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Dissolved Oxygen Measurements in Sea Water at the Woods Hole Oceanographic Institution

by

George P. Knapp, Marvel C. Stalcup and Robert J. Stanley

July1989

Technical Report

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Robert C Beardsley

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Department of Physical Oceanography

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ABSTRACT

This report describes a modified Winkler titration technique that has been used for the past 25 years at the Woods Hole Oceanographic Institution (WHOI). During this time most of the dissolved oxygen measurements made at sea by WHOI personnel have been analysed with this technique and only relatively minor, evolutionary changes in the procedures and equipment have occurred. These changes, however, have improved the precision and accuracy of deep-sea dissolved oxygen measurements to 0.005 ml/1 and 0.02 ml/1 respectively.

DISSOLVED OXYGEN MEASUREMENTS IN SEA WATER

at the Woods Hole Oceanographic Institution

by George P. Knapp, Marvel C. Stalcup and Robert J. Stanley

Sampling Technique

The oxygen samples are collected as soon as possible after each cast is completed beginning with the deepest sample. This sample is collected first since it is generally the water furthest from equilibrium with surface temperature and pressure. However, before each water sample is collected the spigot on the sampling bottle is opened while keeping the breather valve closed. If water flows out of the spigot then air must be entering the bottle through a leak and the water within the sampling bottle is contaminated. This information should be noted on the log to identify this sample as suspect. If water does not come out of the spigot it is unlikely that the bottle has leaked. In this case the breather valve is opened to start the flow of water through the spigot and the oxygen sample can be drawn. The samples are collected in cases of sequentially numbered, brown glass, Tincture bottles with nearly identical capacities. Each bottle has a volume of about 150 ml (±1 ml) and is equipped with a ground glass stopper attached with a rubber leash. The bottle is first rinsed with the sample water and then filled slowly using a hose inserted to the bottom of the bottle. Special care is taken to minimize turbulence and aeration of the sample. Approximately 150 ml of the sample water is allowed to overflow the bottle. One ml of $MnCl_2$ (3 molar) and one ml of NaI-NaOH (8 normal) are added to the sample using high quality 1 ml dispensors which have an accuracy of better than ±1%. As discussed in Strickland and Parsons (1972), the tip of each dispensor is inserted about 1 cm beneath the surface of the sample to avoid the introduction of bubbles and the unwanted addition of atmospheric oxygen into the sample. The dense reagents immediately sink and only sample water is displaced over the rim of the bottle. After the reagents have been added, the stopper is carefully replaced to avoid trapping a bubble. When the stopper is seated, it is pressed firmly in place and the bottle is shaken vigorously 10 to 15 times. The violent agitation of the sample is produced with a downward, snapping movement of the wrist. This motion is mandatory to reduce the size of the flocculent and increase its surface area to ensure that all the dissolved oxygen rapidly oxidizes an equivalent amount of manganous hydroxide. When all the samples have been collected, they are placed in our temperature controlled, portable laboratory to equilibrate and await titration.

Titration Technique

The temperature of the dissolved oxygen samples equilibrates with that in the portable laboratory (22°C ±1°C) while the flocculant precipitates. An hour or so after the last sample was collected, the precipitate has generally settled to about half the volume of the bottle and the samples are shaken a second time. Care is taken while shaking the sample to ensure that the stopper is not inadvertantly opened and air introduced into the bottle. Strickland and Parsons (1972) state that the sample can be allowed to stand indefinitely at this point though care must be exercised to avoid photo-dissociation of the iodine. In practice we seldom wait longer than 8-10 and generally only 2-4 hours before titrating the sample. During this time the samples are in brown glass bottles in subdued light and in a constant temperature environment. Shortly before the samples are to be titrated, one ml of 10 N sulphuric acid is added to each sample bottle which is then vigorously shaken to completely dissolve the precipitate and liberate iodine equivalent to the dissolved oxygen originally contained in the sample. If, 5-10 minutes after acidification, the precipitate is not completely dissolved it may be necessary to add an additional drop of acid and shake the sample again. It is important to remember that the final pH of the sample at the time of titration should be near 2.2. If the precipitate does not readily dissolve or if the pH is much less than 2.0, the NaI-NaOH and H_2SO_4 reagent dispensors should be checked to make certain that they are dispensing 1.0 ml ±5%. A small adjustment to either or both of these dispensors may be necessary to assure that the final pH is correct and that the precipitate dissolves as described above.

