

## **Determination of dissolved oxygen in sea water by Winkler titration**

Andrew G. Dickson  
Scripps Institution of Oceanography  
9500 Gilman Drive  
La Jolla, CA 92093-0902, USA

### **1. Scope and field of application**

This procedure describes a manual method based on the Winkler procedure for the determination of dissolved oxygen in sea water (Footnote 1). The method is suitable for the measurement of oceanic levels of oxygen (0–400  $\mu\text{mol}\cdot\text{kg}^{-1}$ ; Footnote 2) in uncontaminated sea water. (This method is unsuitable in sea water containing hydrogen sulfide.)

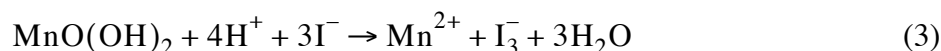
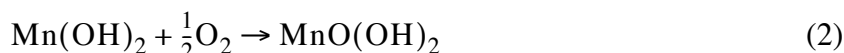
### **2. Definition**

The dissolved oxygen content of sea water is defined as the number of moles of dioxygen gas ( $\text{O}_2$ ) per kilogram of sea water.

### **3. Principle**

The basis of the Winkler procedure is that the oxygen in a sea water sample is made to oxidize iodide ion to iodine quantitatively (in the presence of an alkaline solution of manganese (II) ion); and the amount of iodine generated in this fashion is determined by titration with a standard thiosulfate solution. The end-point is located using starch as a visual indicator for the presence of iodine. The amount of oxygen present in the original sample can then be computed from the titer.

The relevant chemical reactions occurring in the solution are:



---

<sup>1</sup> A number of investigators have automated this procedure (using either changes in the absorption due to the triiodide ion to detect the endpoint—see e.g. Williams & Jenkinson, 1982—or an amperometric technique—see e.g. Culbertson & Huang, 1987). Such approaches are potentially more convenient than the manual method detailed here.

<sup>2</sup> Significantly higher levels of  $\text{O}_2$ —up to 535  $\mu\text{mol}\cdot\text{kg}^{-1}$ —have been observed in cold waters with high plankton blooms. See Note 11 for information on how to adapt this technique to handle such levels.

*i.e.* 1 mol of O<sub>2</sub> reacts with 4 mol of S<sub>4</sub>O<sub>6</sub><sup>2-</sup>. The thiosulfate solution is standardized against a gravimetrically prepared solution of potassium iodate which is in turn used to oxidize iodide ion to iodine:



The experimental measurement using this technique thus essentially determines the ratio between the concentration of iodate in a standard solution and the concentration of oxygen in the sample using thiosulfate as a transfer standard.

## 4. Apparatus

### 4.1 Sampling

- 4.1.1 Sample flasks: Erlenmeyer flasks of 125 cm<sup>3</sup> nominal capacity (“iodine” flasks) with ground glass stoppers (Footnote 3), calibrated in accordance with SOP 13 (Footnote 4).
- 4.1.2 Pickling reagent dispensers: two dispensers capable of dispensing 1 cm<sup>3</sup> aliquots of the pickling reagents (Footnote 5).
- 4.1.3 Flexible plastic drawing tube (Footnote 6), long enough to reach from the drain on the water sampler to the bottom of the sample bottle and with an internal diameter chosen to fit the sample bottle spigot (Footnote 7).
- 4.1.4 Thermometers: one thermometer is used to measure the water temperature at sampling to within 0.5 °C (Footnote 8), another is used to monitor the temperature of the laboratory—also to within 0.5 °C.

### 4.2 Titration apparatus

- 4.2.1 Titration box: an open-front box containing the titration apparatus. The walls of the box are painted white and adequate illumination is provided to enable the operator to see clearly the color change associated with the end point.
- 4.2.2 Burette: a piston burette with a 1 cm<sup>3</sup> capacity and an “anti-diffusion” tip.
- 4.2.3 Dispenser: capable of dispensing 1 cm<sup>3</sup> 5 M H<sub>2</sub>SO<sub>4</sub>.
- 4.2.4 Precise dispenser: capable of dispensing 1 cm<sup>3</sup> KIO<sub>3</sub> solution (used in the blank determination). The volume should be calibrated in accordance with SOP 12 (Note 4).
- 4.2.5 Precise dispenser of 10 cm<sup>3</sup> capacity (Footnote 9), used to dispense the standard KIO<sub>3</sub> solution. The volume should be calibrated in accordance with SOP 12 (Note 4).

