MARINE TECHNICIAN'S

HANDBOOK

Oxygen Analysis

Available from:
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When completed the Marine Technician's Handbook will include sections on most of the techniques used in scientific exploration of the sea.

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"Phosphate Analysis" - IMR TR20 (Sea Grant Ref. No. 11)

GENERAL INTRODUCTION

This publication is one of a series intended to provide explicit instructions for the collection of oceanographic data and samples at sea. Individual chapters are being issued separately so that they may be made available as they are prepared and may be replaced by updated versions without replacing the entire series. It can, therefore, be considered as an open-ended "marine technician's handbook".

For many years there have been such manuals in existence within various groups at the Scripps Institution of Oceanography for internal use. These manuals are being updated, and new ones are being prepared where no satisfactory ones existed; they will be issued as they are ready.

The instructions on physical, biological, and chemical oceanographic data collection and processing have been prepared by members of the Data Collection and Processing Group (DCPG), part of the Marine Life Research Group of Scripps. They cover procedures used by that group. Other chapters on geological and geophysical techniques are based on the "Marine Technician's Handbook" series originally prepared by Mr. Frederick S. Dixon, and issued by the Oceanic Research Division some years ago. It is expected that chapters on techniques used by other groups within Scripps will be added.

Since the sections will be published individually, there will undoubtedly be some repetition. This should not detract from the overall purpose of the manual, since it is expected that a single section will be the only one needed for a particular operation. We do not wish to suggest that the methods described are the only methods; we have merely attempted to describe the methods and procedures which we use and which we have found to be reliable and up-to-date. As new information becomes available, attempts are made to test techniques, incorporate them into routine procedures, and then revise the chapter concerned.

In the final analysis the reliability and quality of the data obtained is in your hands. It is imperative that meticulous attention be given to details to insure reliability and usefulness in the results you obtain.

While we have attempted to be thorough in descriptions of techniques, this cannot be considered to be a complete "cookbook" for the novice. It is in most cases assumed that the reader has some prior knowledge and training in the field concerned. We hope, however, that these instructions can serve as a training aid for the novice marine technician, a "cookbook" for the scientist who is taking his own observations, and a reference manual for the experienced technician.

Preparation of these chapters over the years has been supported by the University of California and by grants and contracts from many federal agencies to the Scripps Institution of Oceanography and to the Institute of Marine Resources. Support for preparation of this more complete and revised manual has come from the National Sea Grant Program.

G. G. Shor, Jr.
Sea Grant Program Manager

OXYGEN ANALYSIS

I. Introduction

A. Technique reference

One of the oceanographic parameters routinely determined by the Data Collection and Processing Group is dissoved Oxygen. The technique used is the modified Winkler technique of Carpenter (Limnol. Oceanog., 10: 141, 1965).

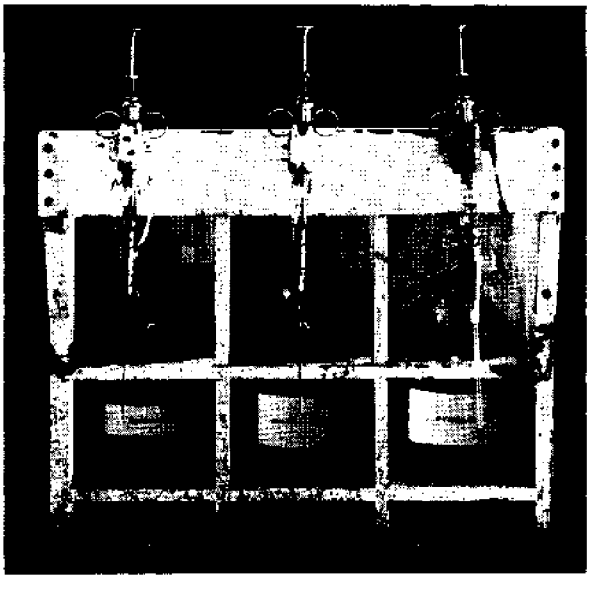
B. Description of Equipment

1. Oxygen flasks

The flasks used are modified iodine flasks of about 100 ml capacity with #22 hollow ⚧ stoppers with elongated penny-heads and extended necks. Most of our samples are drawn from Nansen bottles, approximately 18 samples per hydrocast. For this reason our calibrated oxygen flasks are boxed in groups of 20.

2. Pickling rack

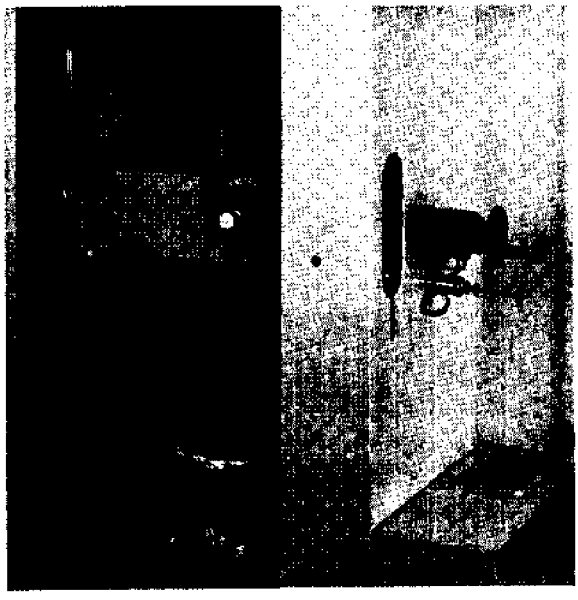
Because of the number of samples done on a cruise, two liter quantities of the pickling reagents are prepared and kept in a pickling rack with reagent dispensers.



Becton-Dickinson 2 ml pipetting syringes with metal double valves are used. A Clay-Adams plastic double valve is used for the acid syringe. The sodium hydroxide syringe has a tendency to freeze; so when use is not anticipated for 2 to 3 days, fill the syringe with distilled water.

