Dissolved Oxygen

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1.   Introduction

This chapter describes procedures to be used for the calibration of volumetric glassware, for the calculation of oxygen concentrations, for the preparation of reagents, and for water sampling in the Winkler method for dissolved oxygen. These procedures are based on the Chesapeake Bay Institute technique for the Winkler dissolved oxygen method (Carpenter, 1965). All participants in WOCE are expected to closely follow Carpenter's method for the measurement of dissolved oxygen in discrete water samples.

Carpenter's (1965) modification of the Winkler technique is reproducible (2 standard deviations) to ± 0.010 mL/L (± 0.4 μmol/kg-sw: approximately 0.2% of air saturated O_2 concentrations). Achieving this level of precision, however, requires scrupulous attention to detail.

The elimination of iodine loss by volatilization is the essential element of Carpenter's technique. This is accomplished by optimizing the concentrations of the pickling reagents ($MnCl_2$, NaOH/NaI, H_2SO_4), and by adopting a whole bottle titration which eliminates iodine loss during sample transfer.

Institutions which titrate aliquots, rather than the entire oxygen sample, must demonstrate that their technique does not exhibit systematic errors, when compared to whole bottle titrations. All institutions muse use the pickling reagent concentrations specified by Carpenter (1965); no exceptions are allowed.

This chapter is not meant to be a cookbook or recipe which lists each step necessary to determine dissolved oxygen. Rather, its purpose if (1) to specify algorithms for calibration of volumetric glassware, and (2) to discuss those aspects of Carpenter's method which are ambiguous or which require modification.

2.   Calibration of Volumetric Apparatus

For ease of use aboard ship, Carpenter's method uses volumetric techniques to dispense solutions and to collect samples. To achieve the highest accuracy, all volumetric glassware must be calibrated. For instance, it is not unusual for the volumes of Class A analytical pipets to differ by 0.3% from the nominal volume.

Volumetric apparatus used in Carpenter's procedure, include the following:

a. oxygen flasks (iodine flasks, 125 cm^3 nominal capacity)

b. 10 cm^3 pipet used to dispense the iodate standard

c. 1 cm^3 pipet used to dispense iodate for blank determinations

d. 1 cm^3 volumetric flask used to prepare the iodate standard

e. piston buret

With the exception of item c, all volumetric apparatus must be calibrated to contain or deliver. Since blanks are determined by difference, the exact calibration of item c is not essential, as long as the same volume is dispensed each time.

The volumetric apparatus should be calibrated by measuring the weight of pure water contained or delivered at a reference temperature of 20.0° C. All weights must be corrected for air buoyancy. The following equations should be used to calculate the true volume from the measured weight of water in air.

2.1   Volume of Apparatus at Calibration Temperature

The volume of glassware at some calibration temperature, $V(t_c)$, is the quotient of the mass of water contained or delivered to the density of pure water,

$$V(t_c) \;=\; W_w \;\cdot\; f_{buoy}/\rho_w \tag{1}$$

where W_w is the weight of water in air, f_{buoy} is the buoyancy correction, and ρ_w is the density of pure water at the calibration temperature, t_c.

2.1.1   Density of pure water

The density of pure water, ρ_w, is needed to transform the measured mass of water into an equivalent volume of water. Over the temperature range, 0 - 40°C, the density of pure water (units: g $\cdot$ cm-3) is (Bigg, 1967):

$$
\begin{aligned}
\rho_w \;=\; & 0.999842594 + 6.793952 \cdot 10^{-5} \cdot t - 9.095290 \cdot 10^{-6} \cdot t^2 + \\[2mm]
& 1.001685 \cdot 10^{-7} \cdot t^3 - 1.120083 \cdot 10^{-9} \cdot t^4 + 6.536332 \cdot 10^{-12} \cdot t^5
\end{aligned}
\tag{2}
$$

where t the water temperature in °C.