---

<sup>3</sup> It is essential that each individual flask/stopper pair be marked to identify them and that they be kept together in subsequent use.

<sup>4</sup> The Standard Operating Procedures (SOPs) cited in this procedure for the volumetric calibration of glassware *etc.* refer to procedures detailed in DOE (1994).

<sup>5</sup> Confirm that the volume dispensed is accurate to ± 0.02 cm<sup>3</sup> by dispensing 10 aliquots into a measuring cylinder.

<sup>6</sup> Tygon<sup>®</sup> tubing is typically used for this purpose, however silicone rubber tubing can also be used.

<sup>7</sup> The drawing tube should be pre-treated by soaking in clean sea water for at least one day. This minimizes the amount of bubble formation in the tube when drawing a sample.

<sup>8</sup> It is convenient to incorporate a thermometer sensor into the drawing tube so that the water flows past the sensor on its way into the sampling bottle.

<sup>9</sup> For example, a Knudsen style pipette.

#### 4.2.6 Magnetic stirrer and a number of stirrer bars.

### 5. Reagents

- 5.1 Manganous chloride solution (3 M): Dissolve 600g of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  in deionized water, then dilute the solution with deionized water to a final volume of  $1 \text{ dm}^3$ . Finally, filter the solution through a coarse filter paper.
- 5.2 Sodium hydroxide (8 M) / sodium iodide solution (4 M): Dissolve 320 g NaOH in about  $500 \text{ cm}^3$  of deionized water, allow to cool, then add 600 g NaI and dilute with deionized water to a final volume of  $1 \text{ dm}^3$  (Footnote 10). Finally, filter the solution through a coarse filter paper.
- 5.3 Sulfuric acid solution (5 M): Slowly add  $280 \text{ cm}^3$  of concentrated  $\text{H}_2\text{SO}_4$  to  $770 \text{ cm}^3$  of deionized water. After cooling the final volume should be  $1 \text{ dm}^3$ .
- 5.4 Starch / glycerol indicator solution: Make a paste of 30 g of soluble starch in  $100 \text{ cm}^3$  glycerol ( $\text{HOCH}_2\text{CHOHCH}_2\text{OH}$ ), stir into about  $900 \text{ cm}^3$  glycerol. Heat the solution until it starts to boil. Cool.
- 5.5 Sodium thiosulfate (0.2 M): Dissolve 50 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in deionized water, then dilute the solution with deionized water to a final volume of  $1 \text{ dm}^3$  (Footnote 11).
- 5.6 Potassium iodate (0.0023 M): Dry high purity  $\text{KIO}_3$  in an oven at  $170^\circ\text{C}$ . Weigh out accurately about 0.5 g of  $\text{KIO}_3$ , dissolve it in deionized water and dilute the solution to a final volume of  $1 \text{ dm}^3$  in a calibrated volumetric flask (see SOP 13—Note 4). Note the temperature of the solution.

### 6. Sampling

#### 6.1 Introduction

Collection of water at sea, from the Niskin bottle or other sampler, must be done soon after opening the sampler and before much other water has been removed from it (Footnote 12). This is necessary to minimize exchange of  $\text{O}_2$  with the head space in the sampler.

---

<sup>10</sup> If sampling in an area of low oxygen ( $<5 \mu\text{mol} \cdot \text{kg}^{-1}$ ) with known high nitrite ( $>5 \mu\text{mol} \cdot \text{kg}^{-1}$ ), add 2 g of sodium azide ( $\text{NaN}_3$ ) to the solution before diluting to the final volume (Note:  $\text{NaN}_3$  is considered an extremely hazardous substance and should be handled appropriately).

