



**INTERNAL DOCUMENT No. 20**

**Procedures for the determination of dissolved  
oxygen in seawater**

**S E Holley & D J Hydes**

**1995**



**Institute of  
Oceanographic Sciences  
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**JAMES RENNELL CENTRE FOR  
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# DOCUMENT DATA SHEET

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<b>ABSTRACT</b> <p>WOCE requires an accuracy of &lt;1% and precision of 0.1% for dissolved oxygen measurements. The present IOS equipment used to achieve these aims includes a Metrohm Titrino, with amperometric end point detection. In order to achieve a high quality data set consistent procedures must be followed at every stage from sampling through to reporting the data. The procedures used in the analysis of dissolved oxygen have been documented. Possible sources of error that may affect the precision of the final results are discussed.</p>	
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## 1. PROCEDURE RECOMMENDATIONS

On all future WOCE cruises in which IOS is responsible for the determination of dissolved oxygen these procedures will be followed in order to achieve the WOCE criteria for accuracy and precision. An accuracy of <1% is required, with a precision of 0.1%. The end point of the standard Winkler Titration will be measured amperometrically by a dead stop titration.

## 2. BRIEF PROCEDURE OUTLINE

The basic outline of the procedure is as follows:

- 1) Collect a bubble free sample of seawater.
- 2) React oxygen in the sample with a mixture of manganous chloride and alkaline iodide, immediately sealing the bottle, at a known temperature.
- 3) Shake bottle vigorously to mix sample and reagents.
- 4) After thirty minutes shake again.
- 5) Add acid and titrate the liberated iodine against sodium thiosulphate, using an amperometric dead stop titration.

## 3. REAGENTS

All the reagents follow the WOCE recommended use of the Carpenter (1965) solutions. In this document concentrations are expressed both in terms of molarity and normality. The old chemical term normality is retained for consistency with earlier documentation, and because of its convenience for use in titration calculations. The molarity (M) is defined as the number of gram molecular weights (moles) of solute in 1L of the final solution. The normality (N) is defined as the number of gram-equivalent weights of the reactant in 1L of solution.

### 3.1 Reagent 1:- Manganous Chloride 3M

Dissolve 600g of Analar grade  $MnCl_2 \cdot 4H_2O$  in 600 ml of distilled water in a beaker. Filter through a GF/F grade filter, to minimise blank readings, before making up to 1L.

Dedicated glassware should be used in the preparation to avoid manganese contamination in other reagents.

**3.2 Reagent 2:- Alkaline iodide** - Sodium hydroxide (8M) and sodium iodide (4M)

Dissolve 600g of Analar grade NaI in 600 ml distilled water and then slowly add 320g NaOH. Care should be taken as the reactions are exothermic. Discard the solution if, at any stage it is cloudy or a yellow-brown colour develops. Filter through GF/F filter papers before making up to 1L.

**3.3 Reagent 3:- Sulphuric acid** 10N(5M)

Slowly add 280 ml concentrated acid to 600 ml of distilled water then allow the solution to cool before dilution to 1 L

**3.4 Sodium Thiosulphate** 0.02N (0.01M)

Dissolve 25g of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in 1L of distilled water to be used with the 5 ml Metrohm burette exchange unit. Bulk quantities can be prepared onboard and stored in Winchester. The solution is stable if kept in a dark, sealed bottle.

**3.5 Potassium Iodate Standard** 0.01N (0.0016M)

Potassium iodate ( $\text{KIO}_3$ ) is dried overnight at  $110^\circ\text{C}$ , cooled in a desiccator then weighed out to five decimal places and the weight recorded. For a 0.01N solution 0.3567g is dissolved in a calibrated 1L volumetric flask at a recorded temperature. The weight does not have to be exactly 0.3567g but the weight must be precisely recorded to 5 decimal places. The solution is stable indefinitely.

Note:

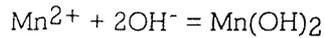
It is required that sodium hydroxide and sulphuric acid should be taken to sea in 2.5L Winchester bottles, in dangerous goods packaging. Manganous chloride is also taken in liquid form but as it is not classed as a dangerous chemical it can be taken to sea in 'Safepak' containers. These reagents are prepared on shore to minimise the risk involved in handling caustic exothermic solutions at sea. Bulk quantities should be made up, sufficient for the proposed cruise campaign. The thiosulphate is taken to sea in dried form packed in sealed plastic vials. It is not made up on shore due to the large quantities used on a cruise. The quantities needed for a typical cruise are detailed in Appendix (7).

#### 4. CHEMISTRY OF THE METHOD

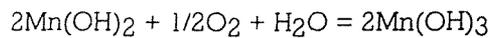
##### 4.1 Equations of the Winkler titration

The equations involved in the Winkler Titration (Grasshoff et al. 1983) are as follows:

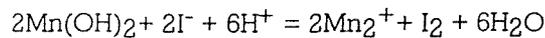
- 1) Precipitation of manganous hydroxide.



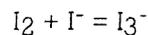
- 2) Uptake of oxygen by conversion of Mn(II) to Mn(III). Dissolved oxygen becomes chemically bound by manganese (II) hydroxide in a strongly alkaline medium. This is the key reaction of the Winkler method. The oxidation results in a mixed precipitate of manganese (II) and (III) hydroxides.



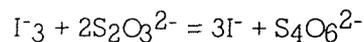
- 3) Acidic oxidation of iodide to iodine when acidified to a pH of 1.0 - 2.5. The precipitated hydroxides dissolve and Mn (III) ions are liberated.



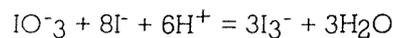
- 4) Complexing of iodine with excess iodide to form a less volatile ionic species.



- 5) Iodine is titrated with thiosulphate resulting in the reduction of iodine by the thiosulphate to iodide, in turn the thiosulphate is reduced to the tetrathionate ion.



- 6) In the standardisation of thiosulphate, using the primary potassium iodate standard, iodate oxidises iodide to titratable iodine (then equations 4 and 5 above).

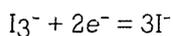
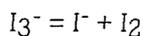


## 4.2 Titration equivalences

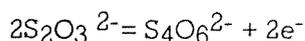
The endpoint of the titration is given when the number of equivalents of thiosulphate added and the number of equivalents of iodate balance and the fraction of iodate neutralised reaches unity. One mole of iodate is equivalent to six moles of thiosulphate and one mole of oxygen is equivalent to four moles of thiosulphate. The oxygen concentration in the sample is calculated by proportion.

## 4.3 Basis of the endpoint detection.

In the dead stop titration two bright platinum electrodes with small surface areas are used as indicator electrodes. A dc voltage of 200 mV is applied to the electrodes. The cathode is depolarised by the reaction shown below:



The anode is depolarised by the reverse reaction. A current flows only if iodine and iodide coexist in the solution. The oxidation of thiosulphate is irreversible and cannot depolarise the electrodes.



