

Dissolved Oxygen

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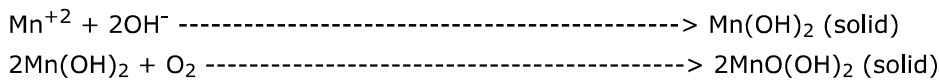
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DISSOLVED OXYGEN

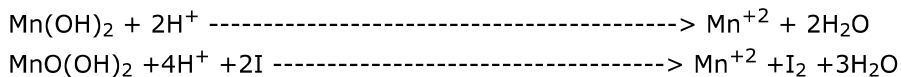
SUMMARY: The amount of dissolved oxygen in seawater is measured using the Carpenter modification of the Winkler method. Carpenters modification (1965) was designed to increase the accuracy of the original method devised by Winkler in 1889. Using Carpenters modification, the significant loss of iodine is reduced and air oxidation of iodide is minimized. Rather than using the visible color of the iodine-starch complex as an indicator of the titration end-point, we use an automated titrator that measures the absorption of ultraviolet light by the tri-iodide ion, which is centered at a wavelength of 350 nm.

1. Principle

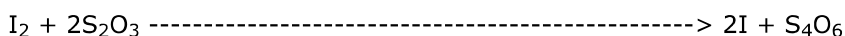
Manganous chloride solution is added to a known quantity of seawater and is immediately followed by the addition of sodium hydroxide iodide solution. Manganous hydroxide is oxidized by the dissolved oxygen in the seawater sample and precipitates forming hydrated tetravalent oxides of manganese.



Upon acidification of the sample, the manganese hydroxides dissolve and the tetravalent manganese in MnO(OH)_2 acts as an oxidizing agent, setting free iodine from the iodide ions.



The liberated iodine, equivalent to the dissolved oxygen present in the sample, is then titrated with a standardized sodium thiosulfate solution and the dissolved oxygen present in the sample is calculated. The reaction is as follows:



2. Reagent Preparation

2.1. The manganous chloride solution (3M) is prepared by dissolving 600g of reagent grade manganous chloride tetrahydrate, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, in Milli-Q water to a final volume of 1 liter. This solution is then filtered using 47mm glass fiber filters (Whatman GF/F).

2.2 The sodium hydroxide (8M)-sodium iodide (4M) solution is prepared by first dissolving 600g sodium iodide (NaI) in approximately 600ml Milli-Q water. After the NaI is dissolved, 320g of NaOH is added slowly (caution-the solution will get hot) and the volume is adjusted to 1 liter with Milli-Q. The solution is then filtered through a GF/F.

2.3. Sulfuric acid solution (10N) is prepared by slowly adding 280ml of reagent grade concentrated sulfuric acid, H_2SO_4 , to 770ml of Milli-Q water. This should be prepared with caution as it gets very hot.

2.4. The sodium thiosulfate solution (0.2N) is prepared by dissolving 50g sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) and 0.1g anhydrous sodium carbonate (Na_2CO_3) in Milli-Q water to a final volume of 1 liter. This solution is prepared approximately 2 weeks before use and stored in an amber glass bottles.

2.5. The potassium iodate standard (0.0100N) is prepared by first drying potassium iodate (KIO_3) in a drying oven for approximately one hour. Once the KIO_3 is dried, carefully measure out 0.3567g, using a 5-place balance, and dissolve in Milli-Q water to a final volume of 1 liter.

3. Sample Drawing

3.1. Oxygen samples are always drawn first from the Niskin bottles and should be drawn as soon as possible to avoid contamination from atmospheric oxygen. Approximately 6 inches of Tygon tubing connected to a temperature probe via a y-connector is slipped onto the discharge valve of the Niskin.

3.2. A calibrated volumetric flask is rinsed three times, then with the seawater still flowing, the end of the tygon tubing is placed into the flask nearing the bottom. The sample is then overflowed with twice the sample volume while making sure that there are no bubbles in the tubing during the overflow process. The tubing is then carefully removed from the sample flask to prevent the influx of bubbles.

3.3. Immediately after drawing the sample, 1 ml of manganous chloride solution is added into the flask. This is followed by the addition of 1ml of sodium hydroxide-sodium iodide solution to the sample. Both dispensers should be purged to remove air bubbles prior to the addition of these reagents.

