DEPARTMENT OF ECOLOGY
State of Washington

Standard Operating Procedure EAP027 Version 4.1

Seawater Dissolved Oxygen Analysis

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Purpose of this Document

The Washington State Department of Ecology develops Standard Operating Procedures (SOPs) to document agency practices related to sampling, field and laboratory analysis, and other aspects of the agency's technical operations.

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The Washington State Department of Ecology's (Ecology's) Standard Operating Procedures (SOPs) are adapted from published methods, or developed by in-house technical and administrative experts. Their primary purpose is for internal Ecology use, although sampling and administrative SOPs may have a wider utility. Our SOPs do not supplant official published methods. Distribution of these SOPs does not constitute an endorsement of a particular procedure or method.

Any reference to specific equipment, manufacturer, or supplies is for descriptive purposes only and does not constitute an endorsement of a particular product or service by the author or by Ecology.

Although Ecology follows the SOP in most instances, there may be instances in which Ecology uses an alternative methodology, procedure, or process.

SOP Revision History

Revision Date	Revision History	Summary of changes	Sections	Reviser(s)
3/19/2007	1.0	Added “Seawater” to title; footer	all	Bill Kammin
8/22/2007	1.1	Minor changes to procedure	all	Adrienne Stutes
2/17/2012	2.1	Added picture, additional details for sample holding & treatment, Dosimat manual link and reference.	4.0, 7.0, 5.0 bibliography	Mya Keyzers, Julia Bos
3/19/2012	2.1	Recertified	All	Bill Kammin
1/9/2015	3.0	Added neutralization procedure, updated MSDS links, additions of apparatus and materials, minor edits and clarifications	5.0, 6.0, 7.0 (added new 7.7), 10.0, 13.0, 14.0	Laura Hermanson, Suzan Pool
1/9/2015	3.0	Recertified	All	Bill Kammin
4/5/2017	4.0	Complete re-edit of text, revised footer format	All	Bill Kammin
12/5/2017	4.0	Added neutralization step after standards and samples.	7.0	Mya Keyzers
5/3/2021	4.1	Revised several sections, clarified steps, eliminated erroneous instructions for blanks, formatted sections, added more info on result calculation, equations and QC & data management.	All	Julia Bos

1.0 Purpose and Scope

1.1 This Standard Operating Procedure (SOP) is for the analysis of dissolved oxygen (DO) samples collected during all seawater sampling events conducted by the Marine Monitoring Unit. This SOP describes the Winkler titration, azide modification method using a Dosimat Titrator.

1.2 This SOP does not attempt to describe the entire procedure for marine waters dissolved oxygen determination, but only the laboratory portion. It assumes that proper sampling protocols have been followed, that the sample was collected in a 130 mL DO flask, and that the sample has had 1 mL manganous chloride solution, followed by 1 mL of alkaline sodium hydroxide-sodium iodide reagent added soon after sampling. Care must have been taken to cap the sample bottle(s), excluding all air bubbles. This is an analytical chemistry technique. The glasswater, equipment, sample bottles, pipettes, stir bars, and buret tip must be kept scrupulous clean. Thoroughly rinse the glassware with clean hot water after every analysis. Clean every three months using Liqui-Nox® and water. Clean the dosimat as needed.

2.0 Applicability

2.1 This method is applicable for use with most freshwater, saltwater and wastewater samples. In instances where azide modification is not applicable, other Winkler modification methods may be used.

3.0 Definitions

3.1 Blank: A synthetic sample used to determine the volume of thiosulfate needed to titrate 1 ml of KIO3 in reagents MnCl2 + NaOH-NaI-Azide + H2SO4. Used to assess possible contamination of reagents. Synonym: Method Blank

3.2 Correction Blank: A factor for assessing contamination by comparing two blanks, and used in final calculation of sample concentration e.g.. Blank 1- Blank 2 = correction factor to account for any impurities in regents.

3.3 Dissolved Oxygen: The concentration of dissolved oxygen (mg/L) in a water sample.

3.4 Indicator solution: A solution used to determine the endpoint (usually a color change) when titrating.

3.5 Measurement Quality Objectives (MQOs): Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness. (USEPA, 2006)

3.6 Normality: The number of mole equivalents per liter of solution or the molar concentration divided by an equivalence factor. The capital letter N is used to indicate concentration in terms of normality. It can also be expressed as eq/L (equivalent per liter) or meq/L (milliequivalent per liter).