With decreasing iodine concentration during the titration the initial current drops until it is almost zero when all the iodine is reduced at the end-point of the titration. If the stirring of the solution is constant the decrease in the current is directly proportional to the decrease in iodine concentration. The small remaining current after the end-point is caused by minor components of the solution.

## 5.0 EQUIPMENT

### 5.1 Equipment calibration

All volumetric apparatus must be calibrated on shore before a cruise, this includes the following equipment:

10 ml Knudsen pipette or 10ml exchange unit, for dispensing iodate standard (spares must also be calibrated);

1 ml fixed volume Eppendorf pipette, for iodate when measuring blanks although the precision is more important than the accuracy in this case;

piston burette in the exchange unit;

Anachem repeat dispensing pipettes used for sulphuric acid, manganous chloride and alkaline iodide;

1L volumetric flask for iodate standard preparation.

The calibration is done by finding the mean weight of pure water contained in, or delivered by, the apparatus at the calibration temperature. Adjustments are made to take account of buoyancy correction and the density of pure water at this temperature. The buoyancy correction factor is necessary as the weight of an object is less in air than in a vacuum. Calibration is normally done at 20°C which is close to working in the ships constant temperature laboratory, set at 20°C. The calibration equations whereby buoyancy, temperature and density corrections are made to arrive at the true volume at 20°C are given by Culberson in the WOCE operations manual and are illustrated in the appendix (5). Even if a class A flask is used it must still be checked as the calibrations are only certified to 0.3%.

## **5.2 Equipment descriptions and set-up**

### 5.2.1 Sample bottles

Wide neck borosilicate glass bottles with an approximate volume of 120ml. The elongated bottle stoppers are unique to each bottle and have the same number engraved onto them, they have been produced to have a sloping surface to break the water tension of the solution. The bottles are supplied by HGL, Hampshire, ready calibrated to three decimal places.

At least three boxes of twenty four bottles should be taken to sea on any one cruise. They should be stored for transport with tissue around the stoppers to prevent them locking in the bottles. Checks should be made onboard for cracks and chips in the bottles and stoppers. All bottles should be checked at the start of the cruise by taking a test station to duplicate every sample to ensure reproducibility.

### 5.2.2 Anachem dispensers

Repeat dispensers supplied by Anachem (part number 5.370.001) for 500 ml amber Safebreak glass bottles. They are used for sulphuric acid, manganous chloride and sodium hydroxide/iodide, set and pre calibrated to dispense 1 ml. A reproducibility of 0.1% is quoted by the manufactures.

### 5.2.3 Thermometer

Supplied by Jenway (model 2052), used with spare sample bottles to determine water temperature at the time of sampling. An accuracy is quoted as  $\pm 0.1^{\circ}\text{C}$  by the manufactures.

### 5.2.4 Tubing

A 15 cm length of silicon tubing is attached to the Niskin bottle tap to transfer water to the oxygen sample bottle. It must be soaked for 2-3 days before use then kept wet between uses in a beaker of seawater, to reduce the tendency of bubbles to stick in tube.

### 5.2.5 Automatic burette

A 5 ml automatic burette, or exchange unit, supplied by Metrohm. The exchange units includes: a 1L titrant reservoir bottle which is to be filled with thiosulphate (includes a lid with air outlet); a stand for the reservoir bottle and piston which locks onto the top of the Titrino unit; three pieces of tubing which must be connected up; and the piston body. All of these parts are removable for transport.

When connecting the unit up after transport the piston unit is screwed into place first and the bottle, filled up with thiosulphate, is put into its stand. The lid, with a straw attached which goes to the base of the reagent bottle, must be screwed on and then the three tubes can be attached to the unit. The small piece of tubing connects from the front to the piston; the medium piece connects from the front left to the top of the 1L reservoir bottle; the large piece connects from the front right to the aspirator tip.

The fittings must all be tightened with the plastic spanner provided. The whole unit is then lined up in front of the Titrino and pushed along the runner until it locks in place on top of the unit. Once the Titrino has been powered up an error message will result on the Titrino screen if the exchange unit is not correctly in place.

### 5.2.6 Titrino unit

A diagram representing the 716 DMS Titrino unit (supplied by Metrohm) is shown in Figure 1. The front panel consists of a screen and three press buttons. When the DOS button is pressed the reservoir empties for as long as the button is pressed, when the FILL button is pressed the unit will fill up ready to dispense up to its full capacity of 5 ml.

When the reservoir bottle is first topped up with thiosulphate the burette must be fully filled and emptied on a slow speed at least five times, checking for bubbles. The speed can be adjusted using the  $dV/dt$  control. At the start of each run it is sufficient to lightly swirl the contents of the reservoir bottle and then fill and empty the burette three times checking for bubbles. This is necessary as the thiosulphate may evaporate or bubbles may form at the top of the piston, as the unit is left standing.

Figure 1 includes a diagram of the back of the Titrino unit. When setting up the equipment the leads connect from the back of the Titrino to the other units as described below:

- 1) Power lead into the power socket;
- 2) Printer lead to socket 'A';
- 3) Electrode lead into 'pol';
- 4) Stirrer lead into 'E';
- 5) Keyboard lead into 'C'.

There is also an on/off button on the back of the Titrino unit.

#### 5.2.7 Printer

The Diconix 180si printer, supplied from Kodak, has two leads: one to the power supply and the other attaches into the back of the Titrino unit.

#### 5.2.8 Stirrer

The stirrer unit (Metrohm 649) connects to the Titrino as described above. The unit has a speed setting which is usually set to 3 for an optimum between rapid stirring (to react the thiosulphate and iodine in sufficient time to prevent significant iodine losses) and a small vortex (a large vortex may introduce bubbles into the sample and result in excessive iodine losses).

The stand is held in the back of the stirrer by a screw fitting, this can be removed for transportation. The aspirator tip and electrode fit into the same holder on the top of the stand. The Knudsen pipette, used to dispense the standard, can be placed on the stand with its own holder so that it can be moved aside until required.

The position of the aspirator tip with respect to the electrode is important. The aspirator is placed slightly below the electrode tip in the stand so that when the unit is lowered into the solution the thiosulphate will be immediately drawn into the stirrer vortex. The stand

can be adjusted so that it can always be lowered to the same height to avoid damage to the electrode by the stir bar.

#### 5.2.9 Electrode

The electrode (Metrohm, part number 6.0341.100) connects to the Titrino unit by a lead running from the 'pol' socket at the back of the Titrino, which attaches to the top of the electrode. The electrode has a plastic cover used for transportation but when it is in place in the stand the electrode is kept in a conical flask of distilled water to keep it clean.