3.4. The stopper is then carefully placed in the bottle to avoid the trapping of air and the temperature of the seawater at the time of sample draw is recorded.

3.5. After all samples are drawn, they are shaken vigorously to disperse the precipitate uniformly through the flask. This process is repeated again after the precipitate has settled to the bottom of the flask, or after at least ten minutes.

4. Standardization of thiosulfate

4.1. Proper care in the setup of the auto-titrator is required before running blanks, standards and samples. The UV lamp is turned on at least 30 minutes prior to the run and should have a stable voltage of 2.4-2.5 volts for the run. The dosimat tubing is carefully purged so that the lines are completely free of air bubbles, and the water bath inside the auto-titrator is clean and filled with Milli-Q water prior to analysis. Make sure, prior to your first run, any thiosulfide solution is rinsed off the tip of the line with Milli-Q after purging.

4.2. Using a Metrohm 655 Dosimat, dispense 10 ml of the standard potassium iodate solution into a clean oxygen flask. Add a stir bar and rinse down the sides with a small amount of Milli-Q water. Add 1 ml of the 10N sulfuric acid solution and swirl to ensure the solution is well mixed before adding the pickling reagents.

4.3. Add 1 ml sodium hydroxide-sodium iodide solution to the acidified flask and swirl gently. Then add 1ml of Manganous chloride solution, swirl gently, and fill the solution to the neck of the flask with Milli-Q water.

4.4. The UV detector on the auto-titrator measures the transmission of ultra-violet light through the standard (as well as seawater sample and blank) as a Metrohm 665 Dosimat dispenses thiosulfate at increasingly slower rates. The endpoint is reached when no further change in absorption is detected by the detector. At this point all of the iodine has been consumed.

5. Blank determination

5.1. Using the Metrohm 655 Dosimat, dispense 1 ml of the standard Potassium Iodate solution into a clean oxygen flask. Add a stir bar and rinse down the sides with a small amount of Milli-Q water. Add 1 ml of the 10N sulfuric acid solution and swirl to ensure the solution is well mixed before adding the pickling reagents.

5.2. Add 1 ml sodium hydroxide-sodium iodide solution to the acidified flask and swirl gently. Then add 1ml of Manganous chloride solution, swirl gently, and fill the solution to the neck of the flask with Milli-Q water. The solution is then titrated to the end-point as described in section 4.3 above.

5.3. A second 1 ml aliquot is added to the same solution which is then titrated to a second end-point. The difference between the first and second titration is used as the reagent blank.

6. Sample analysis

6.1. Samples are analyzed after all of the precipitate settles to the bottom of the flask, after the second shake. The top of the flask is wiped with a kimwipe to remove moisture containing excess reagent around the stopper and then the stopper is carefully removed.

6.2. 1ml of 10N sulfuric acid is added to the sample and a stir bar is placed inside the flask. The flask is then secured inside the clean water bath. The tip of the thiosulfate dispenser is placed inside the sample flask and the automated titration can begin with the use of an auto-titrator program.

7. Certified Standard Comparison

7.1 Presented here are the results of a comparison of several certified standards with a CalCOFI prepared standard (weighed and diluted up to set normality in 1 liter volumetric) standard. Three certified iodate solutions, (Table 1) were tested using the same 0.2N thiosulphate solution. Iodate concentrations are back calculated from defined thiosulphate concentrations for comparison purposes. It is noteworthy that the Acculute and Fisher solutions had to be diluted before use. The same volumetric was used for all dilutions, the same Dosimat and piston was used for all titrations, extensive rinsing between uses. Titration n=9 as dictated by the maximum number of samples that could be acquired from the 100ml portion for the OSIL standard. CalCOFI values are a result of cruise and shore based titrations to demonstrate an integrated real use sampling. Differences between all standards represent less than +/- 0.5 percent of the signal.