<sup>11</sup> The concentrations for the  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{KIO}_3$  reagents used here are higher than were originally recommended by Carpenter (1965). This allows most oceanic  $\text{O}_2$  concentrations to be analyzed. If the highest concentrations of  $\text{O}_2$  expected are  $<280 \mu\text{mol} \cdot \text{kg}^{-1}$ , the original concentrations (0.14 M  $\text{Na}_2\text{S}_2\text{O}_3$  and 0.0017 M  $\text{KIO}_3$ ) are appropriate. If concentrations

In such cases, it may be appropriate to adjust the reagent concentrations (if a number of samples with high oxygen concentrations are expected), or simply to refill the burette and continue with the titration (for individual samples).

<sup>12</sup> It is difficult to collect an  $\text{O}_2$  sample without atmospheric contamination from a Niskin sampler with a volume of less than  $2 \text{ dm}^3$ .

## 6.2 Sampling procedure

6.2.1 *Confirm that the flask and stopper pair match.*

6.2.2 *Rinse the drawing tube*—Run a small volume of sample water through the drawing tube to remove air.

6.2.3 *Rinse the sample bottle*—If the bottle is not already clean and dry, it is rinsed twice by swirling with 30 cm<sup>3</sup> of fresh sample so as to remove any traces of reagents from a previous analysis (Footnote 13).

6.2.4 *Fill the sample bottle*—The bottle is filled smoothly, minimizing turbulence and avoiding aeration, from the bottom using a Tygon® tube which extends from the Niskin drain to the bottom of the glass sample bottle. The water is overflowed by three flask volumes (Footnote 14).

6.2.5 *Note sampling temperature*—Record the temperature of the water being sampled while the sample is overflowing the flask (Footnote 15).

6.2.6 *Add pickling reagents* —The MnCl<sub>2</sub> and the NaOH/NaI reagents should be added immediately after the sample is drawn (Footnote 16). The dispenser tips should be submerged at least 1 cm below the neck of the sample flasks before dispensing (Footnote 17).

6.2.7 *Close the bottle and mix*—The stopper is then inserted carefully into the flask, displacing the excess sea water but without trapping bubbles. The flask is then shaken vigorously to mix the contents thoroughly and to disperse the precipitate finely throughout.

6.2.8 *Shake the bottle a second time*—After the precipitate has settled at least halfway down the bottle (about 20 minutes), shake the bottle vigorously to disperse the precipitate.

6.2.9 *Storage*—Flasks containing pickled samples should be stored in a cool, dark, location until they are titrated.

## 7. Titration procedures

### 7.1 Determination of the blank (Footnote 18)

7.1.1 Place 50 cm<sup>3</sup> deionized water in a clean flask and add a magnetic stirring bar.

7.1.2 Add 1 cm<sup>3</sup> of standard potassium iodate solution using the calibrated dispenser.

7.1.3 Add 1 cm<sup>3</sup> of 5 M H<sub>2</sub>SO<sub>4</sub> and stir thoroughly.

7.1.4 Add 1 cm<sup>3</sup> of the NaOH / NaI reagent and stir thoroughly.

---

<sup>13</sup> This rinse water will leave a film that is approximately in equilibrium with atmospheric oxygen levels. For uncontaminated measurement of low oxygen levels it is best to use clean, dry, bottles.

<sup>14</sup> The amount of overflow water can be estimated by measuring how long it takes to fill a sample flask and allowing the water to overflow for a period of 3 times that.

<sup>15</sup> In subsequent calculations, it is assumed that the sample flask has also reached this temperature.

<sup>16</sup> Keep these reagents at about 25 °C as long as possible. The oxygen solubility is known at this temperature. If they are cooled, *e.g.* by being outside in cold weather, they will absorb additional oxygen from the atmosphere.

<sup>17</sup> This reduces contamination with atmospheric oxygen and ensures that the precipitate does not form in the excess sea water above the neck of the flask.

<sup>18</sup> A duplicate determination should always be done.