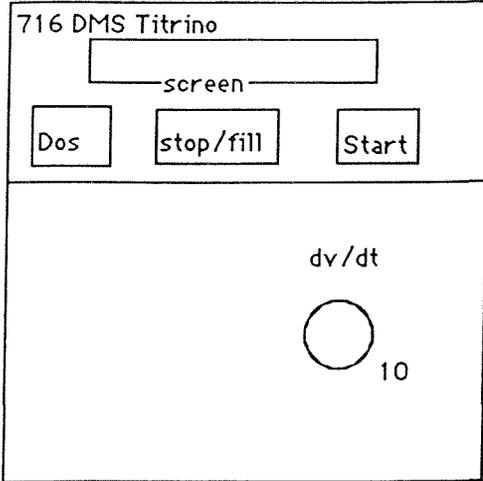
#### 5.2.10 Keypad

The 716 DMS Titrino keypad is attached by a lead to the Titrino. The titration is controlled through this keypad by using the STOP and START keys. The parameters can be set-up in the unit using the PARAMETERS key, this is a rolling function key so that the parameter menu is explored by continuing to press the key. At any time the menu is left by pressing QUIT and the last variable keyed in will be stored provided that the ENTER key had been pressed after each entry. For example, when changing the start volume from 0.5 ml to 0 ml for blank measurements: key down to the start volume (Start V) prompt and ENTER the new volume, then QUIT.

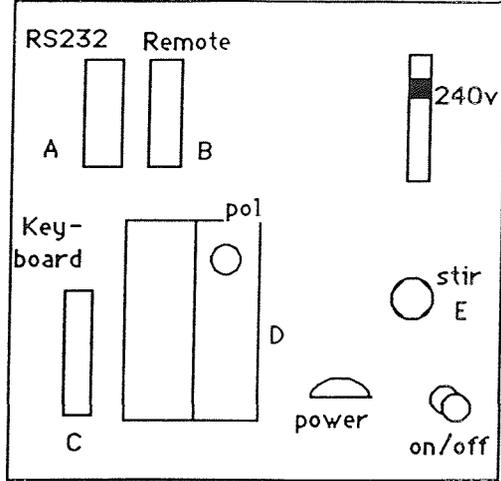
**Figure 1**  
**Equipment set-up**

Titrimo

Front

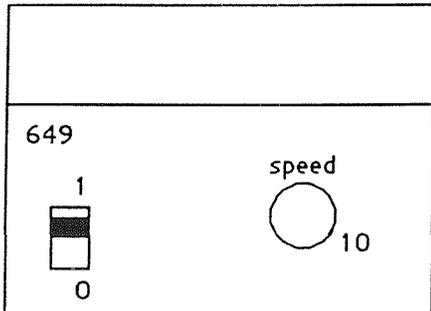


Back

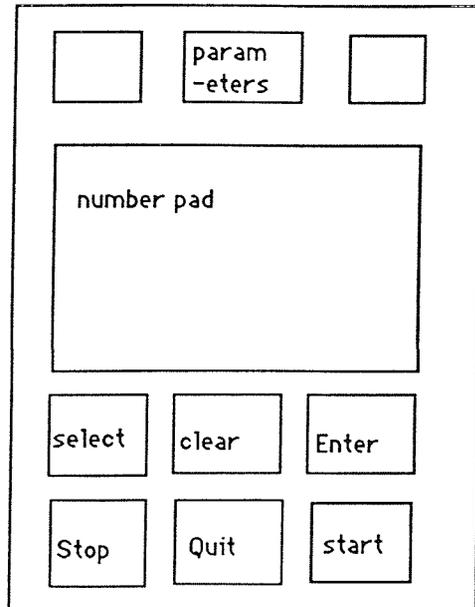


Stirrer (front)

lead from the back connects to E above



Keyboard (connects to C above)



**Table 1**

**Parameter listing as programmed into the Titrino keyboard.**

<u>Parameter:</u>	<u>Setting:</u>	<u>Description:</u>
<u>&gt;SET1</u>		
EP at I	0.1 uA	Parameters for first endpoint (only one end point in this case)
dynamics	10 uA	End point set to 0.1 uA
max.rate	1 ml/min	distance from end point where controlled additions begin.
min.rate	2 ul/min	maximum rate of dosing
stop.crit	drift	type of stop criteria
stop drift	2 ul/min	titration stops if stop drift reached.
<u>&gt;SET 2</u>		
EP at I	OFF	no second end point.
<u>&gt;titration parameters</u>		
titration direction	(-)	direction towards lower current
start V:	abs.	absolute start volume used
start V	0.3 ml	Primary shot for standards and samples. NB: change to 0 ml for blank measurements
dos.rate	max. ml/min	Dosing rate for start volume
pause	10s	wait time following addition of start volume.
U (pol)	200 mV	polarisation of the electrode
electrode test	ON	
temperature	20.0°C	
<u>&gt;stop conditions</u>		
stop V:	abs.	type of stop volume is absolute
stop V	5 ml	set to 5 ml for 5 ml exchange unit
filling rate	max.ml/min	burette fills after titration
<u>&gt;statistics</u>		
status	OFF	calculations mode off
<u>&gt;presentations</u>		
conditioning	OFF	All other parameters off

Sample data can be entered into the SILO but usually the printout is annotated with the sample number instead. The oxygen calculation can also be carried out by specifying USER METHODS and FORMULA VARIABLES however as these stages are potential sources of error all information is recorded onto the worksheets for transcription to the spreadsheets where the oxygen calculations are made.

On the auxiliaries setting, the unit can be setup to send to a PC or printer. The titration results are usually sent to the PC, the software on the PC is loaded by typing '716' from the C: prompt. To collect data from the Titrino go into 'Edit' from the menu (using the 'ALT' keys) then select 'info'. Select 'trace' to put a file name and path into the memory (or overwrite the previous file when first prompted to do so) then select 'wait'. The titration is then started from the 'start' key on the Titrino keypad. The computer will wait to collect the data, each result flashes up on the screen, then it continues to wait for the next sample until the titration run has finished. Press 'esc' to get out of the collection window and 'Alt X' to quit the program.

When the run has finished the data is printed to a hard copy (or to a disk) from the C: prompt the data file and path name (/716/data) having been previously defined as described above. The RS232 settings must also be specified to the default settings of baud rate 9600, data bit 8, stop bit 1, handshake HWs and RS control 'ON'. On the Keypad the '2/DEF' key is set to define the mode of report, this should be set to 'FULL' for routine analysis.

## **6.0 SAMPLING**

### **6.1 Worksheets**

Prior to sample collection prepare an oxygen worksheet for each station to include the following information:- sample number; Niskin number; station number; oxygen sampling bottle number (each has a different three place calibrated volume with an identifying number on the stopper and bottle); and room for the bottle temperature data.