2.1.2 Buoyancy correction

Since the weight of objects in air is less than that in vacuum, a buoyancy correction must be applied to the weight of pure water contained or delivered by volumetric glassware. This correction is given by,

$$f_{\text{buoy}} = \frac{1 - \rho_{\text{air}}/\rho_{\text{weights}}}{1 - \rho_{\text{air}}/\rho_{\text{w}}} \qquad (3)$$

where,

ρ_{air} = density of air at the temperature and pressure of the weighing operation (≈ 0.0012 g $\cdot$ cm^{-3} at $20°$C),

ρ_{w} = density of pure water (≈ 1.0 g $\cdot$ cm^{-3} for water), and

ρ_{weights} = density of balance calibration weights (≈ 8.0 g $\cdot$ cm^{-3}) for stainless steel, ≈ 8.4 g $\cdot$ cm^{-3} for brass).

For weighing temperature between 10 and $30°$C, use of the approximate buoyancy factor,

$$f_{\text{buoy}} = 1.00105 \qquad (4)$$

will result in an error of less than 0.01%.

2.2 Change of Glass Volume with Temperature

Since glass expends upon heating, the volume of glassware increases slightly with increasing temperature. The volume at temperature t_2 $°$C, $V(t_2)$, is related to the volume at temperature t_1 $°$C, $V(t_1)$, by the formula,

$$V(t_2) = V(t_1) \cdot [1 + \alpha_{\text{v}}(t_2 - t_1)] \qquad (5)$$

where α_{v} is the cubical coefficient of thermal expansion for the particular glass. For borosilicate glass, α_{v} is approximately $1.0 \cdot 10^{-5}$; for soft glass, α_{v} is approximately $2.5 \cdot 10^{-5}$. The change in volume of glass apparatus with temperature is quite small. For borosilicate glass, the volume changes only 0.01% for a $10°$C temperature difference.

Equation (5) is used to reduce calibrated glassware volumes to the standard temperature, $20°$C; and to reduce oxygen flask volumes from the standard temperature to the sampling temperature.

2.2.1   Volume of apparatus at standard temperature

The volume of glassware, calibrated at temperature t_c ° C, at a reference temperature of 20°C can be calculated from equation (5). Setting t_1 equal to the calibration temperature, t_c °C; and t_2 to the reference temperature, 20°C; yields,

$$V(20) \;=\; V(t_c) \cdot [1 + \alpha_v (20 \;-\; t_c)] \tag{6}$$

where,

$V(20)$ = volume of oxygen flask at reference temperature, 20°C,
$V(t_c)$ = volume of oxygen flask at calibration temperature, t_c °C, from
equation (1).

2.2.2   Volume of oxygen flask at sampling temperature

To calculate the concentration of oxygen in a seawater sample, the volume of seawater contained in the oxygen flask when the sample was pickled must be known.

Due to the thermal expansion of glass, the volume of the oxygen flask will depend slightly on the temperature of the seawater used to fill the flask (see equation (5) above),

$$V_{bot} \;=\; V(20) \cdot [1 + \alpha_v (t_{sw} - 20)] \tag{7}$$

where,

V_{bot} = volume of oxygen flask at temperature t_{sw}°C,

$V(20)$ = volume of oxygen flask at reference temperature, 20°C, from equation (6), and

t_{sw} = seawater temperature at the time of pickling.

2.2.3   Sample calculations of glassware calibration

Tables 1 and 2 give actual calibration data and calculated volumes for an oxygen flask and a 10 cm^3 pipet. The density of pure water was calculated from equation (2), the buoyancy factor from equation (3), the volume at the calibration temperature from equation (1), and the volume at 20°C from equation (6).

Table 1

Sample calibration of an oxygen flask using WOCE equations. Calibration temperature, 21.7°C; buoyancy factor calculated using density of stainless steel weights, and the cubical coefficient of thermal expansion for borosilicate glass.