3. Titrating Apparatus

The titrating apparatus (see right) contains a modified 1 ml Manostat Digipet 3 way stopcock (Kimble #41044F), a B-D 2 ml syringe for addition of the starch indicator, an electric stirring motor with a swivel mounting and a 10 ml automatic filling pipet. Reservoirs of iodate standard (1 liter) and thiosulfate solution (1 liter) are connected to the automatic filling pipet and the microburette stopcock respectively. The 500 ml starch indicator reservoir (not shown in photograph) is connected to the B-D 2 ml syringe. Connections are made with tygon tubing. This is all mounted in a white box 23" x 23" x 11" deep, illuminated by two fluorescent lamps (Sylvania F6T5/CW) mounted on the rear side of the two small front panels.



II. Method Outline

A divalent manganese solution, followed by strong alkali, is added to the sample. The precipitated manganous hydroxide is dispersed evenly throughout the seawater sample which completely fills a stoppered oxygen flask. Any dissolved oxygen rapidly oxidizes an equivalent amount of divalent manganese to basic hydroxides of higher valency states. When the solution is acidified in the presence of iodide, the oxidized manganese again reverts to the divalent state, and iodine, equivalent to the original dissolved oxygen content of the water, is liberated. This iodine is titrated with standardized sodium thiosulfate. (Strickland and Parsons, A Practical Handbook of Seawater Analysis, Bull. Fish. Res. Bd. Canada, No. 167: 21, 1968).

The method is approximated by the following chemical reactions:

$Mn^{++} + 2OH^- \rightleftarrows$ (or =) $Mn(OH)_2$	(Forms white precipitate)
$2Mn(OH)_2 + O_2 = 2MnO(OH)_2$	(Forms brown precipitate)
$MnO(OH)_2 + 4H^+ + 3I^- = Mn^{++} + I_3^- + 3H_2O$	(Dissolves precipitate to give a clear brown iodine solution)
$I_3^- = I_2 + I^-$	
$I_3^- + 2S_2O_3^{--} = 3I^- + S_4O_6^{--}$	(Consumes the free iodine)
$KH(IO_3)_2 = I^-$	(Transfer of 12 electrons)
$KIO_3 = I^-$	(Transfer of 6 electrons)

(Martin, Marine Chemistry, vol. I: 88, 1968)

III. Reagents and preparation

All the reagents should be prepared by the chemist before the cruise.

1. Manganous chloride solution (3M)

Dissolve 600 g manganous chloride tetrahydrate, $MnCl_2.4H_2O$, or 507 g manganous sulfate monohydrate, $MnSO_4.H_2O$, in distilled water and bring the final volume up to 1 liter. Stir until completely dissolved.

2. Sodium hydroxide (8N) - sodium iodide (4M) solution

Dissolve 320 g sodium hydroxide, NaOH, in 500 ml of distilled water. Cool the solution. Add, while stirring, 600 g of sodium iodide, NaI, and 2 g sodium azide, NaN_3. Bring the final volume up to 1 liter.

3. Sulfuric acid solution (10N)

Slowly add 280 ml of concentrated sulfuric acid, H_2SO_4, (sp. gr. of 1.84) to 770 ml of distilled water. After cooling the final volume should be 1 liter.

4. Starch - glycerin indicator solution (2.3%)

Dissolve 30 g soluble starch (potato powder) in 1 liter of glycerin (glycerol). This is best accomplished by making a paste of the starch and approximately 100 ml of glycerin. If this is not done, large clumps will form which are very difficult to dissolve. Pour the paste into the rest of the glycerin while stirring. Heat the solution until it just starts to boil. Cool.

5. Glycerol (glycerin) $HOCH_2CHOHCH_2OH$.

6. Sodium thiosulfate (0.14N) micropipet-buret solution

Dissolve 35 g sodium thiosulfate pentahydrate, $Na_2S_2O_3.5H_2O$, in distilled water which has been boiled for about 10 minutes to expel CO_2 (allow to cool before adding the sodium thiosulfate). Bring to a final volume of 1 liter in a volumetric flask. Add a few drops of chloroform (preservative) and 0.1 g sodium carbonate, Na_2CO_3; the solution is stable for several months.

7. Standard iodate solution (0.010N)

With an oven temperature of 170°C dry some potassium iodate, KIO_3, for approximately one hour. Weigh out 0.3567 g and dissolve in distilled water in a 1 liter volumetric flask. If well stoppered, the solution is quite stable.

As an alternative potassium biiodate, $KH(IO_3)_2$ can be used. Since this decomposes at temperatures above 100°C, it should be vacuum desiccated for about 1 week prior to use. Dissolve 0.3250 g in 1 liter of distilled water to give a 0.010 Normal solution.

IV. Sample Collection

Oxygen samples are always the first to be drawn from the Nansen bottle and should be drawn as soon as possible.

Draw the samples while the cast is coming up. A six inch piece of 1/4" I.D. tygon tubing is slipped over the discharge valve of the Nansen bottle. If the sample flasks have been pre-rinsed and dried, fill from the Nansen bottle without rinsing. First run a small volume of sample water through the delivery tube to remove all the air. Then with the tip of the tube near the bottom of the flask, fill slowly without agitating the sample. Overflow one full flask volume. When inserting the stopper avoid trapping air bubbles.

If the flasks have not been pre-rinsed and dried, rinse once with a small amount of Nansen bottle water by gently swirling the sample around the walls of the flask and discarding. Running this first volume of water through the tygon tubing will also serve to remove bubbles from the tubing. Fill the flask and stopper as outlined above.

Bubbles are very likely to form on the sides of a new piece of tygon tubing. This problem can be avoided by soaking the tubing in sea water for 2 or 3 days prior to use.

V. Pickling procedure

Before adding any reagents to the samples be sure the reagent dispensers are delivering exactly 1.0 ml. Then discard three squirts of each reagent into a waste container. Add 1 ml $MnCl_2$ (manganous chloride) solution and then 1 ml NaOH-NaI (sodium hydroxide-sodium iodide) solution to each sample as soon as possible after the samples have been drawn. In adding the reagents keep the cannula tip approximately one inch above the bottom of the flask, carefully holding the plunger down until the sample flask has been removed (otherwise some of the sample may be sucked into the cannula tip and will contaminate the following sample).

When replacing the stopper it is essential to avoid trapping air bubbles. This is best accomplished by tilting the flask slightly and inserting the stopper with a twisting motion.