A 50 ml aliquot of the iodine solution is drawn up with a calibrated, automatic pipette. When this sample is sucked up into the pipette, the top 10-15 ml of the sample is allowed to overflow into the vacuum sump. This volume will be slightly deficient in iodine (Strickland and Parsons, 1972). The 50 ml sample is dispensed into a 100 ml beaker and quickly titrated with 0.01N sodium thiosulphate until the solution is a light straw color. Two drops of the starch solution are added at this point to produce a dark blue color. Thiosulphate is added slowly until the solution is colorless and the end point is reached. Recently the end point has been determined and the titrant dispensed automatically using a Metrohm Titroprocessor equipped with a combination massive platinum electrode and a Dosimat reagent dispensor. The operation of this equipment wll be described later.

Historically the oxygen sample was always the first to be drawn once the water sampling bottles were aboard the ship. Recently, however, priorities have dictated that other samples must be collected first. When this occurs, the oxygen samples are sometimes drawn 30 or more minutes after the cast is completed. Sometimes oxygen samples are collected from the water used to rinse the copper tubes in which Tritium samples are collected. The effects of delays in drawing oxygen samples and the use of rinse water on the quality of the dissolved oxygen measurements was assessed during a recent cruise to the tropical Pacific ocean. No differences were found between samples collected immediately from 10 liter Niskin bottles or samples collected 30 minutes later. Samples drawn through copper tubing were not affected.

The preparation of the reagents used in the WHOI modification of the standard Winkler titration and the techniques employed to measure the normality of the thiosulphate and to determine the reagent blank correction are described next. Although the potassium biniodate standard is employed at WHOI, Carritt and Carpenter (1966) recommend using a potassium iodate standard. Both of these reagents are stored in a vacuum jar with dessicant and comparisons are made each time a batch of reagents is mixed. Directions for mixing both reagents are given below. The formula used to calculate the dissolved oxygen content in ml/l is presented next and is followed by a description of the Titroprocessor and a discussion of the accuracy of the dissolved oxygen measurements presently made by WHOI personnel at sea. Much of the credit for the consistency and accuracy of our oxygen measurements over the years can be attributed to the high quality of the reagents and standards prepared by Nathaniel Corwin.

Reagent Preparation

Manganese Chloride (3 M)

.........Six hundred grams of analytical reagent grade $MnCl_2 \cdot 4H2O$ are dissolved in 600 ml of distilled water. This solution is filtered and distilled water is added to make one liter.

Sodium Iodide(4M)- Sodium Hydroxide (8N)

.........Dissolve 600 grams of analytical reagent grade NaI in 600 ml of distilled water and note the color of the solution. If the solution is not clear (i.e. yellow-brown), it must be discarded and a new reagent used. Slowly add 320 grams of analytical reagent grade NaOH while continuously stirring. Cool this mixture to room temperature and filter it before adding distilled water to make one liter.

Sulphuric Acid (10 N)

.........Slowly add 280 ml of concentrated reagent grade H_2SO_4 to 600 ml of distilled water. Cool this mixture to room temperature and add distilled water to make one liter.

Sodium Thiosulphate (0.01 N)

.........Weigh 5.0 grams of $Na_2S_2O_3 \cdot 5H_2O$ crystals, add 0.25 grams of sodium borate for a preservative and place in a small plastic vial. When dissolved in two liters of distilled water, each vial will make a solution approximately 0.01 normal. This solution is stable for many months if kept in a dark well-stoppered bottle. Note... Dilute thiosulphate solution in a burette or in tubing deteriorates quite rapidly. The burette or Dosimat cylinder and tubing should be flushed three times before beginning any titrations.

Potassium biniodate Standard (0.0100 N)
........Carefully weigh 0.3250 grams of $KH(IO_3)_2$. Transfer to 1000 ml volumetric flask and make to the mark with distilled water. This solution is stable indefinitely.