	Weights in air		Density	Buoyancy	Volume at	
Empty	Full	Water	water	factor	21.7°C	20.0°C
84.51	230.58	146.07	0.997841	1.001054	146.540	146.538

Table 2

Sample calibration of a 10 mL pipet using WOCE equations. Calibration temperature, 24.0°C; buoyancy factor calculated using density of stainless steel weights, and the cubical coefficient of thermal expansion for borosilicate glass.

	Weights in air		Density	Buoyancy	Volume at	
Empty	Full	Water	water	factor	24.0°C	20.0°C
17.2015	27.1273	9.9258	0.997299	1.001055	9.9632	9.9628

3.   Calculation of Dissolved Oxygen Concentration

3.1   Titration of an Aliquot

Equations for calculating the concentration of dissolved oxygen from the results of aliquot titrations of acidified oxygen samples are more complex than those for whole bottle titrations (equation (8) below); the exact form of the equations will depend on the titration and standardization procedures used by each institution. Consequently, no general algorithm can be given for calculating the oxygen concentration from the results of aliquot titrations. Institutions performing aliquot titrations must submit the equations that they use to calculate dissolved oxygen concentration to the WOCE Hydrographic Programme Office for verification and approval.

3.2   Whole Bottle Titrations

The concentration of dissolved oxygen, determined from whole bottle titrations, should be calculated form equation (8). Equation (8) differs from Carpenter's (1965) equation for whole bottle titrations in the correction for oxygen added with the reagents. In equation (8), the correction for oxygen added with the reagents is a function of the flask volume; whereas, in Carpenter's equation, a constant correction, 0.018 mL/L, is used.. The use of a constant value for the concentration of oxygen added with the reagents is only correct if all flasks have identical volumes. The value of DO_{reg} in (8) is a measured value (Murray $et~al$, 1968), rather than the estimated value used by Carpenter (1965).

$$
O_2 ~=~ \frac{\dfrac{(V_x - V_{blk,dw}) \cdot V_{IO_3} \cdot N_{IO_3} \cdot 5598}{(V_{std} - V_{blk,dw})} - 1000 \cdot DO_{reg}}{(V_{bot} - V_{reg})} \tag{8}
$$

Terms in equation (8) have the following meaning. All volumes are expressed in cubic centimeters.

$$
\begin{aligned}
V_x \quad &= \quad \text{thiosulfate titer of sample (cm}^3) \\[2mm]
V_{\text{blk,dw}} \quad &= \quad \text{thiosulfate titer of pure water blank (cm}^3) \\[2mm]
V_{\text{std}} \quad &= \quad \text{thiosulfate titer of standard (cm}^3)
\end{aligned}
$$

V_{bot} = volume of sample bottle (cm^3) at the temperature of sampling

V_{reg} = volume (2 cm^3) of sample displaced by reagents

V_{IO3} = volume of iodate standard (cm^3) at temperature of standardization

N_{IO3} = normality of iodate standard (=6·molarity) at temperature of standardization

DO_{reg} = absolute amount of oxygen added with reagents, 0.0017 mL (Murray *et al*, 1968)

O_2 = oxygen concentration in sample (mL/L)

3.3   Conversion of Volumetric to Weight Concentrations

Oxygen concentrations must be reported in units of micromol per kilogram of seawater (μmol/kg-sw). Oxygen concentrations in mL/L calculated from equation (8) can be converted to units of μmol/kg-sw by the following equation,

$$
O_2(\mu\text{mol/kg} - \text{sw}) \; = \; 44.660 \cdot O_2(\text{mL/L})/\rho_{\text{sw}} \tag{9}
$$

where ρ_{sw} is the density of seawater at the temperature at which the oxygen sample was pickled. If the seawater temperature at the time of pickling is not known, the density of seawater in equation (9) should be calculated at the potential temperature of the water sample. The value 44.660 equals (1000/molar volume of oxygen gas at STP) (Weiss, 1981).