Run your thumb and forefinger around the neck of the flask to remove any mist which might have formed and check for the presence of air bubbles. Misting is often a problem with deep water samples. If bubbles are present, carefully remove the stopper, reseating it again so as to eliminate the bubbles. When you are sure there are no bubbles trapped inside the flask, pour off the 2 ml of displaced sample and shake to disperse the precipitate uniformly through the flask.

Allow the precipitate to settle about half way. This may take 10 to 20 minutes. Shake again, thoroughly dispersing the precipitate throughout the flask.

At this point the pickled oxygen samples can be left in the box and if covered with a towel or cloth, can be left for as long as a week before titrating. However, the titrations are generally done within a few hours.

VI. Titration procedures

A. Pre-titrating checks

1. Carefully remove the iodate and the thiosulfate bottles from the rack and shake. This will insure that the two solutions are homogeneous. After shaking, replace these bottles in the rack. It is neither necessary nor advisable to remove the stoppers in the bottles.

2. The thiosulfate petcock can be put into three positions. One will allow the thiosulfate to run directly from the reagent bottle out the top of the micropipet-buret. With the petcock in this position, run out approximately 3 ml of thiosulfate. This will remove any 'old' thiosulfate from the tubing connecting the reagent bottle to the micropipet-buret.

3. After flushing the thiosulfate tubing, change the position of the petcock so that the thiosulfate in the micropipet-buret barrel can be discharged out the tip. With the petcock in the third position fill the barrel from the reservoir and again discard. Repeat this a total of four times. After filling the barrel for the fifth time, run a little distilled water over the micropipet-buret tip to wash off any thiosulfate which might have collected there.

4. Using the zero reset on the micropipet-buret, set the zero at a point which allows you to run the plunger back to a reading of approximately 0.9500. This is the only time the zero reset should be used. Whenever filling the micropipet-buret always run the plunger back to this point, 0.9500, and then run it forward to the zero point, 0.0000. This eliminates one of the back lash problems and is also a check on whether the counter is working properly. It is best to make this adjustment at the very beginning of the cruise before the first set of standards and blanks are run.

5. Drain any of the iodate in the 10 ml automatic filling pipet. Refill from the iodate reagent bottle and again discard. Repeat this a second time. Note: when the pipet drains there will be a small amount of liquid in the tip and an air space between it and the petcock. THIS IS CORRECT. The pipet is calibrated to have this airspace. Before the third filling, touch the tip of the pipet briefly to the side of a beaker to remove the last drop that may be clinging there.

A pressure bulb is used with the iodate reservoir to force the iodate out when the level of the liquid gets low.

6. Discard three shots from the starch dispenser which should be set at 0.3 ml. If it is not, set it at this point.

7. Discard three squirts from the H_2SO_4 reagent syringe and if more than one hour has passed since the pickling of the samples, discard two squirts from the $MnCl_2$ and the NaOH-NaI dispensers. IT IS ONLY AT THIS POINT THAT YOU ARE READY TO START YOUR STANDARDS, BLANKS IF NECESSARY, AND SAMPLES. ALWAYS DO STANDARDS BEFORE RUNNING ANY SET OF SAMPLES.

B. Standardization

RUN STANDARDS BEFORE EVERY SET OF SAMPLES. RUN STANDARDS UNTIL TWO AGREE WITHIN $\pm$ 0.0020.

1. Clean two oxygen flasks by scrubbing with soapy water. Rinse them with tap water and then distilled water. If possible set these two flasks aside to be used for standards and blanks only.

2. Pipet 10 ml iodate into each flask and add a magnetic stirring bar.

3. Fill the flasks to the bottom of the neck with distilled water. Sea water can also be used but if it is, add the 3 reagents to the 10 ml iodate before adding the sea water.

4. Add 1 ml H_2SO_4 solution and stir by swirling. DO NOT put the cannula tip into the solution.

5. Add 1 ml NaOH-NaI solution and stir by swirling. DO NOT put the cannula tip into the solution. Note: This is a departure from the technique used in pickling samples.

6. Add 1 ml $MnCl_2$ solution. DO NOT put the cannula tip into the solution.

7. Raise the oxygen flask so that the micropipet-buret tip is approximately 1 1/2 inches below the surface of the liquid. Swivel the stirring motor under the flask. Now lower the flask onto the stirring motor. In this rest position the tip should be one inch below the surface of the liquid. The vertical positioning of the stirring motor is usually set when doing the first set of standards.

8. Begin stirring. Titrate immediately because iodine is lost quickly through volatization. Add the thiosulfate rapidly at first, to consume the bulk of the free iodine. Titrate to a

light straw yellow color. Then add 0.3 ml starch solution. This should give the sample a blue or violet color. Continue titrating to a clear end-point.

Avoid a large vortex when stirring to minimize iodine loss. However, after adding the starch, more rapid stirring is suggested.

9. Record the results on the data sheet in the standardization block on the oxygen form (Form 9).

10. Refill the micropipet-buret past zero and then crank forward to the zero point.

11. Repeat the above procedure with the second standard. If the results do not agree within $\pm$ 0.0020, run as many additional standards as necessary to get this agreement. It is very important that the flasks be thoroughly cleaned after each standard determination to remove all manganous ions (Mn^{++}). Failure to do so will lead to bad subsequent standards.

After completing the standards, leave the 10 ml automatic filling pipet full of iodate, and if it was necessary to loosen the top of the iodate bottle to get flow, re-tighten the top at this point.

C. Sample titrations

1. Remove the stopper and add a magnetic stirring bar to the first sample.

2. Add 1 ml H_2SO_4 solution. DO NOT put the cannula tip into the solution.

3. Put the flask on the stirring motor as was done with the standards and begin stirring.

4. After most of the precipitate has dissolved, titrate to a starch end-point. Starch that gives a reddish end-point should be replaced with freshly prepared starch-glycerin solution.

If the sample is low in oxygen, the precipitate will be white and the addition of the acid will show little color. With these samples it is best to add the starch immediately.

5. Record the oxygen flask number and buret reading on the oxygen form. Since each flask and stopper combination are unique, the flask number is just as important as the buret reading.

Should a flask be used with a stopper other than its own, make a note to that effect on the data sheet. This combination of flask and stopper must be put aside for calibration either ashore or on the ship before the dissolved oxygen can be calculated (See Section X, B-2).