Potassium iodate Standard (0.0100 N)
........Carefully weigh 0.3567 grams of KIO_3. Transfer to 1000 ml volumetric flask and make to the mark with distilled water. This solution is stable indefinitely.

Starch Indicator
.........Weigh 5 grams of potato starch, add 5 mg of mercuric iodide for preservative, and place in a small plastic vial. To make a solution, add distilled water to the starch to make a paste and, while stirring, slowly pour the paste into 500 ml of boiling, distilled water. Continue stirring until cool. The solution is stable for several months.

Storage during cruise
..........The sodium thiosulphate reagent is pre-weighed and placed in plastic vials to be mixed with 2 liters of distilled water as required for titrations. The starch is pre-weighed and kept in plastic vials to make 500 ml solution. These vials are stored in an air-tight container with dessicant. All the other reagents are mixed in the shore based-laboratory, carefully sealed and taken to sea in brown, one-liter PVC bottles.

Standardization and blank determination

To determine normality of sodium thiosulphate solution:
.........Add exactly 150 ml (±0.01 ml) of distilled water to a flask which has been thoroughly cleaned to remove any trace of manganese. Add 1 ml of the 10 N sulphuric acid and stir, add 1 ml of the sodium iodide-sodium hydroxide reagent and stir. If the solution is not colorless at this point, the sample has been contaminated with manganese which has liberated iodine and discolored the solution. This sample should be discarded and the flask carefully washed and dried before trying again. Add 1 ml of the manganese chloride reagent and stir. Add exactly 15 ml of the 0.0100 N standard solution and stir thoroughly. The concentration of this solution is similar to that of the average water sample and requires about 4.3 ml of thiosulphate to titrate to the endpoint. Collect exactly 50 ml of this solution in the 50 ml automatic pipette and allow 10-15 ml of the sample to overflow as described in the collection of the sea water sample. Titrate with the thiosulphate and note the amount needed to reach the endpoint. Three standardizations should be performed with agreement to at least 0.01 ml of thiosulphate. The formula used to calculate the normality of the thiosulphate is given below.

Carritt and Carpenter (1966) note that "The complexity of the behavior of thiosulphate suggests that the solutions must be standardized with the particular oxidant under precisely the same conditions that exist during sample analysis". The standardization technique described above has been designed to follow this suggestion and closely parallels the method used to analyze the seawater samples. Any iodine lost through volatilization or gained by the oxidation of iodide while analyzing the seawater samples will be equal to similar errors occurring during this standardization procedure. This method of standardization automatically compensates for these errors.

To measure the reagent blank:
.........Add about 50 ml of distilled water to a clean flask. Add 1 ml of the 10N sulphuric acid and stir, add 1 ml of the sodium iodide-sodium hydroxide reagent and stir. If the solution is not colorless at this point, the sample has been contaminated with manganese which has liberated iodine. This sample should be discarded and the flask carefully washed before trying again. Add 1 ml of the manganese chloride reagent and stir. Next add exactly 1.0 ml of the 0.0100 normal potassium biniodate reagent and titrate with the thiosulphate. When the end point is reached, record the amount of thiosulphate used, add another 1 ml of standard and titrate again. The difference between the amount of thiosulphate used for the first and the second titration is the reagent blank and can be either positive (iodine producing) or negative (iodine consuming). Our blanks are typically less than 0.01 presumably because we carefully filter the manganese chloride and sodium iodide-hydroxide reagents. Contaminated reagents (manganese chloride) have been found only once in the past 25 years and blanks are generally zero. The reproducibility of both the standardization and the blank titrations should always be better than +/-0.01 ml. The normality of the thiosulphate and the reagent blanks are determined frequently during each cruise.