- 7.1.5 Add 1 cm<sup>3</sup> of the MnCl<sub>2</sub> reagent and stir thoroughly.
- 7.1.6 Fill flask to the neck with deionized water.
- 7.1.7 Titrate the liberated iodine with thiosulfate immediately to minimize loss of iodine by volatilization. Add thiosulfate, titrating the solution until it is a light straw color.
- 7.1.8 Add 0.3 cm<sup>3</sup> starch solution. This should give the sample a deep blue color.
- 7.1.9 Titrate precisely to the end-point—a clear solution—with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution.
- 7.1.10 Add a further 1 cm<sup>3</sup> of standard iodate solution.
- 7.1.11 Titrate the liberated iodine.

## 7.2 *Standardization of sodium thiosulfate titrant (Note 18)*

- 7.2.1 Place 50 cm<sup>3</sup> deionized water in a clean flask and add a magnetic stirring bar.
- 7.2.2 Add 10 cm<sup>3</sup> of standard potassium iodate solution using the calibrated dispenser.
- 7.2.3 Add 1 cm<sup>3</sup> of 5 M H<sub>2</sub>SO<sub>4</sub> and stir thoroughly.
- 7.2.4 Add 1 cm<sup>3</sup> of the NaOH / NaI reagent and stir thoroughly.
- 7.2.5 Add 1 cm<sup>3</sup> of the MnCl<sub>2</sub> reagent and stir thoroughly.
- 7.2.6 Fill flask to the neck with deionized water.
- 7.2.7 Titrate the liberated iodine with thiosulfate immediately to minimize loss of iodine by volatilization. Add thiosulfate rapidly at first, titrating the solution until it is a light straw color.
- 7.2.8 Add 0.3 cm<sup>3</sup> starch solution. This should give the sample a deep blue color.
- 7.2.9 Continue titrating to the end-point—a clear solution.
- 7.2.10 Record the room temperature.

## 7.3 *Titration of a sample*

- 7.3.1 Remove the ground-glass stopper.
- 7.3.2 Add 1 cm<sup>3</sup> of 5 M H<sub>2</sub>SO<sub>4</sub>.
- 7.3.3 Add a magnetic stirrer bar to the solution and begin stirring.
- 7.3.4 After most of the precipitate has dissolved, titrate the liberated iodine with thiosulfate immediately to minimize loss of iodine by volatilization. Add the thiosulfate rapidly at first, titrating the solution until it is a light straw color.
- 7.3.5 Add 0.3 cm<sup>3</sup> starch solution. This should give the sample a deep blue color.
- 7.3.6 Continue titrating to the endpoint—a clear solution (Footnote 19).
- 7.3.7 Record the room temperature.

## 7.4 *Clean flasks*

The flasks should be rinsed thoroughly with fresh water to remove traces of the reagents prior to their next use.

---

<sup>19</sup> If the endpoint is overtitrated, the sample can be “rescued” by the addition of 1.000 cm<sup>3</sup> of KIO<sub>3</sub> and then titrating to a new endpoint. It is then necessary to correct the final titre by  $V_1$  to obtain the titre appropriate to the original sample.

## 8. Calculation and expression of results

### 8.1 Titration blank

The “blank” results from the presence of redox species apart from oxygen in the reagents which can behave equivalently to oxygen in the analysis. It is given by the expression

$$V_{\text{blank}} = V_2 - V_1, \quad (6)$$

where  $V_1$  and  $V_2$  are the volumes of  $\text{Na}_2\text{S}_2\text{O}_3$  used to titrate the first and second aliquots of  $\text{KIO}_3$  respectively (Footnote 20).

### 8.2 Concentration of standard $\text{KIO}_3$ solution

The concentration of the standard  $\text{KIO}_3$  solution—corrected to 20 °C—is given by the expression:

$$M(\text{KIO}_3, 20\text{ °C}) = \frac{m(\text{KIO}_3)/(213.995\text{ g}\cdot\text{mol}^{-1})}{V_{\text{S}}} \times \frac{\rho_{\text{w}}(20\text{ °C})}{\rho_{\text{w}}(t_{\text{L}})}; \quad (7)$$

where  $m(\text{KIO}_3)$  is the mass of  $\text{KIO}_3$  that was made up with deionized water to a total volume,  $V_{\text{S}}$  (Footnote 21);

$$V_{\text{S}} = V_{\text{S}}(20\text{ °C})\{1 + \alpha_{\text{V}}(t_{\text{L}} - 20\text{ °C})\}. \quad (8)$$

213.995 g·mol<sup>-1</sup> is the molar mass of  $\text{KIO}_3$ ;  $\rho_{\text{w}}(t_{\text{L}})$  is the density of pure water at the laboratory temperature when the solution was prepared ( $t_{\text{L}}$ ) — see Appendix (A.1).