3.3.1   Density of seawater

The density of seawater, ρ_{sw}, is needed to convert volumetric oxygen concentrations (mL/L) to mass concentrations (ρmol/kg-sw). Between 0 and 40°C, and 0.5 to 43 salinity, the density of seawater at 1 atmosphere (units: g $\cdot$ cm^{-3}) is Millero and Poisson, 1981),

$$
\rho_{\text{sw}} = \rho_{\text{w}} + A \cdot S + B \cdot S^{1.5} + C \cdot S^2 \tag{10}
$$

where S is the salinity, t is the temperature, in °C, and

$$A = 8.24493 \cdot 10^{-4} - 4.0899 \cdot 10^{-6} \cdot t + 7.6438 \cdot 10^{-8} \cdot t^2 -$$
$$8.2467 \cdot 10^{-10} \cdot t^3 + 5.3875 \cdot 10^{-12} \cdot t^4 \tag{11}$$

$$B = -5.72466 \cdot 10^{-6} + 1.0227 \cdot 10^{-7} \cdot t - 1.6546 \cdot 10^{-9} \cdot t^2 \tag{12}$$

$$C = 4.8314 \cdot 10^{-7} \tag{13}$$

3.3.2 Sample calculation of oxygen concentration

Table 3 provides actual titration data and calculated oxygen calculations for 2 whole bottle titrations.

Table 3

Sample calculations of dissolved oxygen concentration.

Oxygen flask volume at 20°C: 146.538 mL

Parameters in equation (8):

V_{blk}	=	-0.0004
V_{IO3}	=	9.9784
N_{IO3}	=	0.01014
V_{std}	=	0.7180
V_{reg}	=	2
DO_{reg}	=	0.0017

Temperature of sampling	Salinity	Oxygen flask volume at sampling temperature	Dissolved Oxygen	
			mL/L	μmol/kg-sw
10.78°C	35.398	146.524 mL	3.3738	147.06
2.19°C	34.915	146.512 mL	6.1839	269.64

3.4   Effect of Temperature on Mass of Thiosulfate and Iodate Dispensed

The thermal expansion of aqueous solutions is much greater than that of glass. Consequently, the mass of solution dispensed by pipets and burets depends on the temperature of the solution. In figure 1, the ratio of the mass of pure water dispensed at temperature t °C to the mass dispensed at 20°C is plotted versus the solution temperature. The values plotted in the figure are corrected for the thermal expansions of both water and glass. However, almost all of the variation is due to the thermal expansion of water.

The figure shows that, at 20°C, the mass of solution dispensed changes about 0.1% for a 5°change in solution temperature. In equation (8), it is the masses of thiosulfate and of the iodate standard which will be affected by thermal expansion of the solution.

The thiosulfate volumes (V_x, V_{std}) occur as a ratio in equation (8). Consequently, mass changes due to thermal expansion of the thiosulfate titrant will cancel if temperatures during standardization are close to those during sample analysis.

The effects of thermal expansion are more serious for the iodate standard. Room temperature should be measured during each thiosulfate standardization so that the mass of the iodate standard dispensed can be calculated. Assuming a reference temperature of 20 °C, the volume of the iodate pipet at the standardization temperature, t_{std} °C;, is (see equation (5)),

$$V_{IO3} = V(t_{std} = V(20) \cdot [1 + \alpha_v (t_{std} - 20)]. \tag{14}$$

The iodate normality (= 6· molarity) at temperature, t_{std} °C, can be calculated as,

$$N_{IO3}(t_{std} = N_{IO3}(20) \cdot [\rho_w(t_{std})/\rho_w(20)] \tag{15}$$

where,

$N_{IO3}(20)$ = normality of iodate standard (= 6·molarity) at 20°C,

$\rho_w(t_{std})$ = density of pure water at standardization temperature, and

$\rho_w(20)$ = density of pure water at reference temperature, 20°C.

