml graduated cylinder with 1-ml subdivisions. This is used to check sample flow rate, if necessary.

##### F. BOTTLE CONTAINER

The sample container should be as shown in Figure 5. The thermometer may be deleted if another means of temperature measurement is available.

#### G. TITRATION CONTAINER

The titration container should be as described in Section VII, C, 2 and shown photographically in Figure 6.

#### H. POTENTIOMETRIC END POINT APPARATUS

The apparatus consists of (1) a pH meter with a total range of  $\pm 1400$  mv and a limit of error of not greater than 3 mv, (2) a platinum sensing electrode, and (3) a saturated calomel reference electrode of either the glass sleeve or asbestos wick type.

#### I. STIRRING BARS

Two Pyrex-coated stirring bars approximately 1-1/8-in. long by 1/4-in. diameter.

#### J. MAGNETIC STIRRER

Two variable-speed motor-driven magnetic stirrers are required.

#### K. PIPET

One 100-ml or 200-ml pipet.

#### L. PURGE TUBES

Two purge tubes, each consisting of a 1-ft. section of 9-mm O. D. Pyrex tubing connected via rubber or Tygon tubing to a source of  $N_2$  for purging.

### III. REAGENTS

Reagent grade chemicals shall be used in all tests.

#### A. IODINE SOLUTION

Dissolve 6.346 g of resublimed iodine in a solution of 75 g of KI in 60 ml of distilled water and dilute with distilled water to 500 ml in a volumetric flask. Store in a dark, stoppered bottle.

B. SULFURIC ACID

Concentrated sulfuric acid is used for acidification.

C. MANGANOUS SULFATE SOLUTION

Dissolve 364 g of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  in water, dilute to 1 liter, and filter.

D. IODIZED ALKALINE IODIDE SOLUTION

Dissolve 700 g KOH in enough distilled water to make approximately 700 ml of solution. Cool to room temperature. Dissolve 150 g of iodate-free KI in 200 ml of distilled water. Add the KI solution and 10 ml of the iodine solution to the KOH solution. Mix. Dilute to 1 liter with distilled water, mix, and store in a stoppered flask.

E. SODIUM THIOSULFATE SOLUTION

Dissolve 24.82 g of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in 800 ml of distilled water that has just been boiled and cooled. Dissolve 1 g  $\text{Na}_2\text{CO}_3$  in the solution to stabilize it. Dilute to 1 liter with boiled distilled water.

Standardize the sodium thiosulfate solution against primary standard or known purity  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{KIO}_3$  as follows: Dissolve 2 g of iodate-free KI and 2 g of  $\text{NaHCO}_3$  in 300 ml of distilled water in a 500-ml iodine flask containing a stirring bar. Add 12 ml conc. HCl (sp. g. 1.19) slowly. Swirl the flask and stopper lightly. Place a small quantity of distilled water around the stopper to effect a seal. Weigh out 100 mg  $\text{KIO}_3$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ . Add the weighed salt to the flask. Calculate the normality of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution as follows:

$$N = \frac{1000 A}{M B}$$

where: N = normality of  $\text{Na}_2\text{S}_2\text{O}_3$  solution

A = grams of standard salt used

M = equivalent weight of standard salt

B = ml of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration.

It has been our experience that either  $\text{KIO}_3$  or  $\text{K}_2\text{Cr}_2\text{O}_7$  may be used. The same normalities are obtained for each. The preferred standard is  $\text{KIO}_3$  because of the more distinctive color change at the end point. Wash down the inside of the flask with a small amount of distilled water. Restopper. Swirl to dissolve the salt. Place a small quantity of distilled water around the stopper to effect a seal. Allow to stand for 10 min. Titrate with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution using starch solution as the indicator. If  $\text{KIO}_3$  is used as the standard the solution color will change from blue to colorless; if  $\text{K}_2\text{Cr}_2\text{O}_7$  is used the change will be from blue to green.

#### F. SODIUM THIOSULFATE, TITRANT SOLUTION

With a calibrated pipet transfer 10.00 ml of the standardized 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution to a 200-ml volumetric flask. Dilute to the mark with distilled water and mix completely. This solution should be prepared fresh daily just before use.

#### G. POTASSIUM IODATE OR POTASSIUM DICHROMATE

These should be primary standard or known-purity salts.

### IV. PROCEDURE

#### A. PREPARATION

##### 1. Winkler Reagents

These solutions should be made up several days or more before the time of use and set aside to equilibrate with  $\text{O}_2$  in the atmosphere. At the time of use the three 5-ml burets should be set up and filled with the three solutions in preparation for the fixing step. The reagents may be stored in these Koch-type burets provided that the reservoir is covered to prevent changes in concentration or contamination.

##### 2. Sodium Thiosulfate Titrant Solution

This solution should be made up daily in the morning in preparation for the day's analyses. The 1-ml Koch-type buret should be rinsed several times with the titrant and then filled in preparation for the titrations. Normally a single filling of the buret and reservoir will be adequate for a day's work.