### 8.3 Molarity of $\text{Na}_2\text{S}_2\text{O}_3$ titrant

The molarity of the titrant can be calculated from the expression:

$$M(\text{Na}_2\text{S}_2\text{O}_3) = \frac{6 \cdot V(\text{KIO}_3) \cdot M(\text{KIO}_3)}{V_{\text{std}} - V_{\text{blank}}}, \quad (9)$$

where  $V_{\text{std}}$  is the average volume of titrant used to titrate  $V(\text{KIO}_3)$  of standard  $\text{KIO}_3$  solution. This expression is only exact if the measurements are performed at 20 °C: however, if the titrant is at approximately the same temperature as the  $\text{KIO}_3$  standard solution, errors in volume measurement will tend to cancel. Then, if the value used for  $M(\text{KIO}_3)$  refers to 20 °C, so will  $M(\text{Na}_2\text{S}_2\text{O}_3)$ .

<sup>20</sup> Some investigators also make a correction for the presence of other redox species apart from oxygen in the sample which can behave equivalently to oxygen in the analysis. These are typically estimated by measuring the “blank” directly in an aliquot of the sea water. This is not done here.

<sup>21</sup> The volume of the flask is corrected to the actual temperature measured when making up the solution (see SOP 13—Note 4).

#### 8.4 Oxygen in a sea water sample

Oxygen dissolved in the pickling reagents introduces oxygen into the sample prior to the analysis. The total number of moles of  $O_2$  reacted (sample + reagents) can be calculated from the expression

$$n(O_2) = \frac{1.5 \cdot (V - V_{\text{blank}}) \cdot V(KIO_3) \cdot M(KIO_3)}{V_{\text{std}} - V_{\text{blank}}}, \quad (10)$$

where  $V$  is the volume of titrant needed to titrate the sample. The factor 1.5 results from the fact that 1 mol of  $O_2$  can be considered to react with 4 mol of  $Na_2S_2O_3$  and 1 mol of  $KIO_3$  reacts with 6 mol of  $Na_2S_2O_3$  (see § 3)

It is assumed in writing (10) that the titrant had approximately the same temperature when titrating both the standards and the samples. It is, however, necessary to use values for  $V(KIO_3)$  and for  $M(KIO_3)$  appropriate to the laboratory temperature ( $t_L$ ).  $V(KIO_3)$  can be estimated using the expression:

$$V(KIO_3) = V(\text{pipette}, 20^\circ\text{C}) \{1 + \alpha_V(t_L - 20^\circ\text{C})\} \quad (11)$$

and

$$M(KIO_3) \approx M(KIO_3, 20^\circ\text{C}) \frac{\rho_w(t_L)}{\rho_w(20^\circ\text{C})} \quad (12)$$

The concentration of oxygen in sea water is then given by

$$C(O_2) = \frac{n(O_2) - 7.6 \times 10^{-8} \text{ mol}}{m(\text{sample})}, \quad (13)$$

where  $m(\text{sample})$  is the mass of sea water that was pickled, and the amount of oxygen introduced to the sample in  $1 \text{ cm}^3 \text{ MnCl}_2$  and  $1 \text{ cm}^3 \text{ NaOH/NaI}$  reagent at about  $25^\circ\text{C}$  has been estimated at  $7.6 \times 10^{-8} \text{ mol}$ ;

$$m(\text{sample}) = (V(O_2\text{-flask}) - 2 \text{ cm}^3) \cdot \rho_{\text{sw}}(S, t). \quad (14)$$

The volume of the oxygen flask,  $V(O_2\text{-flask})$  is that appropriate to the temperature at which the sample was pickled ( $t$ );

$$V(O_2\text{-flask}) = V(O_2\text{-flask}, 20^\circ\text{C}) \{1 + \alpha_V(t - 20^\circ\text{C})\} \quad ; \quad (15)$$

the density of sea water used— $\rho_{\text{sw}}(S, t)$ ; see Appendix (A.2)—is also that appropriate to the temperature at which the oxygen sample was pickled.