Average[KIO ₃] mM	STDEV mM	% Diff from CC mM
CalCOFI iodate 12/16/2012 used on 1301 10.015722	0.009609	n.a.
OSIL iodate oxygen standard 9.972671	0.013310	99.57
Acculute iodate Lot 00702 10.049259	0.007684	100.33
Fisher iodate Lot 125009 10.044804	0.007650	100.29

7.2 These results are consistent with previously published methods comparison for precision of oxygen measurements¹ (WOCE Report 73/91) and previous replicate analysis to verify precision with auto-titration methods². Although the Ocean Data Facility (ODF) performed the 1991 comparisons for Scripps and was different than CalCOFI, the Winkler techniques

used then and now are the same. Presently, CalCOFI methods employ a UV end point auto-titrator made by ODF that produces a precision of 0.005-.01 ml/L. The difference between high and low samples in replicate analysis equals ~0.5% with a standard deviation typically under 0.010 ml/L. See references:

1. oceaninformatics.ucsd.edu/calcofi/docs/CCConf06Wolgast.ppt
(<http://oceaninformatics.ucsd.edu/calcofi/docs/CCConf06Wolgast.ppt>)
2. odf.ucsd.edu/index.php?id=56 (<http://odf.ucsd.edu/index.php?id=56>)

8. Calculation and Expression of Results

8.1. The auto-titrator uses a UV detector that detects changes in voltage as thiosulfate is added to the sample. The volume of thiosulfate added is recorded at an endpoint once there is no change in voltage. The end point is determined by a least squares fit using a group of data points just prior to the end point, where the slope of the titration curve is steep, and a group of data points just after the endpoint, where the slope of the curve is close to zero. The intersection of the two lines is taken as the endpoint.

8.2. The calculation of dissolved oxygen follows the same principle outlined by Carpenter (1965). Our results are expressed in mL/L.

$$O_2(\text{ml/L}) = \frac{(R - R_{\text{blk}}) V_{\text{IO}_3} \cdot N_{\text{IO}_3} \cdot E}{(R_{\text{std}} - R_{\text{blk}}) \cdot (V_b - V_{\text{reg}})} - \frac{DO_{\text{reg}}}{V_b}$$

Where:

R = Sample titration (mL)

R_{blk} = Blank value (mL)

V_{IO₃} = Volume of KIO₃ standard (mL)

N_{IO₃} - Normality of KIO₃ standard

E = 5,598 mL O₂/equivalent

R_{std} = Volume used to titrate standard

V_b - Volume of sample bottle

V_{reg} = Volume of reagents

DO_{reg} = Oxygen added in reagents

9. Equipment/Supplies

- Volumetrically calibrated 100ml Glass Erlenmeyer flasks with paired ground glass stoppers
- 3 - 1ml Brinkman reagent dispensers
- Tygon tubing
- Fisher Scientific UV Longwave Pencil Lamp, 365 nm and power supply, 115 VAC
- 2 Metrohm Dosimat 665 Automatic Burets
- 10ml Metrohm Dosimat Exchange unit
- 1ml Metrohm Dosimat Exchange unit
- Metrohm Dosimat Keypad
- Spare 1ml and 10ml dispenser pistons for the Metrohm Dosimat Exchange units
- Scripps/STS Auto-titrator Unit and Software
- PC Computer
- Waterproof sampling thermometer

- Concentrated Sulfuric Acid, H₂SO₄, ACS Grade
- Manganous Chloride Tetrahydrate, MnCl₂•4H₂O, ACS Grade
- Sodium Hydroxide, NaOH, ACS Grade
- Sodium Thiosulfate, Na₂S₂O₃•5H₂O, ACS Grade
- Potassium Iodate, Dry high purity KIO₃, Alfa Aesar
- Granular Sodium Iodide, EMD Chemicals via VWR
- Magnetic Stir Bars

10. References

- Anderson, G. C., compiler, 1971. "Oxygen Analysis," Marine Technician's Handbook, SIO Ref. No. 71-8, Sea Grant Pub. No. 9.
- Carpenter, J. H., 1965. The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method. *Limnol. Oceanogr.*, 10: 141-143.
- Culberson, C. H. 1991. Dissolved oxygen. WHP Operations and Methods -- July 1991.
- Parsons, T. R., Y. Maita, C. M. Lalli, 1984. A Manual of Chemical and Biological Methods for Seawater Analysis. Pergamon Press Ltd., 3-28.
- oceaninformatics.ucsd.edu/calcofi/docs/CCConf06Wolgast.ppt
(<http://oceaninformatics.ucsd.edu/calcofi/docs/CCConf06Wolgast.ppt>)