To calculate the normality (N) of the sodium thiosulphate
.........N = std * (S/(B+std+reagents)) * nrm)/(thio-blank)

To calculate dissolved oxygen (ml/l) in sea water:
....oxygen = N * (V-blank) * (B/(B-reagents)) * 5.6 * (1000/S)

where std = ml of standard solution (15.0 ml)
nrm = normality of standard solution (0.0100 N)
thio = ml of thiosulphate to titrate sample (about 4.35 ml)
N = normality of sodium thiosulphate (approx. 0.01 N)
V = ml of thio needed to titrate sample (variable)
B = volume of sample bottle (approx. 147 ml)
S = capacity of calibrated automatic burette
blank = reagent blank correction (generally 0.00)
reagents = volume of reagents added to sample (2 ml)

Titroprocessor

In 1985 a Metrohm Titroprocessor was purchased to control the modified Winkler titration used at WHOI. This equipment consists of electronic circuitry to measure the electric potential of a combination platinum electrode and a microprocessor to control the titration. The proprietary program in the microprocessor continuously monitors the potential of the electrode and controls the dispensing of the sodium thiosulphate reagent during the titration of the iodine solution. Depending upon parameters selected by the analyst, the program adjusts the rate at which the reagent is dispensed from quite fast during the initial stages of the titration (when the concentration of iodine is high) to very slow as the end point is approached (when the concentration is low). This pattern of dispensing thiosulphate closely mimics that employed by a skilled analyst but does so with greater precision and consistency. The addition of a non-diffusing tip on the Dosimat reagent dispensor reduces the minimum dosage of thiosulphate from about 0.02 to 0.001 ml. This equipment has been successfully used during several cruises in both the temperate and tropical Atlantic and Pacific Oceans during which thousands of analyses have been performed. The automatic titration of 24 oxygen samples typically requires about 40 minutes. Neither the collection and handling of the oxygen samples nor the preparation of the reagents has been substantially changed from that employed at WHOI for the past 25 years. The main difference between the previous manual system and the new automatic Titroprocessor based system is that the end point is now sensed electronically instead of relying upon an operator to determine the disappearance of the blue starch color. Other slight modifications to the technique include the use of high quality 1 ml automatic reagent dispensors to improve repeatability, a standardization technique that closely mimics the titration of seawater samples and the overflow of 10-15 ml of iodine depleted sample from the automatic pipette. Comparisons between the Titroprocessor's potentiometric end point and the amperometric end point, with the starch end point determined by several experienced analysts, shows that the former are about 0.02 ml past the visual end point at average oceanic values. Strickland and Parsons (1972) point out that "the true stoichiometric end point is a little after the starch end point". The differences among a series of 80 automatic titrations of a prepared sample indicates a precision of 0.005 ml/l.

Currently undergoing development is an evaluation and modification of the technique of Culberson and Huang (1987) where an amperometric endpoint scheme is utilized. This has certain advantages over the present method in that less operator dependance is required. Instead of ending the titration at a predetermined (by the operator) set voltage, the titration stops as the current thru the electrode drops to near zero when a slight excess of thiosulphate is dispensed. The slope of the final portion of the titration curve is calculated and its intercept with the "zero" line is calculated. This method should eliminate problems created by electrode drift.

Data handling

The Titroprocessor prints out a complete record of each titration.

1. Date and time
2. Program #
3. Sample #
4. Sample volume
5. Initial electrode voltage
6. Final electrode voltage
7. Volume of thiosulphate dispensed

The sample number, the initial and final electrode voltages, and the volume of thiosulphate dispensed are presently transmitted to a Commodore B-128 computer system for calculation of dissolved oxygen, interim storage and various quality control procedures. Recent problems with these computers have mandated their replacement. A NEC Powermate 2, PC compatible computer has been purchased and software is being rewritten for this machine. When both the salinity and oxygen samples for a station have been analyzed, the data are merged with the CTD temperatures and pressures from the same station. Plots are then made of potential temperature versus the water sample salinity and oxygen values for comparison with nearby stations and historical data. This procedure is used to identify errors and suspect data which are either edited or flagged as questionable. When these quality control measures have been completed, the data are transmitted to the computer used by the WHOI CTD group to calibrate the CTD salinity and oxygen sensors. The differences between the water sample and the CTD salinities and dissolved oxygen values are calculated to provide continuous monitoring of sensor reliability.