If a sample flask gets broken, record this on the data sheet and note which flask will be used in its place. Save the stopper, or save the flask should a stopper get broken.

Do not use oxygen flasks if they are cracked or if the stoppers are severely chipped.

6. Refill the micropipet-buret past the zero point, zero, add a magnetic stirring bar and acid to the next sample and titrate as above.

D. Salvaging overtitrated samples

In the event that a sample is accidentally overtitrated (titrated beyond its end-point), the sample can often be salvaged by back titration. Add 1 ml of the iodate standard to the sample flask and titrate to a new end-point. Make a note in the remarks section on the oxygen form. Be sure to record the first titration value (the over titrated value) and the value after the addition of the 1 ml of iodate. Both numbers are important for correcting the mistake.

Some people prefer to add 10 ml from the automatic filling pipet. This is quite acceptable if there is enough room in the flask for the extra 10 ml.

E. Reagent blanks

Run reagent blanks at the beginning of the cruise, and about once a week from then until the end. Also, it will be necessary to run blanks whenever a reagent is changed. Note: when reagents are changed be sure to indicate this on the data sheet.

Run at least four blanks whenever they are run. It may be necessary to run more than four unless you get reasonable agreement on at least three of the four that you do.

1. Clean two flasks with soap and rinse thoroughly first with tap water and then with distilled water. You may use the same flasks which you have set aside for the standards.

2. Since you have just run standards, the standard line and pipet are thoroughly purged of 'old' iodate. Run approximately 5 ml from the pipet into a small screw top bottle. Rinse and discard. Repeat with a second portion of iodate. Then run approximately 20 ml of iodate into the bottle. This you will use for your blanks and for overtitrated samples.

3. Using a 1 ml pipet, put 1 ml of the iodate solution into each of the two flasks.

4. Add 10 ml distilled water to each flask.

5. Add a magnetic stirring bar to one flask.

6. Add 1 ml of H_2SO_4 solution and stir.

7. Add 1 ml of the NaOH-NaI solution and stir.

8. Add 1 ml of the $MnCl_2$ solution and stir very well.

9. Fill to the bottom of the neck with sea water obtained from intermediate depth Nansen bottles, 300 to 1000 meters.

10. Add the starch and titrate to the end-point.

11. Record the reading and then add approximately 90% of the thiosulfate required for the first titration. Stir on the magnetic stirring unit.

12. Add a second 1 ml of iodate using the 1 ml pipet.

13. Titrate to a second end-point. No other reagents or additional starch need be added. Record this reading. If you fail to get any blue color with the addition of the second 1 ml of iodate, add less thiosulfate, as noted in 11 above.

14. The reagent blank is the first titration value minus the second titration value, or as shown on the sample Form 9, 2 x 2nd counter reading minus the (3rd + 1st). Note the first counter reading is 0.0000.

It is very important that the flasks be thoroughly cleaned after each blank determination to remove all manganous ions (Mn^{++}). Failure to do so will lead to bad subsequent blanks.

VII. Calculations

Dissolved oxygen in units of milliliters per liter is calculated as follows:

$$\text{Dissolved oxygen} = \frac{(R-b)}{(S-b)} \times \frac{559.8}{(V_f-2)} - 0.014$$

Where:

- R = sample titration buret reading
- S = mean of the standard titrations for those values within $\pm$ 0.0020
- b = mean reagent blank
- V_f = volume of the oxygen flask (ml)
- 2 = volume of sample displaced by the reagent additions (ml)
- 559.8 = constant for this procedure relating the volume of iodate standard, its normality, and its oxygen equivalence in ml/l
- 0.014 = amount of oxygen added to the samples with the $MnCl_2$ and NaOH-NaI when 1 ml of each reagent is added to a 115 ml sample

Since 559.8 is a constant and (V_f-2) is a constant for any particular flask, the oxygen "bottle factors" are tabulated in the form: $\frac{559.8}{V_f-2}$

Our equation can then be written:

$$\text{Dissolved oxygen} = (R-b) \times (\text{oxygen "bottle factor"}) \times \frac{1}{(S-b)} - 0.014$$

Where: $(R-b)$ is called "ml $Na_2S_2O_3$ MINUS BLANK" on the oxygen form

and $\frac{1}{(S-b)}$ is called the "STANDARD FACTOR" on the oxygen form

List the results to the nearest 0.01 ml/l.

OXYGEN TITRATION

UNIVERSITY OF CALIFORNIA
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	OXYGEN FLASK NUMBER	MICRO BURET READING 2nd	MICRO BURET READING 1st	ml. $Na_2S_2O_3$ (2nd − 1st)	ml. $Na_2S_2O_3$ MINUS BLANK	BOTTLE FACTOR	TIMES "STANDARD" FACTOR	−0.014	O_2 CONC. ml/l.	REMARKS
1	A-5	0.7837	0.0000	0.7837	0.7898	4.969	1.4106	−.014	5.56	
2	A-3	.7661	.	0.7661	.7722	5.203	.	.	5.70	
3	A-4	.8172	.	. etc.	.8233	5.011	.	.	5.85	
4	A-6	.9264	.	.	.9325	5.001	.	.	6.61	
5	A-7	*CORRECTED VALUE .8587	.	.	.8648	4.986	.	.	6.11	*OVERTITRATE
6	A-8	.8594	.	.	.8655	5.108	.	.	6.27	
7	A-9	.8486	.	.	.8547	4.985	.	.	6.04	
8	A-10	.8051	.	.	.8112	4.910	.	.	5.65	
9	A-11	.7649	.	.	.7710	5.081	.	.	5.56	
10	A-12	.7214	.	.	.7275	5.205	.	.	5.37	
11	A-13	.7416	.	.	.7477	4.987	.	.	5.29	
12	A-14	.6634	.	.	.6695	5.080	.	.	4.83	
13	A-15	.5353	.	.	.5414	4.953	.	.	3.81	
14	A-16	.3698	.	.	.3759	5.037	.	.	2.70	
15	A-17	.2517	.	.	.2578	5.038	.	.	1.86	
	A-18	.1305	0.0000	0.1305	.1366	5.153	.	.	1.02	
17	A-19	.1737	.1305	0.0432	.0493	5.080	.	.	0.38	
18	A-20	.2014	.1737	0.0277	.0338	5.039	1.4106	−.014	0.27	
19		.	.	.	.	.	.	.	.	
20		.	.	.	.	.	.	.	.	
21		.	.	.	.	.	.	.	.	
22		.	.	.	.	.	.	.	.	