Sample worksheets should be signed and dated, any notes such as which pipettes were used on deck to add the fixing reagents and when new batches of reagents were used should be detailed on this form. Other notes to be recorded here during analysis include: the weight of iodate used to prepare the primary standard; the volumetric flask used in its preparation and the pipette used to dispense it; any bubbles noted in the system; any bottles not sampled; and any other problems which may arise. Sample titration volumes are recorded on this form, a template is shown in the appendix (1).

## 6.2 Procedure

Oxygen samples are taken as soon as possible after each station cast is completed, following sampling for CFCs. The deepest sample is collected first as it is generally the water furthest from equilibrium with the surface temperature and pressure and may become supersaturated and out-gas as the sample warms up.

- 1) Top up the Anachem repeat dispensers with the fixing reagents if necessary and take the reagents out onto deck in a rack just prior to sampling so that the reagents remain at 20°C for as long as possible. Remove the cover from the dispenser arm and clear out the first 2 ml from the pipette tips to reduce the risk of injecting bubbles into the sample. Take the sample bottles out onto the deck with extra bottles to allow for duplicate samples and for measuring the temperatures. Also take out the thermometer, tubing and the prepared worksheet on a clipboard.
- 2) The tubing is attached to the water bottle spigot and the tap opened to run water through the tube to clear any bubbles. If the tap does not run then the breather valve must be opened by the person taking the oxygen samples if no CFC samples are to be taken. It is also the responsibility of the first person taking samples to check for any leaks from the tap or around the base of the Niskin bottle. Once the water is flowing it may be necessary to pinch the tubing to remove bubbles. The tubing is then bent upwards and the sample bottle is inverted over the end of the tube which is pushed to the bottom of the bottle. This gives a rapid flow of water over the bottle walls to give effective washing and temperature equilibration of the bottle.
- 3) The bottle is then righted and filled to overflowing. At least three bottle volumes are allowed to flow through the bottle. The tube may be tapped to dislodge any bubbles but sample agitation must be avoided to minimise aeration of the sample.
- 4) The filling tube is removed and 1 ml of manganous chloride solution is injected into the sample bottle, immediately followed by 1 ml of alkaline iodide solution. The reagents are dense and will sink to the bottom of the bottle. The tips of the Anachem dispensers must be below the neck of the bottle, about 1 cm beneath the surface of the sample, to avoid reaction with water which is displaced when the stopper is inserted into the sample.
- 5) The stopper must be inserted slowly into the sample, with a firm twisting motion, immediately after adding the alkaline iodide solution and care should be taken to ensure no bubbles are trapped below the stopper and that a tight seal is achieved.

- 6) The sample bottle must be shaken vigorously for 30 seconds to disperse the manganous precipitate which scavenges oxygen from the sample. This reduces the flocculent size and increases the surface area, increasing the efficiency of the oxidation of  $\text{Mn}(\text{OH})_2$ .
  
- 7) The tightness of the stopper must be checked before returning the sample to the rack as 'pop back' may occur due to nitrogen coming out of solution, if the stopper has not remained tightened a bubble will have formed under the lid and the Niskin bottle must be resampled. At least 10% of the samples must be taken in duplicate to check the method reproducibility and these are usually taken from the first four bottles of each cast, although all samples are usually duplicated on the first few stations. The duplicate samples are taken straight away using sample bottles from another box. The next water bottle is then sampled. When all of the samples have been collected they are stored in subdued light (close the lid of the sampling rack) in the temperature controlled laboratory to thermally equilibrate and await titration.
  
- 8) A second bottle is filled for recording the fixing temperature (bubbles are not of concern this time but it must be flushed sufficiently to be the same temperature as the oxygen sample bottle.) The temperature probe is placed in the temperature bottle and the temperature of the second bottle is recorded on the worksheet.
  
- 9) Thirty minutes after the sample bottles have been returned to the laboratory they should be shaken a second time. All analysis takes place in a temperature controlled lab  $20^\circ\text{C} \pm 2$ . The analysis may be started one hour after the samples were collected.
  
- 10) All samples should be titrated within two hours if possible.

## **7.0 ANALYSIS**

### **7.1 Reagent blank measurements**

The reagent blank should be determined at the start of each run. It may change whenever a new batch of manganous chloride, sulphuric acid or sodium iodide-hydroxide is opened. It must be checked when the Anachem dispensers are topped up in case of contamination of the reagents. Carpenters' (1965) method of reverse 1 ml reagent addition is used.

- 1) When the Titrino unit is first switched on the exchange unit burette is flushed out using the DOS and FILL keys on the Titrino unit. This is done three or four times, or until the piston burette is bubble free, before each run. It is usually best to reduce the  $dV/dt$  setting to 2.5 to fill the flask so as to avoid drawing bubbles into the system. If bubbles do get into the exchange unit they can usually be cleared from the top of the burette by introducing a larger bubble into the system to mop the smaller ones up; it may be necessary to remove the reservoir and invert the whole exchange unit to mop up bubbles on the top of the piston.
- 2) Make sure that the Titrino keypad PARAMETERS are set-up so that the start volume is set to zero ml addition for blank measurements.
- 3) Blank measurements are made in the 125 ml conical flasks which must be thoroughly washed in tap water three times then in distilled water before being filled to about 100 ml with distilled water. Put a stir bar into the flask then add 1 ml of sulphuric acid and place the conical flask on the stirrer.
- 4) Add 1 ml of sodium hydroxide-sodium iodide and stir, check the solution is clear before adding 1 ml of manganous chloride. If the solution is not clear wash the flask and start again, as some manganese contamination may be present. If clear carefully add 1 ml of the iodate standard. Note on the worksheet the pipette used to add the standard material. The same dispensers must be used for the manganous chloride and alkaline iodide as used on deck. Make sure that the iodate standard is dispensed into the solution and any left of the walls of the conical flask must be washed down into the solution using distilled water.
- 5) Titrate to a dead stop (use the keypad START key, this will automatically fill up the burette with thiosulphate for each titration). Note the result on the worksheet.
- 6) Add a second 1 ml aliquot of iodate and titrate to a dead stop, then a third aliquot and titrate again to a dead stop. Record each result on the worksheet.

The values are written on the worksheet then typed into the spreadsheet with the sample values, to calculate the blank value. The blank measurement is calculated from the first reading minus the mean of the second and third reading; the blank reading is calculated from the mean of the blank measurements made for each conical flask. This whole procedure should be repeated for a minimum of three readings which must be consistent to within 0.002 ml. A 0.002 ml difference in blank measurements results in a 0.0334% change in the oxygen result calculated.

## 7.2 Standardisation of the thiosulphate titrant

The thiosulphate normality is checked against an iodate standard of known normality. The normality of the titrant should be checked every time the thiosulphate reservoir is topped up, it is also checked when a new batch of iodate standard is prepared. The volumetric flask used to prepare the iodate, the weight of iodate used and the calibration of the pipette or exchange unit used to dispense it should be noted down on the worksheet.