The automatic transfer of data from the salinometer and Titroprocessor to the computers has eliminated errors introduced by hand entry of these data and decreased the time between sample collection and data availability. The automation of these measurements has also freed the operator of tedious, time-consuming paper work and has resulted in the reduction of personnel needed to perform these analyses. On several recent major oceanographic cruises, during which four or five 24-bottle CTD stations were occupied each day, only one person was required to analyse both the salinity and the oxygen samples and complete the data reduction processes. Thus a single analyst can now analyse and process on the order of 125 salinity and oxygen samples per day.

Accuracy

A study by Saunders (1986) has shown that during 6 cruises in the northeastern Atlantic Ocean during 1980-81 the rms deviation in dissolved oxygen measurements below 3500 m varied by only 0.027 to 0.074 ml/l. The analyses were performed by different investigators employing different techniques. Four of the cruises were aboard WHOI research vessels where analysts used the modified manual Winkler technique described here. The accuracy determined by Saunders (1986) compares well with the 0.1% reported by Carpenter (1965). Since 1981 improvements have been made in the resolution and in the accuracy with which the titrant is measured and the repeatability of the endpoint determination. In addition to these improvements, we have noted that the scatter of the oxygen measurements has been significantly reduced since oxygen analyses have been conducted within our temperature controlled portable laboratories.

Recently Knapp et al. (in prep., a) have described the accuracy of salinity and oxygen measurements made during an extended cruise aboard the R/V Moana Wave operated by the University of Hawaii. The WHOI CTD and Hydrographic groups were responsible for the collection and analysis of the water samples during this cruise which was essentially along 10°N from the Philippines to Costa Rica. During the cruise 221 stations were occupied to the bottom and over 5200 water samples were collected. An analysis of the water sample data interpolated at several potential temperature surfaces showed that the salinity measurements were accurate to about 0.001-0.002 PSU and the oxygen measurements were accurate to about 0.02 ml/l. Duplicate samples from the same 10 liter Niskin bottles and from bottles tripped at the same depth indicate a precision of about 0.001 PSU and 0.005 ml/l. The precision and accuracy of these measurements exceeds those recommended by the WOCE Science Steering Committee.

The accuracy of the dissolved oxygen data collected during WHOI cruises has also been discussed by Knapp and Stalcup (1987) and is clearly dependent on the skill and experience of the individual conducting the analyses. During the past 10 years the quality of the oxygen data from several cruises has been degraded by unskilled technicians. It is generally not possible to train individuals in a shore-based laboratory and expect them to collect the highest quality data at sea without supervision. Several training cruises are generally needed to develop both the skills and confidence required to obtain the quality of the WHOI data described by Knapp et al. (in prep., a).

Iodine Volatility Losses

Green and Carritt (1966) note the problem of volatility losses of iodine during the transfer of samples. They measured a large variability (0.11 ml/l) and an average loss of 0.10 ml/l apparent oxygen when collecting 100 ml aliquot samples and recommend whole-bottle titrations. Knapp, et al. (in prep.) have shown that when aliquot samples are compared with whole-bottle samples there is no significant difference in variability or average value. Saunders's (1986) data show good agreement between WHOI's aliquot oxygen measurements and Scripps Institution of Oceanography's (SIO) whole bottle data. The observations reported by Knapp et al. (in prep., b) show a standard deviation of 0.005 ml/l for replicate samples and an accuracy of 0.02 ml/l suggesting that iodine volatility losses are not a problem in the present method.

Comparisons

We agree with Saunders (1986) that comparisons of temperature, salinity and oxygen measurements between oceanographic institutions are highly desirable. Such comparisons are especially important during multi-institutional experiments such as the forthcoming WOCE measurements. Sites should be identified where the uniformity of the potential temperature-salinity and -oxygen relationship can provide environmental standards for these deep sea measurements. The forthcoming oxygen comparison, scheduled for mid 1990 during the first WOCE cruise in the Pacific, will be useful in defining the precision and accuracy with which various groups measure dissolved oxygen in deep sea samples.

Common Problems

When replacing the ground glass stopper in the sample bottle it is important to avoid trapping an air bubble beneath the stopper. The best technique is to insert the stopper at a slight angle until its base is beneath the surface of the water. Then let it drop into the bottle until it seats itself. Press the stopper firmly to seat it within the neck of the sample bottle and secure it while shaking the bottle.