Substituting the pure water density for the density of dilute KIO_3 in equation (15) will not cause significant error.
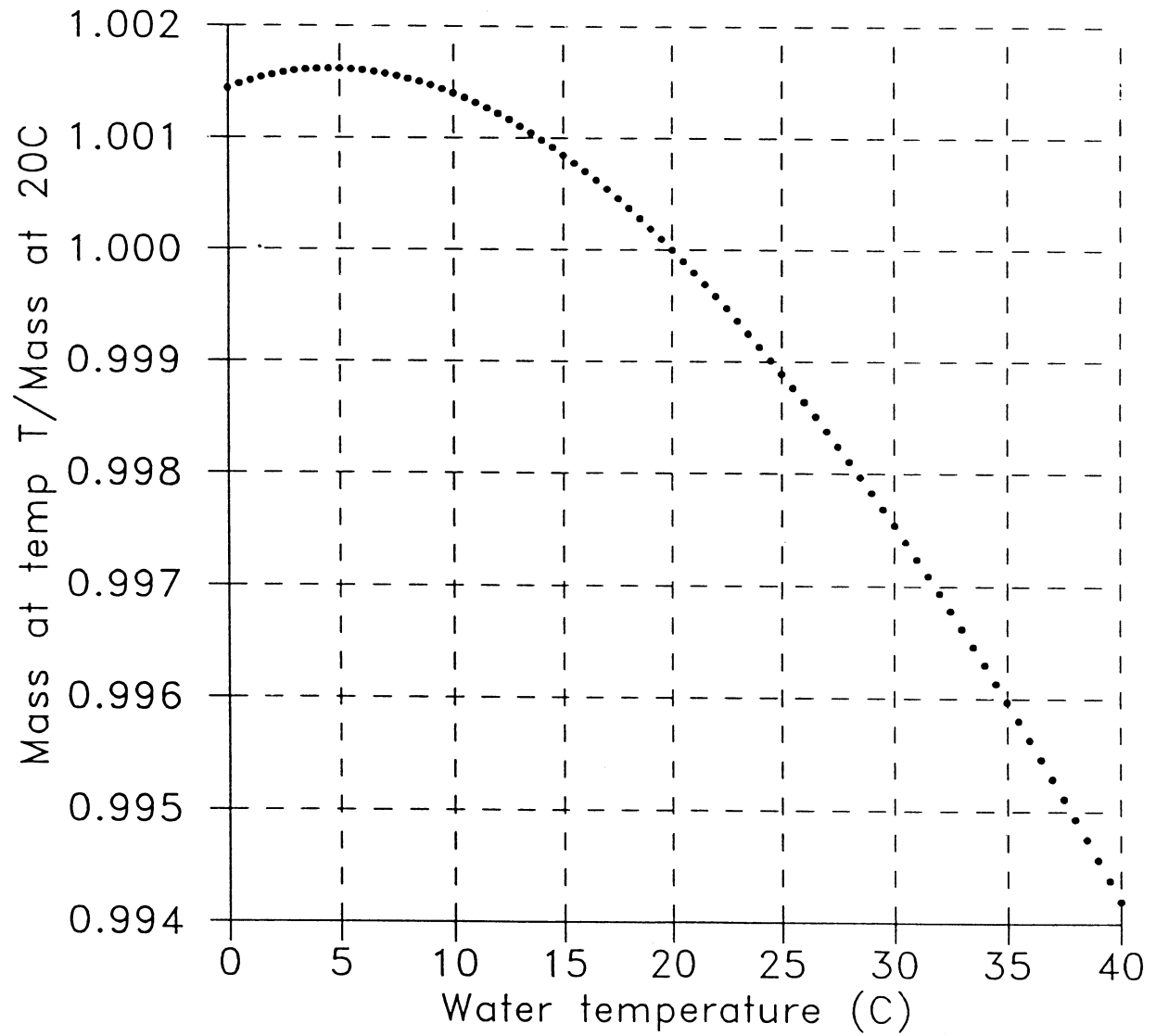
Figure 1: Effect of temperature on mass of water dispensed due to thermal expansion of water and glass.