### 3. Purging of Sampling Vessels

Prior to sampling a BOD bottle containing a Pyrex-coated magnetic stirring bar is placed in the bottle container. Turn on the  $N_2$  to give a flow of approximately 2 liters per minute through the purge tube. Remove the stopper of the BOD bottle and insert the purge tube. Allow the BOD bottle to be swept with  $N_2$  for 5 minutes. Remove the purge tube and restopper the BOD bottle. Disconnect the Pyrex glass tube and connect the rubber or Tygon tubing to the side arm of the bottle container. After 5 minutes or more the sampling vessels are ready for collecting a water sample.

### 4. Titration Container

Place a 250 ml beaker containing a Pyrex-coated stirring bar in the titration container. Position the cover. Turn on the  $N_2$  to give a flow of approximately 2 liters per minute through the purge tube. Insert purge tube into the 250-ml beaker.

### 5. pH Meter

Prepare pH meter for potentiometric measurements. Connect platinum and calomel electrodes. Fill the calomel electrode with a saturated KCl solution, if necessary.

### 6. Pipet Purging

Connect the 100-ml or 200-ml pipet to a stream of  $N_2$  flowing at approximately 1 liter per minute. Allow  $N_2$  to flow until the pipet is used. This purging dries the pipet and sweeps out the air.

## B. SAMPLING

Note: The flow of  $N_2$  through the bottle container is to continue throughout this step. Remove the stopper of the BOD bottle and position the bottle container and BOD bottle under the tube delivering the sample stream so that the tube is approximately 1/4-in. from the bottom of the BOD bottle. Allow the sample water to flow through and sweep out the BOD bottle for 25 to 30 minutes. As a general guide the volume of water passed should be at

least 5 times the volume of the BOD bottle. Samples flowing at flow rates greater than 100 ml/min may be sampled for a shorter time and at rates less than 50 ml/min for correspondingly longer periods of time. Just before the conclusion of sampling, read and record the temperature of the water sample. At the conclusion of sampling, lower the bottle container quickly away from the sample tube and restopper the BOD bottle. The stopper of the BOD bottle should be dry or should be wiped dry with a clean, dry, lint-free cloth or absorbent paper. Wipe the cover of the bottle container inside and outside (without removing from the vessel) to blot up droplets of water. Once these droplets have come into contact with air they must not be allowed to fall back into the water in the BOD bottle. Measure the flow rate of the sample by collecting water from the tube delivering the sample stream for 1 min.; collect the water in a 100-ml graduated cylinder.

### C. FIXING

Fill each of the three burets from the reservoir to just slightly above the zero mark. Wipe the tip of each buret with a clean, dry, lint-free disposable paper. NOTE: The flow of  $N_2$  through the bottle container is to continue throughout the fixing step.

#### 1. Sample (NR)

Add 2.0 ml of the iodized alkaline iodide solution to the sample. This is done in the following manner: Remove the stopper of the BOD bottle and lay it on a clean, dry paper. Insert the tip of the buret inside the bottle container but outside the BOD bottle. Allow the solution to flow out of the buret until the upper liquid level (meniscus) is at the zero mark. Then insert the buret tip to the bottom of the BOD bottle. Allow 2.0 ml of the solution to flow slowly into the BOD bottle. Stop the flow and quickly lower the bottle container and BOD bottle down and away from the tip of the buret. Do not allow liquid running down the tip of the buret to drop into the BOD bottle. Set the bottle container and BOD bottle on the magnetic stirrer. Wipe the stopper of the BOD bottle dry with a clean, dry, lint-free paper and place it lightly into the BOD bottle with a slight

turn. Wipe the tip of the just-used buret and discard the paper. Turn on the magnetic stirrer at a slow speed that is adequate to give complete mixing of the contents of the BOD bottle. Allow the contents to stir 30 seconds. Turn off the stirrer. Add 2.0 ml of the  $\text{MnSO}_4$  solution in exactly the same manner as described above for iodized alkaline iodide solution. After the 30-second stirring allow the precipitate to settle 5 minutes. Then add 2.0 ml of  $\text{H}_2\text{SO}_4$  in exactly the same manner as for the above two solutions, except that the  $\text{H}_2\text{SO}_4$  is delivered near the top of the solution instead of at the bottom. This sample is now ready for titration.

2. Blank (RR)

The blank is fixed by exactly the same procedure except that the reagents are added in the order:  $\text{H}_2\text{SO}_4$ , iodized alkaline iodide solution,  $\text{MnSO}_4$  solution. There need be no waiting after any of these additions inasmuch as the chemical reactions are all rapid. In distilled water it makes no difference whether the  $\text{H}_2\text{SO}_4$  or the iodized alkaline iodide is added first, but in sea water a precipitate is formed in basic solution. Certain metal ions might be present in sea water, especially in sea water which has been in contact with metal parts, and these metal ions might undergo some reaction with D. O. This potential problem is largely avoided by the order of addition suggested above.

3. Sample (DNR)

The fixing procedure is identical to that for Sample (NR) except that 4.0 ml of each reagent is added instead of 2.0 ml.