If the 1 ml automatic reagent dispensors have not been used for a day or more, they should be flushed with several milliliters of solution to ensure that fresh reagents are used in the analyses. The sodium thiosulphate solution deteriorates in the tubing of the Dosimat and its normality decreases. When beginning a series of titrations, the cylinder is flushed three times to make certain that fresh reagent is dispensed.

The NaI-NaOH is corrosive to most materials found in dispensors and occasionally the plungers stick. This problem can be minimized if the dispensor is cleaned every 3-4 days with distilled water. It is especially important that the tip of this dispensor be kept clean and free of manganese contamination. The brown precipitate that sometimes forms on the tip is produced by the oxidation of manganous hydroxide to yield higher valent manganese hydroxide. If this material is accidently introduced into a sample and acidified, it will react with iodide to yield iodine. This contaminated sample will then contain an unknown quantity of excess iodine.

When pipetting the 50 ml aliquot it is important to collect the last drop of sample from the pipet at the same time, every time. The droplet size can increase with time as laminar flow of the sample on the inside walls of the pipet continues.

During titrations it is important to regulate the speed of the stirrer to provide rapid mixing of the thiosulphate into the sample yet not aerate the sample and liberate iodine or oxidize iodide. Best results are obtained when the vortex produced by the stirring bar is about 1 cm deep. The relative position of the dispensor tip and the electrode is critical if the highest quality data are to be obtained. The electrode is placed near the inside edge of the beaker in the fastest flowing portion of the fluid and just above the stirring bar. The dispensor tip is placed near the inside of the beaker and about 90 degrees upstream and at the same depth as the electrode.

All of the glassware used in the Winkler titration should be kept as clean as possible. Manganese contamination of the flasks used during standardization or for the determination of the reagents blank will produce erroneous results, and dirty burettes will not dispense the correct volume of solution. We regularly clean all of the burettes with 'Chromerge' and find that they will stay clean for a week or more if kept filled with distilled water when not in use. Flasks and beakers are scrubbed with a solution of 'Sparkleen'.

The highest quality oxygen measurements are obtained when variations in the sampling, handling and titration techniques are minimized. The collection of the samples, the addition of the reagents and the shaking of the samples before and after acidification should be carried out as uniformly as possible. Such uniformity is best realized when a single analyst is responsible for all of the titrations. The rate at which the titration is conducted during both the standardization and the analysis of the water samples should be similar. In practice this means that the thiosulphate is dispensed rapidly during the beginning of the titration when the concentration of iodine is high and slowly near the end point when the concentration is low.

Carritt and Carpenter (1966) recommend that the pH of the iodine solution be maintained between 2.0 to 2.5 to avoid the air oxidation of iodide to iodine. We set the manganese chloride and sodium iodide-hydroxide automatic pipettes to dispense exactly 1 ml and adjust the sulphuric acid pipette to yield a solution with a pH of about 2.2.

The formula for calculating dissolved oxygen contains the term B/B-2 which is the volume of the sample bottle in ml divided by the volume minus 2 ml. The latter is the volume of the manganese chloride and sodium iodide-sodium hydroxide reagents added to the sea water sample to react with the dissolved oxygen. In the presence of a strong alkali, manganous hydroxides are precipitated from the manganese chloride. Oxygen, dissolved in the sample water, oxidizes an equivalent amount of divalent manganese to hydroxides of higher valency states. The 2 ml correction is needed to account for the change in the volume of the sea water sample resulting from the addition of the two reagents.

The acidification of the sample, in the presence of iodide, causes the manganese to revert to the divalent state and liberate iodine proportional to the higher valent manganese hydroxides. When 1 ml of the acid is added, it displaces water which contains neither dissolved oxygen nor manganese hydroxide. When the stopper is replaced, the volume of the sample remains the same as before the acid was added. Thus the concentration of the iodine produced by this reaction is not affected by the addition of the acid.

CONVERSION FACTORS: from Saunders (1986)

1 ml/l = 43.57 micromoles/kilogram
1 ml/l = 44.660 micromoles/liter
assumed water density = 1.025 kg/l

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16. Abstract (Limit: 200 words)

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