STANDARDIZATION $Na_2S_2O_3$ 10mls $KH(IO_3)_2$, $[KIO_3]$

BURET READING 2nd	BURET READING 1st	RESULT
.6984	.0000	.
.7032	.	.
.7025	.	.
.7028	.0000	.
.	AVERAGE	.7028 = S

REMARKS *SAMPLE *5 OVERTITRATED
OVERTITRATED VALUE WAS 0.8600
ADDED 1 ML IODATE. NEW END PT. 0.9290
0.9290 − .0703 = .8587.

BLANK DETERMINATION

BURET READING 3rd	BURET READING 2nd	BURET READING 1st	BLANK 2 X 2nd MINUS (3rd + 1st)
.1462	.0704	.0000	−.0054
.1474	.0703	.0000	−.0068
.1469	.0704	.0000	−.0061

AVERAGE −.0061 = b

STANDARD FACTOR

$$\frac{1}{\text{STANDARD MINUS BLANK}} = \frac{1}{S-b} = \frac{1}{.7028-(-.0061)} = 1.4106$$

CRUISE: SAMPLE
STATION: TEST

30 DAY MAY MONTH 197 YEAR

START OF TITRATIONS: 0900 TIME
TITRATIONS COMPLETED: 0935 TIME

ANALYST: JOHN DOE

$Na_2S_2O_3$ CHANGED
☐ YES ☑ NO

VIII. Preparation and maintenance of 'Oxygen Standard Tabulation' graph

It is convenient and instructive to keep a running plot of the oxygen standard and blank values. Plot the standard values against the date and the 'start of titrations' time. Each day is divided into 6 four-hour time periods: 0000-0400, 0400-0800, 0800-1200, 1200-1600, 1600-2000, 2000-2400. The time should be plotted as accurately as this scale will permit. Use different symbols for each operator, e.g., operator one , operator two , operator three , etc., or use different color pencils.

Indicate on the graph:

1. all standard values, with indication of which have been rejected.

2. the average of any block of standards.

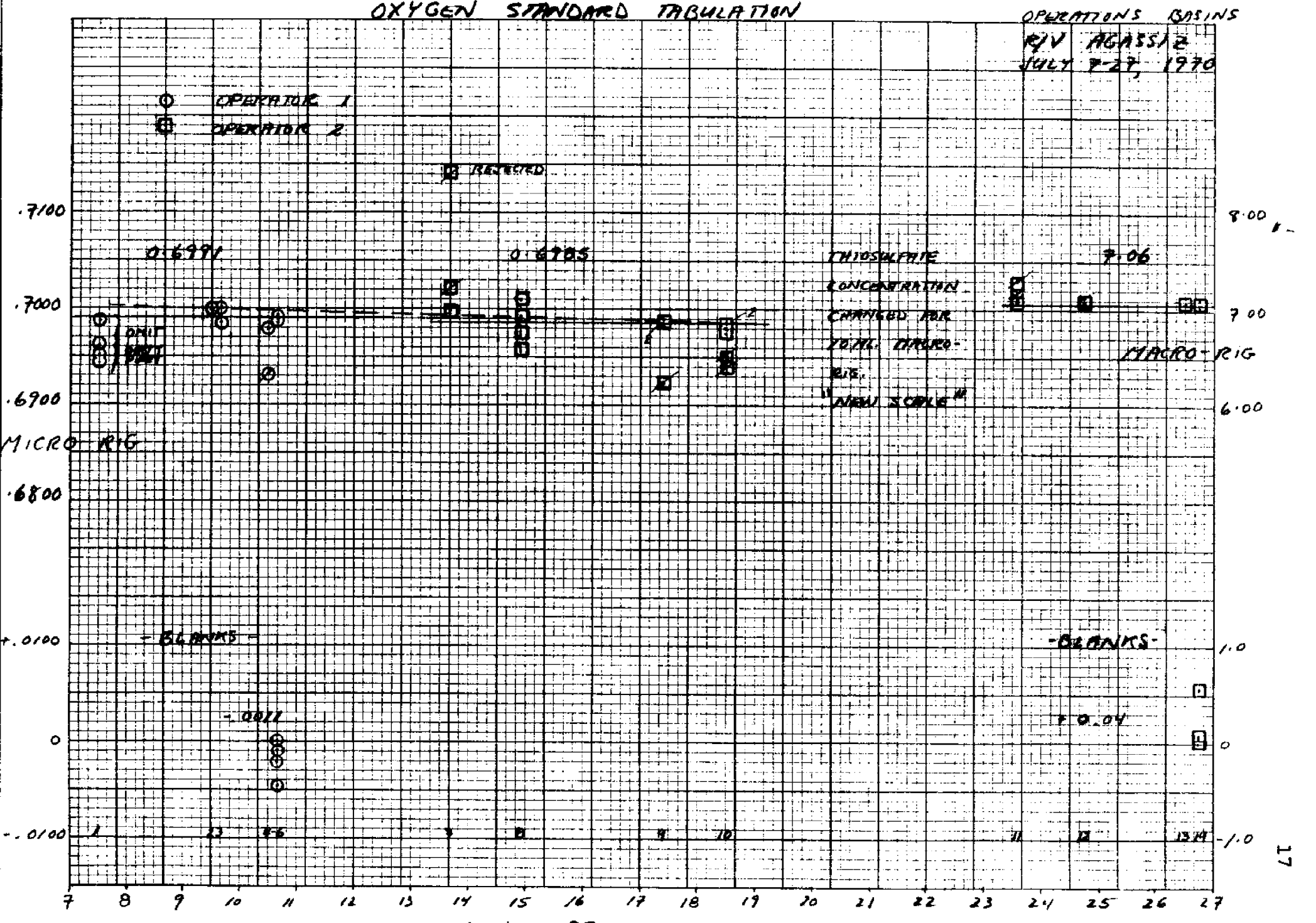
3. all reagent changes, e.g., new iodate (biiodate) standard, new thiosulfate, etc.

4. station numbers.