- 1) The parameter menu on the Titrimo key pad should be set for a 0.3 ml start volume of titrant to reduce the titration time.
- 2) The conical flasks must be thoroughly washed as for the blank measurements to ensure that they are free of manganese contaminants, then filled with about 90 ml of distilled water. Alternatively the same flask and reagents as used to measure the blank can be used for a standard, this appears to give better precision but as the effect of the blank has already been accounted for it must not then be subtracted from the standard measurement in the final spreadsheet. Seawater must not be substituted in either the standardisation or blanking as it has its own 'blank'.
- 3) Add 1 ml sulphuric acid and the stir bar to the distilled water and stir on the mixer before adding 1 ml of sodium iodide-sodium hydroxide then if the solution is colourless add 1 ml of manganous chloride. If the solution is not colourless before the addition of the last reagent discard and wash the flask again. Continue stirring after the addition of each reagent. All reagents must be added using the same pipettes as used for the samples on deck.
- 4) Add exactly 10 ml of potassium iodate standard using a glass Knudsen pipette or the 10ml exchange unit on a Dosimat driver unit. Whichever unit is used the calibration must be known, the reservoir of iodate must be checked regularly and topped up with iodate standard from the same batch when necessary. Wash the standard down into the solution using distilled water if necessary. Stir and then titrate to a dead stop.

Record the results on the worksheet and repeat until the results agree to within 0.5 % for a minimum of three readings. As a guide 10 ml of a 0.01N (0.3567g/l) solution of iodate titrated with a 0.02N (5g/l) solution of thiosulphate, dispensed from a 10 ml exchange unit, results in a titrant addition close to 5 ml. The same iodate quantities measured using 25g/l thiosulphate, dispensed from a 5 ml exchange unit, should give results close to 1 ml of titrant

addition. The results must be transferred to the Macintosh spreadsheet, following transcription checking from the printer.

### **7.3 Sample measurement**

Sample analysis can be started one hour after sample collection, when the precipitate has settled out. The parameter listing should be set up for a start volume of 0.3 ml of titrant using the PARAMETERS settings on the Titrino keypad. Before each run thoroughly flush the burette out. Run at least three dummy samples until the results are consistent. Check that the aspirator tip is close to the electrode to improve precision, preferably below the electrode tips and that the mix speed remains constant at 3 units.

- 1) Slowly remove the stopper from the sample to avoid any sample loss and put a stir bar into the precipitate.
- 2) Mix on the stirrer then add 1 ml of sulphuric acid. Start the titration as soon as the precipitate has disappeared. Titrate to a dead stop. Whilst the automatic titration is being done check the bottle number and record its volume on the logsheet. The next sample can be taken out of the rack ready for titration.
- 3) Record the titration volume on the logsheet. The results are automatically printed out. Annotate the printout, result transcriptions can be checked from the printout before entering the results to a spreadsheet at the end of the run.
- 4) When the titration is complete remove the stir bar using a magnetic stir bar retaining rod, replace the stopper without emptying the contents of the bottle. Soak the stopper to clean away any manganous oxide which may contribute to sample contamination.

At the end of the run all of this waste solution must be disposed of and the oxygen sample flasks and stoppers rinsed out in tap water ready for the next batch of samples. Rinse and store the electrode in distilled water between runs.

If the same batch of sample bottles are used routinely in the same numeric order their unique volumes can be recorded on a template Macintosh spreadsheet to save the need for extra data entering.

## 8.0 CALCULATIONS

### 8.1 Spreadsheets and oxygen calculation

The oxygen spreadsheet contains information such as: new flask calibrations; iodate weights; Knudsen pipette calibrations; and any changes in bottle numbers i.e.: bottle volumes used. Blank and standard measurements are typed in as necessary. This information is held as a locked template spreadsheet, then for each station the new station number, bottle temperatures and titration volumes are added to this spreadsheet and it is saved with the new station number reference. The template spreadsheet in appendix (2) shows the formula and steps used in the calculation of the oxygen results, the equations are explained more fully below.

The oxygen concentration can be summarised as follows:

$$\text{oxygen concentration} = \frac{\text{blank corrected sample titration volume} * \text{thiosulphate normality} - \text{constant}}{\text{corrected bottle volume}}$$

#### 8.1.1 The blank corrected sample titre

This is the volume of thiosulphate dispensed in the titration of each sample minus the blank reading.

#### 8.1.2 The thiosulphate normality

The thiosulphate normality ( $N_{\text{thio}}$ ) is calculated from the mean of the thiosulphate standardisation titrations as follows:

$$N_{\text{thio}} = (N_{\text{IO}_3} * P_{\text{cal}}) / V_{\text{S}}$$

where

$N_{\text{IO}_3}$  = iodate normality

$P_{\text{cal}}$  = 10 ml Knudsen pipette calibration (ml)

$V_{\text{S}}$  = mean standard titration, blank corrected (ml)

The normality of iodate ( $N_{\text{IO}_3}$ ) is calculated as follows:

$$N_{\text{IO}_3} = 0.01 * (w_{\text{I}} / 0.3567) * (1000 / F_{\text{cal}})$$

where:

$w_t$  = weight of potassium iodate (g)

$F_{cal}$  = calibration of 1L volumetric flask (ml)

This assumes 0.3567g/l potassium iodate is 0.01N which is the case in air, when buoyancy corrected it is 0.0100025N. This will result in changes to the final oxygen calculation of 0.0501%.

#### 8.1.3 The constant:

The absolute amount of oxygen added with 2 ml of reagent has been determined by Murray et al. (1968) to be 0.0017 ml. This is multiplied by  $10^3$  to account for changes in the units from ml to  $\mu\text{mol}$  and divided by 22.4 to account for the number of moles of gas in 1 L. This is all multiplied by 4, as one mole of oxygen thiosulphate is equivalent to 4 moles of oxygen, to arrive at the constant 0.3036.

#### 8.1.4 The corrected bottle volume

The corrected bottle volume is calculated using the bottle temperature (the temperature will also be used at a later date in the conversion of  $\mu\text{mol/l}$  to  $\mu\text{mol/kg}$  units). It is calculated as follows using the formula detailed by Culberson in the WOCE manual (1991).

$$V_{cor} = V_{bot} * (1 + (10^{-5} * (T-20))) - V_{reg}$$

where:

$V_{reg}$  = The volume of sample displaced by the addition of reagents on deck (2 ml).

$V_{bot}$  = bottle volume as etched onto the glass (ml)

$T$  = fixing temperature on deck ( $^{\circ}\text{C}$ )

$V_{cor}$  = corrected bottle volume (ml)

20 = The reference temperature ( $^{\circ}\text{C}$ ) ie: of the temperature controlled laboratory, used if the bottle temperature is not known.