4. Blank (DRR)

The fixing procedure is identical to that for Blank (RR) except that 4.0 ml of each reagent is added instead of 2.0 ml.

5. Volume of Reagents

The delivered volume of  $\text{MnSO}_4$  and of iodized alkaline iodide solutions are read at least 15 minutes after the fixing step to allow adequate time for wall drainage. Read to the nearest 0.001 ml and record as  $V_M$  and  $V_I$ , respectively.

## D. TITRATION

NOTE: The flow of  $N_2$  through the bottle container is to continue until the sample is pipetted out for titration.

### 1. Sample (NR)

Remove the purge tube from the titration container. Position the platinum-calomel electrode pair through the cover and in the 250-ml beaker. Fill the buret to above the zero mark and then drain out titrant solution to bring the liquid level (meniscus) down to zero. Wipe the tip of the buret with a clean, dry, lint-free paper wiper. Position the buret so that the tip extends through the cover of the titration container and into the 250-ml beaker.

Remove the stopper from the BOD bottle and pipet 200 ml of the sample into the 250-ml beaker in the titration container. Be sure that the electrodes are positioned properly and that the buret tip touches the surface of the sample. Turn the pH meter dial to read. Start the stirrer. Read and record emf and ml (0). Add titrant in 0.10-ml increments, reading and recording ml and emf in vertical columns at each increment. When the end point is approached, as indicated by a disappearance of any trace of brown or yellow from the solution being titrated and by the lowering of the emf to 300 to 310 mv, reduce the size of increments added to 0.01 ml. Titrate in 0.01-ml increments through and approximately 0.05 ml beyond the end point, recording emf and ml at each increment. In a third column parallel to those in which ml of thiosulfate and emf were recorded, write the  $\Delta$  mef values for the 0.01-ml increments. Estimate the end point to  $\pm 0.001$  ml from a plot of ml vs emf or by interpolation of  $\Delta$  emf values.

### 2. Blank (RR)

This procedure is identical to that for Sample (NR).

### 3. Sample (DNR)

This procedure is identical to that for Sample (NR) except that the potential just before the end point break will be some 20 mv lower.

#### 4. Blank (DRR)

This procedure is identical to that for Sample (DNR).

### V. CALCULATION

#### A. UNCORRECTED VALUES

The volume of thiosulfate titrant required to reach the end point is converted to an uncorrected equivalent D. O. content, as follows:

$$D_u = 40,000 NV$$

where:  $D_u$  = equivalent D. O. content, ppb

$N$  = normality of thiosulfate titrant (nominally, 0.005)

$V$  = ml of thiosulfate solution required for titration of the sample.

$D_u$  corresponds to values for  $NR_u$ ,  $RR_u$ ,  $DNR_u$ , and  $DRR_u$ , depending on whether the volumes were for Sample (NR), Blank (RR), Sample (DNR), or Blank (DRR), respectively.

#### B. CORRECTED VALUES

Uncorrected values for  $R$  and  $R_{O_2}$  ( $R_u$  and  $R_{O_2u}$ ) are calculated from the preceding uncorrected values ( $NR_u$ ,  $RR_u$ ,  $DNR_u$ , and  $DRR_u$ ) as follows:

$$R_u = DRR_u - RR_u$$

$$R_{O_2u} = DNR_u - NR_u - R_u$$

Corrected values for NR, RR, DNR, and DRR are then calculated from uncorrected values ( $NR_u$ ,  $RR_u$ ,  $DNR_u$ , and  $DRR_u$ , respectively) as follows:

$$NR = 1.0506 [NR_u + R_{O_2u} (2.000 - V_M) + R_u (2.000 - V_I)]$$

$$RR = 1.0506 [RR_u + R_u (2.000 - V_I)]$$

$$DNR = 1.040 [DNR_u + R_{O_2u} (4.000 - V_M) + R_u (4.000 - V_I)]$$

$$DRR = 1.040 [DRR_u + R_u (4.000 - V_I)]$$

where:  $V_M$  is in each case the ml of  $MnSO_4$  solution delivered for that specific sample

$V_I$  is in each case the ml of iodized alkaline iodide solution delivered for that specific sample.

These corrected values are then used to calculate R, H,  $R_{O_2}$ , and  $H_{O_2}$ , as follows:

$$R = DRR - RR$$

$$H = 2RR - DRR$$

$$R_{O_2} = DNR - NR - R$$

$$H_{O_2} = 2NR - DNR - H$$

where: R = net redox of the Winkler reagents, ppb (calculated as D.O. equivalent)

H = net redox of the water sample, ppb (calculated as D.O. equivalent)

$R_{O_2}$  = D.O. content of the Winkler reagents, ppb

$H_{O_2}$  = D.O. content of the water sample, ppb.

## VI. PRECISION AND ACCURACY

This method is capable of giving values for R, H,  $R_{O_2}$ , and  $H_{O_2}$  which are precise and accurate to  $\pm 2$  ppb or better.