The value of the graph is in identifying operators that may be doing something wrong or who consistantly 'see' a different end-point. Where only short periods of time are concerned, an average standard value can usually be used for all the stations in a group of stations. Over long periods of time, trends can be spotted. Thiosulfate decomposition, iodate (biiodate) decomposition, and/or concentration of a reagent due to evaporation can readily be spotted.

As can be seen on the sample tabulation graph, operators 1 and 2 had average values very close to each other and an average value for both can be used with little loss in accuracy. The standard minus blank value would be 1/2 (0.6991 + 0.6985) - (0.0011) which equals 0.6999. It would also have been acceptable to have drawn a sloped line (dashed line) from the values of the 9th to the values of the 18th suggesting a change in the thiosulfate concentration with time. However, since the deviations from the two average values are small, using this sloping line is of little advantage.

July 23, operator 2 switched to the 10 ml buret oxygen rig (macro-rig) necessitating a ten fold dilution in the thiosulfate concentration. Here operator 2 obtained a standard minus blank value of 7.02 which when divided by 10 gives 0.702. This is in good agreement with his micro-rig value of 0.6985.



IX. Oxygen flask calibration procedure

1. Cleaning

Wash each flask and stopper thoroughly in hot soapy water. Rinse with tap water, followed by distilled water. Be sure to rinse the outside as well as the inside of the flask. Once the flask has been cleaned do not touch it with your fingers.

2. Weighing

a. Pre-weighing procedure

1) Remove the cover from the Sartorius balance

2) Unscrew the two 10 gram weights (see Sartorius instruction booklet).

3) Set the zero with a 20 gram weight on the pan.

b. Dry weighing

Using the forceps, put the oxygen flask with its stopper on the pan and weigh. Record the weight to four decimals.

c. Wet weighing

1) Slowly fill the flask with distilled water which has been sitting for at least two hours.

2) Replace the stopper.

3) Check for trapped air bubbles in the flask.

4) Pour off the distilled water which has been displaced, and carefully but rapidly wipe off all excess water from around the stopper.

5) Put the flask with its stopper on the balance pan and weigh. Record the weight to four decimals.

d. Temperature

After weighing, remove the flask from the pan. Pull out the stopper and insert a thermometer. (After two minutes) read the temperature to one decimal.

3. Calculations

a. Flask volume

1) Subtract the two weights (c minus b from part 2) giving the weight of the water.

2) Using the temperature, determine the correction factor interpolating to the nearest tenth of a degree. [See Appendix 1]

3) Multiplication of the weight of the water by the correction factor gives the bottle volume in ml.

b. "Bottle factor"

1) Derivation

The expression for calculating the dissolved oxygen (D.O.) value is:

$$D.O.(ml/l) = \frac{(R-b)}{(S-b)} \times \frac{559.8}{V_f-2} - 0.014$$

where V_f is the flask volume calculated above.

Since $559.8/(V_f-2)$ is constant for any flask, we calculate our "bottle factor" as this.

2) Correct the flask volume by subtracting 2 and divide this into 559.8. Report the result to 4 significant figures.

c. Example

1) Raw data

Flask number	A-16
Weight with distilled water	187.9378 g
Dry weight	75.5106 g
Temperature	19.1°C

2) Calculations

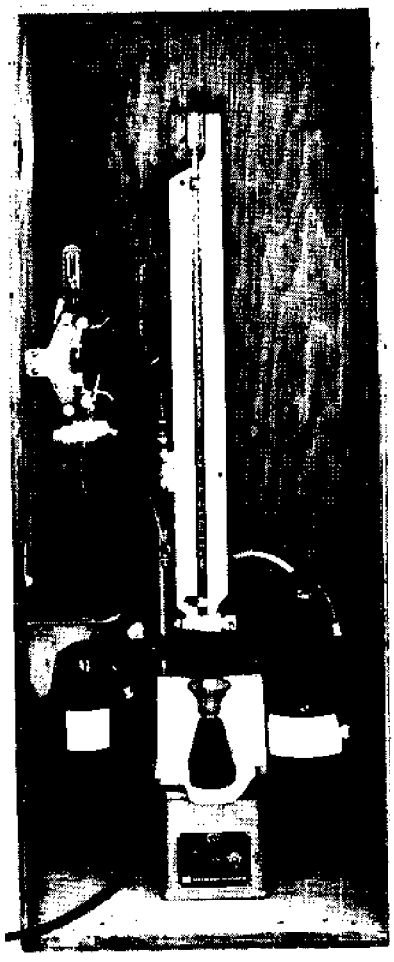
Weight of water	112.4272 g
Temperature correction from the table [Appendix 1]	1.0026257 cm^3/g
Volume	112.7224 cm^3 = ml
(V_f-2)	110.7224 ml
"Bottle factor"	$\frac{559.8}{110.7224}$ = 5.057

X. Miscellaneous notes

A. Use of the 10 ml buret oxygen rig (macro-rig)

There have been occasions when the micropipet-buret has been broken. For this reason one of our 10 ml buret titrating rigs is usually sent on longer cruises or expeditions as back-up equipment. There are two major differences between this unit and the micropipet-buret unit:

First, the titrating buret is a conventional 10 ml buret with automatic zeroing; and second, the thiosulfate concentration is 0.014 Normal (3.5 gms per liter). To prepare this concentration dilute 200 ml of the micropipet-buret solution (measured in a 250 ml ~~gra~~ graduated cylinder or preferably a 200 ml volumetric) to 2 liters (a 2 liter volumetric if possible) with distilled water. If working with the 35 g quantity of the pre-packaged $Na_2S_2O_3.5H_2O$, prepare the micropipet-buret solution and then dilute as above. Standardization values of about 7 ml are common for this concentration.



It should be noted that when using this oxygen rig, care must be taken to adequately flush the 10 ml buret and tubing before starting any titrations. This is best accomplished by draining the buret, filling and draining it twice more. The third filling should find the system thoroughly flushed.