### 8.5 Example calculations (Footnote 22)

#### 8.5.1 Titration blank

$$V_1 = 0.0700 \text{ cm}^3;$$

$$V_2 = 0.0750 \text{ cm}^3;$$

$$V_{\text{blank}} = 0.0050 \text{ cm}^3 \text{ — Equation (6).}$$

#### 8.5.2 Concentration of standard $\text{KIO}_3$ solution

$$m(\text{KIO}_3) = 0.5000 \text{ g};$$

$$t_L = 18.0 \text{ }^\circ\text{C} \text{ (laboratory temperature);}$$

$$V_S(20^\circ\text{C}) = 1.0001 \text{ dm}^3;$$

$$V_S(18^\circ\text{C}) = 1.00008 \text{ dm}^3 \text{ — Equation (8);}$$

$$\rho_W(18^\circ\text{C}) = 0.99859 \text{ g}\cdot\text{cm}^{-3} \text{ — Equation (A.1);}$$

$$\rho_W(20^\circ\text{C}) = 0.99820 \text{ g}\cdot\text{cm}^{-3} \text{ — Equation (A.1);}$$

$$M(\text{KIO}_3, 20^\circ\text{C}) = 0.0023354 \text{ mol}\cdot\text{dm}^{-3} \text{ — Equation (7).}$$

#### 8.5.3 Molarity of $\text{Na}_2\text{S}_2\text{O}_3$ titrant

(Assumes that the  $\text{Na}_2\text{S}_2\text{O}_3$  titrant is at approximately the same temperature as the  $\text{KIO}_3$ .)

$$V_{\text{std}} = 0.7000 \text{ cm}^3;$$

$$V(\text{KIO}_3) = 10.0000 \text{ cm}^3;$$

$$M(\text{Na}_2\text{S}_2\text{O}_3) = 0.20162 \text{ mol}\cdot\text{dm}^{-3} \text{ — Equation (9).}$$

#### 8.5.4 Oxygen in a sea water sample

$$S = 35.0;$$

$$t = 0.0 \text{ }^\circ\text{C} \text{ (sampling temperature);}$$

$$t_L = 23.0 \text{ }^\circ\text{C} \text{ (laboratory temperature);}$$

$$\rho_W(23^\circ\text{C}) = 0.99753 \text{ g}\cdot\text{cm}^{-3} \text{ (Equation A.1);}$$

$$V(\text{KIO}_3, 23^\circ\text{C}) = 10.0003 \text{ cm}^3 \text{ — Equation (11);}$$

$$M(\text{KIO}_3, 23^\circ\text{C}) = 0.0023338 \text{ mol}\cdot\text{dm}^{-3} \text{ — Equation (12);}$$

$$V = 0.9500 \text{ cm}^3;$$

$$n(\text{O}_2) = 47.602 \text{ } \mu\text{mol} \text{ — Equation (10);}$$

$$V(\text{O}_2\text{-flask}, 20^\circ\text{C}) = 125.000 \text{ cm}^3;$$

$$V(\text{O}_2\text{-flask}, 0^\circ\text{C}) = 124.976 \text{ cm}^3;$$

$$\rho_{\text{SW}}(35, 0^\circ\text{C}) = 1.02811 \text{ g}\cdot\text{cm}^{-3} \text{ — Equation (A.2);}$$

$$m(\text{sample}) = 0.12643 \text{ kg} \text{ — Equation (14);}$$

$$C(\text{O}_2) = 375.90 \text{ } \mu\text{mol}\cdot\text{kg}^{-1} \text{ — Equation (13).}$$

---

<sup>22</sup> Note, extra significant figures are provided to assist in checking calculations.



## 9. Quality assurance

Some duplicate sampling is recommended to assess the quality of the sampling procedures; both from the same sampler (*e.g.* Niskin bottle) and ideally from two samplers tripped together at the same depth.