$1.0 * 10^{-5}$  = expansion factor for borosilicate glass

The corrected bottle volume is also multiplied by 4 at this stage (see the final WOCE equation below) to account for the equivalence of 1 mole oxygen to 4 moles of thiosulphate.

### 8.1.5 The WOCE equation

$$O_2 (\mu\text{mol/l}) = \frac{(((V_x - V_{\text{blk,dw}}) * N_{\text{thio}}) * 10^6) - 1000 * 0.303688}{(V_{\text{cor}} * 4)}$$

where:

$V_x$  = thiosulphate titre of the sample (ml)

$V_{\text{blk,dw}}$  = mean thiosulphate titre of pure water blanks (ml)

$N_{\text{thio}}$  = thiosulphate normality

$V_{\text{cor}}$  = corrected bottle volume (ml)

$10^6$  = conversion to  $\mu\text{mol}$  units

1000 = conversion to units per L relative to the  $C_{\text{cor}}$  given in ml.

## 8.2 Data processing

The oxygen spreadsheet used to calculate the results includes information on the bottle volumes and unique number. Individual oxygen spreadsheets for each box of oxygen bottles are created at the start of a cruise on the Macintosh. The spreadsheet can then be 'locked' using FILE INFO from the top menu to avoid errors and used as a template for each station using a particular box of oxygen bottles. The templates can be 'unlocked', changed and then locked again following changes in standardisation, blank measurements, changes in the sample bottle order, or in the volumetric flask or pipette used. An example of a template spreadsheet is shown in Appendix 2.

Some of the cells in the Excel spreadsheet have been highlighted to show where information is usually to be added, the rest of the spreadsheet involves constants and formula for calculating the final oxygen concentrations. At each station the sample titration volumes, temperature data, station number and sample number are added to the file manually, following data transcription checking, from the worksheets. The oxygen values are calculated automatically. The duplicate values must also be added and the duplicate differences checked. The file is then saved with a reference to the station number, for example 'oxy\*\*\*.dat' where '\*\*\*' is the station number.

The sample number, calculated oxygen and temperature data can then be copied and pasted into another locked template file 'oxy.text' (an example is shown in appendix 3). This file separates the sample value, duplicate values and reported values (normally the sample values are reported but if there was a problem with the analysis the value reported may be the

duplicate or '-999' if no reading is made). This file forms the intermediate step for reading the data into PSTAR.

Quality flags are applied to the data such as code '2' for acceptable data, '9' when no sample has been taken or '3' for questionable data. A list of the quality flags is shown in the appendix (4) and the use of these flags for WOCE data is fully explained in the WOCE manual. Quality flags are initially applied to the data in the 'oxy.text' file but can be modified later in PSTAR if necessary. The 'oxy.text' template file can be set up to default to flag '2' for the sample data (acceptable data) and '9' for the duplicates (no sample taken) as shown in appendix 3.

The 'oxy.text' file must be saved as a 'text' file (use 'save as' selecting 'options' then 'text') named as 'oxy\*\*\*.text' with reference to the station number. The duplicate data can be pasted into an ongoing duplicate file at this stage ('oxy.dups'). The duplicate file should include the sample number, bottle number, duplicate values and differences so that any consistent errors, in bottle volumes for example, can be seen. Macros can be set up for each of the three copy /paste stages.

In total there will be three files for each station: 'oxy\*\*\*.dat', 'oxy\*\*\*.text' and 'oxy.dups', which must be backed up on disk daily. The text files can then be copied into PSTAR. Once the data is in PSTAR property plots can be used to examine any trends, bias, flyers which may result in further changes to the data quality flag.

## **9.0 SOURCES OF ERRORS**

### **9.1 Sampling**

A lack of precision in the data may be due to errors occurring at the sampling stage, some of the most common errors are listed below

- 1) Stoppers not on tight enough which may result in losses.
- 2) Samples not shaken long and vigorously enough may not react fully. If the second shaking in the laboratory is not done this can adversely affect the precision.
- 3) Bubbles going unnoticed in the tubing and in the reagent dispensers may result in higher oxygen in the samples.
- 4) Loss of oxygen may result due to corrosion of metal surfaces, for example if the epoxy coating has worn away on the springs in the bottle.
- 5) Inaccurate temperature readings on deck due to faults in the temperature probe going unnoticed.

6) Wrong bottle volumes due to chips in the glass of the bottle or stopper.

It is important to ensure that the people doing the subsampling from the Niskin bottles know the affect of procedures on precision. As many of the errors affecting precision can happen during sample collection it is important to remember to look at the sample closely after the initial shaking on deck for any sign of bubbles, if any bubbles are seen empty the bottle and repeat sampling. Double check that the stoppers are tight and have not 'popped back'.

If precision is poor the following procedures should be checked:

- i) that all procedures used by the people taking the oxygen samples are standardised;
  - ii) that the second shaking in the laboratory is done;
  - iii) that poor duplicate precision does not consistently arise from one pair of oxygen bottles, i.e.: change the bottle used for duplicates and check for cracks and chips;
  - iv) that the pipettes are consistently dispensing the correct volume;
  - v) check that the Anachem dispenser tips are covered between stations to minimise bubble formation in the reagents and wash the whole unit out in distilled water when changing reagents and at least once a week to remove any reagent which may have crystallised out;
  - vi) check that the Niskin bottles are not leaking;
  - vii) check that the tubing is soaking between each station in order to lessen the likelihood of bubbles sticking to the sides and introducing errors;
  - viii) check the thermometer equipment before each run to ensure that there is no damage to the probe or electric components;
  - viii) check that the springs in the Niskin bottles have not been damaged or corroded.
- It is especially important at the start of the cruise that workers on the CTD team realise the importance of not damaging the epoxy coating on the springs when attaching the top and base of the Niskin bottle.

## 9.2 Analysis

Some of the common sources of errors are listed below

- 1) Volatilisation of iodine may occur resulting in losses if the titration is started too long after the acid has been added.
- 2) Bubbles in the burette. These may go unnoticed especially if they are at the top of the piston or in the darker tubing.

- 3) Sample spillage or loss due to stoppers being put on too tight or from not taking care to drag the last drop of sample from the stopper and into the bottle on removal of the stopper.
- 4) Contamination due to dirty stoppers.

All titrations should be started as soon as possible after the acid is added, as soon as the precipitate disappears to minimise volatilisation losses. All samples should be analysed within four hours.

Make sure the burette is filled and emptied two to three times before each run on a slow speed. Frequently check for bubbles at the top of the piston and also in the delivery tip. Check that all connections are tight. Make sure there is sufficient thiosulphate in the reservoir at the start of a run to complete it. Run dummy samples before each run to check the reproducibility of the readings.