4.   Preparation of Reagents

Reagents used in Carpenter's procedure include the following:

a.	$MnCl_2 \cdot 4H_2O$	600 g/liter, 3 molar
b.	NaOH	320 g/liter, 8 molar
	NaI	600 g/liter, 4 molar
c.	H_2SO_4	280 mL concentrated H_2SO_4/liter, 5 molar
d.	Starch	1% solution
e.	$Na_2S_2O_3 \cdot 5H_2O$	35 g/liter, 0.14 molar
f.	KIO_3	0.3567 g/liter, 0.001667 molar

With the possible exceptions of the starch, thiosulfate and iodate solutions, all institutions involved in WOCE oxygen measurements must use the reagent concentrations specified by Carpenter (1965). Reagent solutions should be prepared from reagent grade (or better) chemicals.

4.1   Manganous Chloride

The substitution of manganous sulfate for manganous chloride is allowed because the solubility of oxygen in 3 molar $MnSO_4$ does not appear to have been measured (Murray *et al*, 1968). Consequently, the correction for oxygen added with the reagents, DO_{reg}, in equation (8) is uncertain when manganous sulfate is used in place of $MnCl_2$.

4.2   Sodium Thiosulfate

Note that the chemical formula for sodium thiosulfate is misprinted in the table labeled *Reagent Solutions* on page 141 of Carpenter's (1965) paper. The correct formula is $Na_2S_2O_3 \cdot 5H_2O$.

4.3   Potassium Iodate Standard

The measured weight of KIO_3 used to prepare the iodate standard must be corrected for air buoyancy. The buoyancy factor for KIO_3 calculated from equation (3), assuming the density of KIO_3 equals 3.89 g·cm^{-3} (Hodgman, 1958), is 1.000159. The molecular weight of KIO_3 equals 214.001 (Commission on atomic weights and isotopic abundances, 1988).

Commercially prepared KIO_3 solutions are not allowed as standards. Experience has shown that the concentration of commercial standards may be in error by 0.5%.

The normality ($= 6 \cdot$molarity) of the KIO_3 standard at the temperature of preparation should be calculated from the following equations,

$$N_{IO3}(t_p) \;=\; \frac{W_{KIO3} \cdot f_{buoy,KIO3} \cdot 6}{V(t_p) \cdot 214.001} \tag{16}$$

$$V(t_p) \;=\; V(20) \cdot [1 \;+\; \alpha_v(t_p - 20)] \tag{17}$$

where,

$N_{IO3}(t_p)$	=	normality of iodate standard ($= 6 \cdot$molarity) at $t_p°C$,
W_{KIO3}	=	weight of KIO_3 in air,
$f_{buoy,KIO3}$	=	buoyancy correction for solid KIO_3 ($= 1.000159$),
214.001	=	1987 molecular weight KIO_3,
t_p	=	preparation temperature of KIO_3 solution,
$V(t_p)$	=	volume of volumetric flask at temperature, $t_p°C$, and
$V(20)$	=	volume of volumetric flask at $20°C$ reference temperature.

The normality ($= 6 \cdot$molarity) of the KIO_3 standard at the reference temperature $20°C$, is calculated from the following equation,

$$N_{IO3}(20) \;=\; N_{IO3}(t_p) \;\cdot\; [\rho_w(20)/\rho_w(t_p)]. \tag{18}$$

Substituting the pure water density for the density of dilute KIO_3 in equation (18) will not cause significant error.

5.   Water Sampling and Oxygen Analysis

Except for the changes noted below, all participants in WOCE are expected to adhere to the procedures given by Carpenter (1965) for the measurement of dissolved oxygen in discrete water samples.