The control limits outlined below are necessary to ensure that the accuracy and precision of the data are adequate for the purposes of the WOCE Hydrographic Program. The initial targets specified for this are: a maximum within cruise precision (1 std. dev.) of  $0.5 \mu\text{mol}\cdot\text{kg}^{-1}$  and an overall, between cruise (and between laboratory), range of bias of less than  $2.0 \mu\text{mol}\cdot\text{kg}^{-1}$ . Results from an intercalibration exercise including an implementation of this method indicate that these targets are attainable.

Preliminary results should be calculated immediately and the control charts outlined below should be updated as soon as possible. A logbook should be maintained detailing all the analyses carried out and describing any adjustments made to the analytical system. The following goals are recommended:

### 9.0.1 *Reagent and titration blank*

This should be less than  $0.01 \text{ cm}^3$ , otherwise it is indicative of problems. A property control chart should be kept of this parameter (SOP 22— Note 4).

### 9.0.2 *Precision of titration of standard $\text{KIO}_3$ solution*

A duplicate titration of the standard  $\text{KIO}_3$  solution should be made for every set of samples. The difference in volume of  $\text{Na}_2\text{S}_2\text{O}_3$  used for each pair of analyses should be plotted on a range control chart (SOP 22— Note 4). This difference should typically be less than  $0.0020 \text{ cm}^3$ .

### 9.0.3 *Molarity of $\text{Na}_2\text{S}_2\text{O}_3$ solution*

The molarity of the  $\text{Na}_2\text{S}_2\text{O}_3$  titrant ( $20^\circ\text{C}$ ) should be calculated for each standardization and the results should be plotted on a property control chart (SOP 22— Note 4). This will show any gradual change of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution with time and will allow an early identification of any problems.

### 9.0.4 *Precision of oxygen analysis*

A duplicate sample should be taken and titrated approximately every 10–15 analyses. The difference in oxygen concentration obtained for each pair of analyses should be plotted on a range control chart (SOP 22— Note 4).

## Acknowledgments

I should like to thank the following people, each of whom helped clarify my thoughts about the procedure detailed here: George Anderson, Robert Williams and Arnold Mantyla of the Scripps Institution of Oceanography. Additional, helpful comments were received from George Knapp (Woods Hole Oceanographic Institution) and Allyn Clarke (Bedford Institute of Oceanography).

## References

- Bigg P. H. (1967) Density of water in SI units over the range 0–40 °C. *British Journal of Applied Physics* **18**, 521–525.
- Carpenter J. H. (1965) The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method. *Limnology and Oceanography* **10**, 141–143.
- Commission on Atomic Weights and Isotopic Abundances (1988) Atomic weights of the elements 1987. *Pure & Applied Chemistry* **60**, 841–854.
- Craig H. (1961) Standards for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science* **133**, 1833–1834.
- Culberson C. H. & S. Huang (1987) Automated amperometric oxygen titration. *Deep-Sea Research* **34**, 875–880.
- Culberson C. H. (1991) Dissolved oxygen. In WOCE Operations Manual. Volume 3: The Observational Program. Section 3.1: WOCE Hydrographic Program. Part 3.1.3: WHP Operations and Methods. WHP Office Report WHPO 91-1 / WOCE Report No. 68/91.
- Culberson C. H., G. Knapp, M. C. Stalcup, R. T. Williams & F. Zemlyak (1991) A comparison of methods for the determination of dissolved oxygen in sea water. WHP Office Report WHPO-91-2.
- DOE (1994) *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2*. A. G. Dickson & C. Goyet (eds.), ORNL/CDIAC-74. (This document is available on request from the Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, TN37831-6335, USA)
- Jones F. E. & G. L. Harris (1992) ITS<sub>90</sub> density of water formulation for volumetric standards calibration. *Journal of Research of the National Institute of Standards and Technology* **97**, 335–340.
- Millero F. J. & A. Poisson (1981) International one-atmosphere equation of state for sea water. *Deep-Sea Research* **28**, 625–629.
- Murray C. N., J. P. Riley & T. R. S. Wilson (1968) The solubility of oxygen in Winkler reagents used for the determination of dissolved oxygen. *Deep-Sea Research* **15**, 237–238.
- Williams P. J. LeB. & N. W. Jenkinson (1982) A transportable microprocessor-controlled precise Winkler titration suitable for field station and shipboard use. *Limnology & Oceanography* **27**, 576–584.