Take care when removing stoppers to minimise losses, if they are too tight there is an increased risk of sample loss through spillage. Also some of the sample remains on the stopper, this last drop must be pulled off the stopper by dragging it across the top of the sample bottle. Make sure bottles are clean as the presence of stain from precipitate may contaminate samples.

To minimise problems of drift all analysis should be started one hour after sampling and should be carried out in one batch. Any drift across a run should be noted by running blanks or standards at the start and end of runs.

### **9.3 Calculations**

Care must be taken in ensuring that the right figures have been used in the spreadsheet to calculate the oxygen results. Transcription checking of the titrant volumes can be done from the printout. All of the other information, such as blank and standardisation results, can be checked from the worksheets. Errors in the calculation of the thiosulphate for example can result in over 5% changes to the results for a 0.002 change in the normality calculated. If the sample temperature differs by 2°C for example then the change in the calculated oxygen result of the samples will be in the order of 0.003%, likewise changes in the blank measurement of 0.02 units can change the oxygen result by 0.05%.

Table 2 illustrates the relative importance of the variables used in the calculation and details the effect of individual changes to these variables which result in a 0.1% change in the

final oxygen result. As the errors are additive then only much smaller changes could be tolerated to achieve the WOCE aim of 0.1% precision in results.

**Table 2**

**Percentage change in individual variables which result in a 0.1% change to the final oxygen calculation.**

Variable	% change in variable leading to a 0.1% change to the final result
Normality of thiosulphate	0.1
10 ml Knudsen pipette calibration	0.1
1L flask calibration	0.1
Total on deck reagent volume (2 ml)	5.6

Table 3 illustrates the percentage change on the oxygen result when the precision quotes made by the manufacturer are considered. Although the quoted estimates may be allowing for the worst these errors are still additive and the overall effect on data precision may be considerable aside from errors introduced through the technique or the method itself.

**Table 3**

**The % change in the final oxygen calculation resulting from the manufactures quotes of precision made for some of the equipment used in the analysis.**

Equipment	Error quoted	Change to final result (%)
Thermometer probe (Jenway)	0.1% accuracy	0.00002
Reagent dispenser (Anachem)	0.1 % precision	0.00075
Repeat pipette (Eppendorf)	0.2 % precision	0.00252
Standard pipette (Finn)	0.3 % CV precision	0.30061
Volumetric flask for std. (BDH)	0.04 % precision (0.4ml tolerance on 1000ml)	0.04007

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**Appendix 2:** Spreadsheet to calculate oxygen concentrations ('oxy\*\*\*.dat' template), formula and cells identified for each calculation (information normally hidden). Highlighted areas indicate where information is to be added for each run or on standardisation of the thiosulphate.

	A	B	C	D	E	F	G	H	I
1					Cell specific formula				
2	Cruise	D 213			B8=0.01*(B7/0.3567)*(1000/B6)				
3	Station No	example			D14=D11-((D12+D13)/2)				
4					B15=SUM(B14:D14)/3				
5	Iodate standard				B22=(B8*B17)/B21				
6	Vol flask calib.	1000.09			B26=B25*44.66*4				
7	wt.Iodate (g)	0.3602			F32=C32*(1+(10^-5*(D32-20)))-2				
8	Normality 20oC	0.01			I32=H58-H32				
9	Reagent Blank Correction				H32=(((E32-\$B\$15)*\$B\$22)*10^6)-1000*\$B\$26)				
10		First	Second	Third					/(F32*4)
11	1ml iodate	0.116	0.116	0.117					
12	second 1ml	0.115	0.114	0.115					
13	third 1ml	0.115	0.115	0.115					
14	Blank Vol	0.001	0.0015	0.002					
15	Mean Blank Vol	0.0015							
16	Standardisation of Thiosulphate Titrant								
17	Cor. Vol. 20oC	10.059							
18		first	second	third	fourth				
19	Titration Vol.	1.003	1.004	1.003	1.004				
20	mean	1.0035							
21	blank correct	1.002							
22	N(thio)	0.10038922							
23									
24	Reagent Dissolved O2 Correction (Murray,Riley and Wilson)								
25	Abs DO reg	0.0017	ml						
26	uequi-O2	0.3037							
27									
28	Oxygen results Page 2 Sample titration results								
29	Cruise	D 201							
30	Station No	example		fix T	titration	corr bo	sample	O2	Duplicate
31	Sample No	Ox Bot No	Bot Vol	(oC)	vol (ml)	volume	number	(uM/l)	Difference
32	1	1	115.05	3.79	0.632	113.026	1	139.33	-0.692
33	2	2	114.39	3.79	0.63	112.375	2	139.69	0.325
34	3	3	113.17	4.11	0.604	111.152	3	135.36	0.897
35	4	4	112.92	4.63	0.623	110.900	4	139.96	0.003
36	5	6	112.87	4.85	0.695	110.853	5	156.32	
37	6	7	114.25	5.16	0.728	112.233	6	161.78	
38	7	8	114.28	5.27	0.7	112.263	7	155.48	
39	8	9	114.33	5.8	0.677	112.318	8	150.26	
40	9	10	114.07	6.01	0.62	112.057	9	137.85	
41	10	11	116.38	6.22	0.557	114.362	10	121.24	
42	11	13	113.63	6.65	0.365	111.619	11	81.05	
43	12	14	114.69	7.39	0.357	112.678	12	78.51	
44	13	15	114.54	7.28	0.524	112.525	13	115.86	
45	14	17	114.02	10.45	0.55	112.010	14	122.22	
46	15	19	113.45	10.56	0.541	111.440	15	120.82	
47	16	20	114.71	12.05	0.719	112.705	16	159.10	
48	17	21	115.89	13.1	0.731	113.879	17	160.10	
49	18	22	113.08	13.42	0.745	111.069	18	167.32	
50	19	25	115.6	13.42	0.814	113.591	19	178.85	
51	20	26	113.77	13.63	0.928	111.759	20	207.38	
52	21	24	114.3	16.17	0.68	112.295	21	150.97	
53	22	57	113.61	18.39	0.68	111.604	22	151.90	
54	23								
55	24								
56									
57	Duplicates:-								
58	1	58	115.61	3.79	0.632	113.590	1	138.64	
59	2	23	114.13	3.79	0.63	112.114	2	140.02	
60	3	27	116.31	4.11	0.625	114.289	3	136.25	
61	4	28	113.27	4.63	0.625	111.256	4	139.97	

**Appendix 3:**

Template of the 'oxy\*\*\*.text' file. Calculated results are transferred to this file and quality flags attached to the data.