B. Oxygen flask calibration at sea

1. Checking existing "bottle factors"

As part of the shakedown station a check should be made on the oxygen flask calibrations. This is done rather easily and does not require more than two hours. Fill a clean plastic 3 gallon pail with surface sea water. It is much better to fill it by dipping the pail over the side of the ship than from a shipboard seawater faucet. Using a 2 or 3 foot length of 3/16 inch tygon tubing, syphon water from the pail into the oxygen flasks. Make an effort to keep the tygon tubing close to the bottom of the pail. Use the first 30 to 40 ml to rinse the flasks. Fill, overflowing at least two full flask volumes. Treat these samples as you would any others (see sample pickling procedure). Using the average standard and blank values determined just before these samples, calculate the concentration. If any value deviates from the average of all the values by more than 0.02 ml/l, the "bottle factor" is suspect. If there are many such values, operator errors are suspect. In the event of the latter, the procedure should be repeated if only to give the operator some well needed review and practice.

2. Approximate shipboard calibration

In the event a flask is found with an incorrect calibration or should a flask be used with the wrong stopper and it is inconvenient to put this flask aside for future laboratory calibration, the following procedure can be used to get a usable "bottle factor".

Fill the suspect flask and four others with surface sea water as in the calibration check above. After a thorough flushing of the titrating system, titrate the samples and calculate the oxygen concentrations using recent values for the standard and blank. Do this at least three times. Compute the new "bottle factor" as shown in the example.

a. Derivation

D.O. = (R-b) x "bottle factor" x "standard factor" - .014

and "bottle factor" = $\frac{\text{D.O.} + 0.014}{(\text{R-b}) \times \text{"standard factor"}}$

b. Calculation

First run: "bottle factor" =

$$\frac{(4.8217 + 0.014)}{(0.6709 - 0.0020) \times 1.4365} = 5.0325$$

Second run:

$$\frac{(4.8125 + 0.014)}{(0.6702 - 0.0020) \times 1.4365} = 5.0283$$

Third run:

$$\frac{(4.8354 + 0.014)}{(0.6727 - 0.0020) \times 1.4365} = 5.0333$$

$$15.0941$$

$15.0941 \div 3 = 5.031$

The factor as determined in the lab was 5.027. The agreement is quite good demonstrating that the experimentally determined factor could be used with considerable confidence.

OXYGEN TITRATION

UNIVERSITY OF CALIFORNIA
SCRIPPS INSTITUTION OF OCEANOGRAPHY

	OXYGEN BOTTLE NUMBER	BURET READING 2nd	BURET READING 1st	ml. $Na_2S_2O_3$ (2nd − 1st)	ml. $Na_2S_2O_3$ MINUS BLANK	BOTTLE FACTOR	TIMES "STANDARD" FACTOR	−0.014	O_2 CONC. ml/L	REMARKS
1		FIRST	RUN							
2	F-9	.6623				5.096			4.8199	
3	F-10	.6709				5.033			4.8224	4.8217
4	F-11	.6516				5.184			4.8237	
5	F-16	.6722				5.022			4.8211	
6	F-14	.6709				4.938			4.7312	SUSPECT
7										
8										
9		SECOND	RUN							
10	F-9	.6613							4.8126	
11	F-10	.6694							4.8115	4.8125
12	F-11	.6502							4.8133	
13	F-16	.6722							~~4.8211~~	
14	F-14	.6702							4.7261	SUSPECT
15										
17		THIRD	RUN							
18	F-9	.6644							4.8353	
19	F-10	.6729							4.8367	4.8354
20	F11	.6530							4.8342	
21	F16	.6747							~~4.8392~~	
22	F-14	.6727							4.7439	JUSPECT

STANDARDIZATION $Na_2S_2O_3$ 10mls $KH(IO_3)_2$

BURET READING 2nd	BURET READING 1st	RESULT
		.6981 FROM PREVIOUS STATION

REMARKS

BLANK DETERMINATION

BURET READING 3rd	BURET READING 2nd	BURET READING 1st	BLANK 2 X 2nd MINUS (3rd + 1st)
			.0020 FROM EARLIER IN THE CRUISE

STANDARD FACTOR

$\frac{1}{\text{STANDARD MINUS BLANK}} = 1.4365$

CRUISE: PIQUERO

STATION: AFTER 43

DAY 12 MONTH FEB YEAR 69

START OF TITRATIONS 1400 TIME TITRATIONS COMPLETED 1430

ANALYST: A.C.A.

$Na_2S_2O_3$ CHANGED ☐ YES ☒ NO

C. Data quality and sources of error

1. Duplicate Nansen bottle sampling

In the course of many routine analyses, a number of comparisons have been made with duplicate sampling using different sets of oxygen flasks. The results show that the calibration procedure is a good one and duplicate samples are probably not necessary to get good results.

Duplicates were drawn from Nansen bottles from a hydrocast with depths ranging from 1500-4500 meters. The oxygen values ranged from 2.86 to 4.80 ml/l. The average deviation between the two sets of 10 values was 0.01 ml/l, the standard deviation 0.01, and the range 0.00 to 0.04 ml/l.

2. Operator titrating errors

Frequently more than one operator does oxygens on a cruise. Using the procedure outlined in Part IX, Section B-1, 20 samples were prepared. The samples were drawn and pickled by operator 5, who also did all the preliminary steps outlined in the pre-titrating checks. After running standards and four samples, each of the other operators titrated four samples. It should be noted that the flasks were so chosen that there would be as wide a range in titration values as possible for each operator. The results were excellent:

Operator	Average value ml/l	Average deviation	Standard deviation
1	6.423	0.040	0.056
2	6.423	0.004	0.005
3	6.419	0.004	0.005
4	6.419	0.006	0.008
5	6.427	0.004	0.005

It is quite clear from these two tests that flask calibration and titrating need not be the major sources of error. It is recommended that tests such as these be conducted whenever possible to maintain good data quality.

The major sources of error are probably sample collection and standardization. For the best results these two must be tended to with utmost care.

D. Some common problems

In the course of operating the micropipet-buret oxygen rig several minor difficulties have been encountered. Since they occur quite frequently with inexperienced people they will be mentioned here.

1. Indicator quality

After the starch and glycerin have been mixed, it is necessary to heat the mixture to get the starch into solution. As the temperature gets close to the boiling point, the solution will start to clear, the presence of the starch having given the glycerin a cloudy appearance. Continue to heat until the solution just starts to boil. At this stage all the starch should be in solution. If the starch was not adequately dissolved, fine white particles will appear in the oxygen flask after the end point has been reached. Slow reaction on the surface of these particles seems responsible for the poor end point. This starch can be salvaged by proper heating as described above.