## Appendix A

### Density of air-saturated water

The density of air-saturated water in the temperature range 5 to 40 °C—*i.e.* avoiding the temperature of maximum density—is given by the expression (Jones & Harris, 1992):

$$\begin{aligned} \rho_W / (\text{kg}\cdot\text{m}^{-3}) = & 999.84847 + 6.337563 \times 10^{-2} (t/^\circ\text{C}) \\ & - 8.523829 \times 10^{-3} (t/^\circ\text{C})^2 + 6.943248 \times 10^{-5} (t/^\circ\text{C})^3 \\ & - 3.821216 \times 10^{-7} (t/^\circ\text{C})^4, \end{aligned} \quad (\text{A.1})$$

where  $t$  is the temperature on ITS<sub>90</sub> (Footnote 23).

At 25 °C,  $\rho_W = 997.041 \text{ kg}\cdot\text{m}^{-3} = 0.997041 \text{ g}\cdot\text{cm}^{-3}$ .

### Density of sea water

The density of sea water in the temperature range 0 to 40 °C (ITS<sub>68</sub>—see Note 23) and the salinity range 0 to 42 is given by the expression (Millero & Poisson, 1981):

$$\rho_{\text{SW}} / (\text{kg}\cdot\text{m}^{-3}) = \rho_{\text{SMOW}} / (\text{kg}\cdot\text{m}^{-3}) + A S + B S^{1.5} + C S^2 \quad (\text{A.2})$$

where (Footnote 24)

$$\begin{aligned} \rho_{\text{SMOW}} / (\text{kg}\cdot\text{m}^{-3}) = & 999.842594 + 6.793952 \times 10^{-2} (t/^\circ\text{C}) \\ & - 9.095290 \times 10^{-3} (t/^\circ\text{C})^2 + 1.001685 \times 10^{-4} (t/^\circ\text{C})^3 \\ & - 1.120083 \times 10^{-6} (t/^\circ\text{C})^4 + 6.536332 \times 10^{-9} (t/^\circ\text{C})^5, \end{aligned} \quad (\text{A.3})$$

$$\begin{aligned} A = & 8.24493 \times 10^{-1} - 4.0899 \times 10^{-3} (t/^\circ\text{C}) \\ & + 7.6438 \times 10^{-5} (t/^\circ\text{C})^2 - 8.2467 \times 10^{-7} (t/^\circ\text{C})^3 \\ & + 5.3875 \times 10^{-9} (t/^\circ\text{C})^4, \end{aligned} \quad (\text{A.4})$$

$$\begin{aligned} B = & -5.72466 \times 10^{-3} + 1.0227 \times 10^{-4} (t/^\circ\text{C}) \\ & - 1.6546 \times 10^{-6} (t/^\circ\text{C})^2, \end{aligned} \quad (\text{A.5})$$

$$C = 4.8314 \times 10^{-4}; \quad (\text{A.6})$$

$t$  is on ITS<sub>68</sub> and  $S$  is the salinity.

At 25 °C (ITS<sub>68</sub>) and  $S = 35$ ,  $\rho_{\text{SW}} = 1023.343 \text{ kg}\cdot\text{m}^{-3}$ .

---

<sup>23</sup> The International Practical Temperature Scale of 1968 (ITS<sub>68</sub>) has recently been superseded by the International Temperature Scale of 1990 (ITS<sub>90</sub>). A simple equation can be used to relate the two over the oceanographic temperature range 0 to 40 °C (Jones & Harris, 1992):

$$t_{90} / ^\circ\text{C} = 0.0002 + 0.99975 t_{68} / ^\circ\text{C}.$$

<sup>24</sup> SMOW — Standard Mean Ocean Water (Craig, 1961)—is pure water with a specified isotopic composition and free of dissolved gases.