sampnum	statnum	bottemp	botoxya	botoxyaf	botoxyb	botoxybf	botoxy	botoxyfl
23801	12238			2	-999	9	-999	2
23802	12238			2	-999	9	-999	2
23803	12238			2	-999	9	-999	2
23804	12238			2	-999	9	-999	2
23805	12238			2	-999	9	-999	2
23806	12238			2	-999	9	-999	2
23807	12238			2	-999	9	-999	2
23808	12238			2	-999	9	-999	2
23809	12238			2	-999	9	-999	2
23810	12238			2	-999	9	-999	2
23811	12238			2	-999	9	-999	2
23812	12238			2	-999	9	-999	2
23813	12238			2	-999	9	-999	2
23814	12238			2	-999	9	-999	2
23815	12238			2	-999	9	-999	2
23816	12238			2	-999	9	-999	2
23817	12238			2	-999	9	-999	2
23818	12238			2	-999	9	-999	2
23819	12238			2	-999	9	-999	2
23820	12238			2	-999	9	-999	2
23821	12238			2	-999	9	-999	2
23822	12238			2	-999	9	-999	2
23823	12238			2	-999	9	-999	2
23824	12238			2	-999	9	-999	2

**Appendix 4:**

WOCE data quality flags used in oxygen analysis. These are more fully explained in the WOCE manual.

<u>Quality flag</u>	<u>Definitions</u>
1	Sample for this measurement was drawn from the water bottle but analysis was not received
2	Acceptable measurement
3	Questionable measurement
4	Bad measurement value still reported
5	Value not reported, may be due to bad measurement, sample loss or contamination
9	Sample not drawn for this measurement from this bottle

**Appendix 5:**

Calibrations of the 1L flask and the Knudsen pipettes used to show the procedure for calibration involving air buoyancy corrections.

Oxygen corrections								
Calibration of volumetric flasks and Knudsen pipettes								
Density of pure water vs temperature								
formula for								
density	$0.99842594 + 6.793952 \times 10^{-5} \cdot t - 9.09529 \times 10^{-6} \cdot t^2 + 1.001685 \times 10^{-7} \cdot t^3 - 1.120083 \times 10^{-9} \cdot t^4 + 6.536332 \times 10^{-12} \cdot t^5$							
measured								
temperature	0	5	10	15	20	25	21.7	24
density calc								
at obs temp	0.99984	0.99997	0.99970	0.99910	0.99821	0.99705	0.99784	0.99730
Calibration of volumetric flasks								
	weight water	Bouyancy	Density Corrected					
Flask No.	to line at 20oC	corrected	True Volume at 20oC					
1	497.7	498.2226	499.1178					
2	497.74	498.2626	499.158					
3	498	498.5229	499.4187					
4	997.25	998.2971	1000.091					
Calibration of Knudsen Pipettes								
	SUDO	pipetteA	pipetteB					
		170393	17393					
	10.033	9.895	9.893					
	10.042	9.883	9.899					
	10.034	9.881	9.889					
	10.034	9.889	9.896					
	10.031	9.898	9.895					
	10.033	9.892	9.899					
	10.035	9.886	9.898					
	10.035	9.887	9.895					
	10.038	9.896	9.901					
stdev %	0.324037035	0.595819	0.365529					
mean	10.035	9.889667	9.896111					
bouy corr	10.04553675	9.900051	9.906502					
den corr	10.06358761	9.91784	9.924303					

**Appendix 6:**

A list of the wide neck oxygen sample bottles in use with unique number and calibrated volume (ml)

number	volume (ml)	number	volume (ml)	number	volume (ml)
2	114.394	43	113.511	84	116.398
3	113.17	44	112.619	85	116.342
4	112.917	45	114.286	86	116.73
6	112.87	46	114.11	87	115.664
7	114.25	48	113.368	88	116.231
8	114.28	50	115.453	89	117.165
9	114.334	51	115.685	90	114.591
10	114.073	52	113.293	91	117.309
11	114.28	53	114.691	92	116.298
13	113.634	55	113.638	93	116.357
14	114.692	57	113.606	94	116.465
15	114.54	58	115.609	95	115.773
17	114.021	59	112.103	96	116.113
19	113.451	60	113.742	97	116.113
20	114.3714	61	116.525	99	116.782
21	115.887	62	115.595	100	116.401
22	113.076	63	116.277	101	116.998
23	114.133	64	116.03	102	117.267
24	114.299	65	116.858	103	113.89
25	115.599	66	116.317	105	115.893
26	113.766	67	116.118	106	117.053
27	116.307	68	116.143	107	115.977
28	113.273	69	116.298	108	115.845
29	114.602	70	116.78	109	113.465
30	113.046	71	114.74	110	117.496
31	114.439	72	116.796	111	113.918
32	113.218	73	117.367	112	115.204
33	112.856	74	117.474	113	115.429
34	111.729	76	116.759	114	116.047
36	114.559	77	115.709	115	113.595
37	113.205	78	112.957	116	116.376
38	114.539	79	116.209	117	118.395
39	112.983	80	116.477	118	116.709
40	113.868	81	116.117	119	116.329
41	115.078	82	115.938	120	115.779
42	114.361	83	116.312		

number	volume (ml)	number	volume (ml)	number	volume (ml)
121	110.189	157	112.211	193	107.883
122	109.967	158	111.847	194	111.519
123	109.901	159	110.888	195	109.453
124	110.350	160	113.268	196	109.916
125	109.436	161	110.278	197	110.146
126	110.327	162	110.850	198	113.476
127	109.460	163	107.896	199	110.852
128	109.382	164	111.056	200	112.862
129	110.630	165	110.643		
130	110.313	166	111.623		
131	109.766	168	109.081		
132	109.332	169	110.597		
133	109.251	170	113.297		
134	110.273	171	108.810		
135	109.763	172	112.856		
136	111.344	173	111.141		
137	109.205	174	108.694		
138	110.295	175	109.518		
139	110.438	176	110.396		
140	108.319	177	109.324		
141	108.998	178	112.407		
142	111.063	179	108.297		
143	110.230	180	108.486		
144	110.128	181	109.721		
145	110.400	182	109.520		
147	109.445	183	108.840		
148	108.723	184	111.166		
149	110.611	186	108.198		
150	110.027	187	108.694		
151	109.859	188	110.826		
152	110.065	189	110.359		
154	112.132	190	113.074		
155	109.337	191	110.037		
156	111.561	192	112.325		

**Appendix 7:**

Quantities of chemicals taken on a typical 6 week cruise (with approximately 100 stations of 24 bottles).

Chemical	Amount used	Quantity to take	Packaging
Sodium thiosulphate	10 x 25g	15 x 25g	dry in vials
Potassium iodate	4 x 0.3567g	8 x 0.3567g	.
Sulphuric acid	3 x 2.5L	6 x 2.5L	dangerous goods
Manganous chloride	2 x 2.5L	4 x 2.5L	packaging
Alkaline iodide	2 x 2.5L	4 x 2.5L	.

Note: Sodium thiosulphate diluted 1/5 from 25g/l to 5g/L if required.