5.1   Procedure for Samples

A six-inch piece of tygon tubing slipped over the outlet valve of the water sampler can be used as the drawing tube. Before filling each oxygen flask, run a small volume of

sample water through the drawing tube to remove air. Air bubbles frequently adhere to the sides of the drawing tube. If this occurs, tap the drawing tube to remove them before filling the oxygen flask. Bubbles are very likely to form on the sides of new tygon tubing. This problem can be avoided by soaking the tubing in seawater for several days prior to use.

Rinse the oxygen flask several times with sample water (≈ 30 cm^3) prior to filling; then fill the flask; and, finally, overflow it with at least 3 bottle volumes of sample water to minimize contamination with atmospheric oxygen. Overflowing the flask with copious amounts of sample water is the single most important factor in producing high-quality oxygen results.

Prior to sampling, the MnC1$_2$ and NaOH/NaI reagents should be placed near where the oxygen samples will be drawn. Add these two reagents immediately after each oxygen sample is drawn. Do not stopper the oxygen flasks before adding the MnC1$_2$ and NaOH/NaI reagents. The tip of the reagent dispensers should extend below the neck of the oxygen flasks, so that precipitate does not form in the excess seawater above the neck of the flasks.

The calculation of dissolved oxygen, equation (8), involves corrections for the volumes of MnC1$_2$ and NaOH/NaI added, and for the oxygen that they contain. The reagent dispensers must dispense exactly 1.00 cm^3. Their calibration should be checked, and adjusted if necessary, by dispensing ten 1 mL volumes into a 10 mL graduated cylinder. The solubility of oxygen in the reagents is temperature dependent. Since the value used for the concentration of oxygen in the reagents, DO$_{reg}$, is the air solubility at 25.5° C, it is important that the reagents be stored at a temperature as close to 25.5° C as possible. To maintain their temperature as constant as possible, the MnC1$_2$ and NaOH/NaI reagents should be stored in the laboratory, and only brought on deck when needed. These reagents should never be stored in the cold, since this will significantly increase their dissolved oxygen content.

5.2   Standardization

Carpenter (1965) does not add 1 mL of MnC1$_2$ to standards, even though it is added to blanks. Carpenter's standardization procedure should be modified to include the addition of 1 mL of MnC1$_2$ after the addition of the NaOH/NaI reagent. Standards should be determined in pure water, not in seawater.

5.3   Blank Determination

Blanks should be determined in pure water, not in seawater. The little information available on the magnitude of seawater blanks suggests that they are not constant but vary with depth and position. Rigorously then, seawater blanks should be determined at each depth that oxygen samples are taken. This does not appear feasible. Ignoring the seawater blank will introduce small, systematic errors into the oxygen calculations, but these errors will be the same for all institutions and will not affect the comparison of results from different institutions.

5.4   Replication and Precision

To provide a reliable estimate of analytical precision, duplicate oxygen samples should be titrated for at least 10% of the total number of samples taken. Duplicates should cover the entire range of observed oxygen concentrations, and should not be concentrated at any one concentration. The reproducibility of oxygen measurements (2σ), calculated from the above duplicates, must be $\leq 0.5\%$ of the highest oxygen concentration encountered. Each set of oxygen data submitted to WOCE must state the standard deviation of the data, and the number of replicates used to calculate the standard deviation.

5.5   Endpoint Detection

Photometric or amperometric endpoint detection may be substituted for the visual starch endpoint specified by Carpenter (1965).

6.   Acknowledgements

Must of the discussion in section 2, Calibration of Volumetric Apparatus, is taken from the unpublished notes of Andrew Dickson (1990). Some of the comments in section 5, Water Sampling and Oxygen Analysis, are based on the Marine Technicians Handbook from the Scripps Institution of Oceanography (Anonymous, 1971).

7.   References

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