2. Bubbles in micropipet-buret cylinder

After completing a titration the three way stopcock is set to refill the micropipet-buret chamber from the thiosulfate reservoir. If this is not done, air will be drawn up the pipet tip and bubbles will appear in the chamber. Removing the bubbles is not difficult, just a nuisance.

With the stopcock in the fill position, fill the micropipet-buret chamber to about 0.2500 with thiosulfate. Then tip the whole rig clockwise from 45 to 90 degrees. Set the stopcock so that air can be drawn up the tip and into the chamber so there is a continuous line of air from the tip to the bubble, which is now in the upper part of the chamber. Without changing the position of the stopcock, run the air and some thiosulfate out of the chamber and out the tip. This is usually sufficient to remove the air from the system.

Before tipping the box be sure the bottle reservoirs are sufficiently secure so they will not fall out and break. Also be sure the tops are secure so that the standard and thiosulfate are not spilled over the inside of the rig.

3. Standards and blanks

It is very important that standard solutions be adequately stirred between the addition of each of the pickling reagents. If a brownish-red precipitate forms after the addition of the manganous chloride solution, the standard (or blank) was not adequately stirred after the introduction of the sodium hydroxide-sodium iodide solution. Further stirring will cause the precipitate to dissolve, but the standard value will be as much as 10% high.

Appendix 1

MEASUREMENT OF BOTTLE CAPACITY

"True capacity of glass vessels from the weight of the contained water or mercury when weighed in air with brass weights". Chemical Rubber Handbook, 44th Edition, page 1678.

A glass vessel containing G grams of water at a temperature of t°C has a capacity of a temperature of 18°C given by $V = W_{18°} \times G$ (cubic centimeters).

To correct the weight of water in the oxygen bottle to a volume, multiply the weight by the corresponding $W_{18°}$ temperature correction, e.g., Temperature = 20°C.

Measured bottle weight = 100.0000 g

$100.0000g \times 1.002785\ cm^3/g = 100.2785\ cm^3$

The $W_{18°}$ values give the oxygen bottle volume in units of cubic centimeters. We desire milliliters.

There are two absolute density tables in the Chemical Rubber Handbook which we can use to convert from cm^3 to ml.

$$cm^3 \times g/cm^3 \times ml/g = ml$$

e.g.: all measurements made at 18°C,

$$1.002441 \times 0.998595 \times 1.00138 = 1.002414$$

$$\frac{1.002441 - 1.002414}{1/2\ (1.002441 + 1.002414)} = 0.00002694$$

or 0.002694%

This difference is hardly worth considering since the overall evaluated accuracy of the Winkler technique is probably not better than $\pm$ 0.02 ml/l ($\pm$ .002%).

OXYGEN BOTTLE CALIBRATION

INTERPOLATED $W_{18°}$ VALUES

	18°	19°	20°	21°	22°
0	1.0024410	1.0026080	1.0027850	1.0029720	1.0031700
.1	1.0024577	1.0026257	1.0028037	1.0029918	1.0031909
.2	1.0024744	1.0026434	1.0028224	1.0030116	1.0032118
.3	1.0024911	1.0026611	1.0028411	1.0030314	1.0032327
.4	1.0025078	1.0026788	1.0028598	1.0030512	1.0032536
.5	1.0025245	1.0026965	1.0028785	1.0030710	1.0032745
.6	1.0025412	1.0027142	1.0028972	1.0030908	1.0032954
.7	1.0025579	1.0027319	1.0029159	1.0031106	1.0033163
.8	1.0025746	1.0027496	1.0029346	1.0031304	1.0033372
.9	1.0025913	1.0027673	1.0029533	1.0031502	1.0033581
	23°	24°	25°	26°	27°
0	1.0033790	1.0035970	1.0038250	1.0040630	1.004310
.1	1.0034008	1.0036198	1.0038488	1.0040877	
.2	1.0034226	1.0036426	1.0038726	1.0041124	
.3	1.0034444	1.0036654	1.0038964	1.0041371	
.4	1.0034662	1.0036882	1.0039202	1.0041618	
.5	1.0034880	1.0037110	1.0039440	1.0041865	
.6	1.0035098	1.0037338	1.0039678	1.0042112	
.7	1.0035316	1.0037566	1.0039916	1.0042359	
.8	1.0035534	1.0037794	1.0040154	1.0042606	
.9	1.0035752	1.0038022	1,0040392	1.0042853	

Chemical Rubber Handbook Ed. 44, page 1678

Appendix 2

CHECKLIST OF SUPPLIES AND EQUIPMENT FOR OXYGEN ANALYSIS

I. EQUIPMENT

Titration rack (23" x 23" x 11", illuminated by 2 Sylvania F6T5 fluorescent lamps).

Pickling rack with three 2L reservoirs.

Becton Dickinson 2 ml pipetting syringes with metal double valves. Clay-Adams plastic double valve used for acid syringe.

1 ml Manostat digipet.

Electric stirring motor with swivel mounting.

Teflon encased stirring bars.

Oxygen data forms (SIO-MLR-DCPG Form 9, Mod. 1967).

Tygon tubing: 1/8" and 1/4" ID

II. GLASSWARE

Oxygen flasks: modified iodine flasks of approximately 100 ml capacity with #22 hollow ⚧ stoppers with elongated penny-heads and extended necks.

10 ml automatic filling pipet.

1 ml pipet.

3-way capillary stopcock (Kimble #41044 F).

Reagent bottles: 50 ml, 500 ml, 1000 ml (2)

1500 ml beaker.

1 L volumetric flask.

III. CHEMICALS

H_2SO_4	Sulphuric acid
$MnCl_2 \cdot 4H_2O$	Manganous chloride
NaOH	Sodium hydroxide
NaI	Sodium iodide
NaN_3	Sodium azide
$Na_2S_2O_3 \cdot 5H_2O$	Sodium thiosulfate pentahydrate
KIO_3	Potassium iodate
$HOCH_2CHOHCH_2OH$	Glycerol
	Starch (potato powder as soluble starch)
$CHCl_3$	Chloroform
	Distilled water (2X)

All chemicals are reagent grade

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