3.7 Standard: A QC sample of known composition analyzed prior to the analysis of any samples to check for acceptable bias and reproducibility in the measurement system, including analyst performance. Results are also used in the final calculation of sample concentration. Synonym: Initial Calibration Verification Standard

3.8 Titrate: To titrate a sample, a chemical solution of known strength is added on a drop by drop basis until a color change, precipitate or pH change in the sample is observed.

4.0 Personnel Qualifications/Responsibilities

4.1 An analyst must be able to demonstrate the preparation and analysis of DO samples, explaining each step of the procedure, using the SOP as an aid. The analyst must be able to conduct quantitative chemistry procedures such as pipetting, handling, preparing and dispensing reagents and analyzing samples, as well as troubleshoot any analytical issues.

4.2 An analyst must be able to produce results for a set QC samples (standards and blanks) that meet MQOs.

4.3 All personnel preparing and analyzing samples for DO will be fully trained by an experienced analyst.

4.4 This procedure requires training for the use of hazardous materials, per the Ecology Chemical Hygiene Plan and Hazardous Material Handling Plan (Section 1) which includes Laboratory Safety Orientation, Job-Specific Orientation and Chemical Safety Procedures. The Standard Operating Procedures in Section 16 of the Chemical Hygiene Plan and Hazardous Material Handling Plan for handling chemicals must also be followed.

4.5 The typical levels of job classes for analysts are Natural Resource Scientist 1- 4; Environmental Specialist 1 – 4 or Chemist 1 – 4.

5.0 Equipment, Reagents, and Supplies

5.1 De-ionized water (18 Megohm)

5.2 Safety apron or laboratory coat

5.3 Safety goggles or glasses

5.4 Nitrile exam gloves

5.5 10 mL pipette and tips

5.6 1.0 mL pipette and tips

5.7 Kimwipes

5.8 Small beakers, one for each reagent

5.9 Desk lamp to illuminate sample

5.10 White background (e.g., white paper or plastic) secured to clamp post

5.11 Metrohm® 775 Dosimat titrator with magnetic stirrer and stir bar

5.12 pH strips

5.13 Plastic bucket

5.14 3 M Manganese chloride (MnCl2) (obtained from the University of Washington's Marine Chemistry Lab). This chemical is stable for 2 years when stored in sealed plastic bottles and kept in the dark.

5.15 8 N Sodium hydroxide-sodium iodide sodium-azide (NaOH-NaI-Azide) (obtained from the University of Washington's Marine Chemistry Lab). This chemical is stable for 2 years when stored in sealed plastic bottles and kept in the dark. Sodium azide is a suspected carcinogen and should be treated with care.

5.16 10 N Sulfuric Acid (H2SO4) (obtained from the University of Washington's Marine Chemistry Lab). This chemical is stable for 2 years when stored in a sealed plastic or glass bottle and kept in an acid cabinet. H2SO4 is extremely poisonous, corrosive, and most likely carcinogenic. Extreme care must be used when handling this chemical.

5.17 0.01 N Sodium Thiosulfate (Na2S2O3 • 5H2O) (obtained from the University of Washington's Marine Chemistry Lab). Sodium thiosulfate is made by dissolving 49.64 g sodium thiosulfate + 0.1g Na2CO3 to 1 liter volume with de-ionized water. This chemical is relatively inert and is stable for 2 years when stored in a sealed plastic bottle and kept in the dark.

5.18 Starch soluble, aqueous solution (obtained from the University of Washington's Marine Chemistry Lab). Starch aqueous solution is a super-saturated solution of starch soluble and de-ionized water. The starch solution does not pose any known health risks. This solution should be kept refrigerated and has a shelf life of about 6-12 months.

5.19 0.01 N Potassium Iodate (KIO3) (obtained from the University of Washington's Marine Chemistry Lab). Potassium iodate is a strong oxidizer and should be handled with care.

5.20 Sodium Bicarbonate (NaHCO3) (obtained from a store). Sodium bicarbonate, or baking soda, is a white powder that is commonly used to neutralize acid.

6.0 Summary of Procedure

After collection, a DO sample is treated with 1 mL manganous sulfate followed by 1 mL Alkali-Iodide-Azide in the field. Dissolved oxygen rapidly oxidizes an equivalent amount of the dispersed divalent manganous hydroxide to form a brown precipitate, Mn(OH)2. Upon acidification with sulfuric acid prior to analysis, manganic hydroxide forms manganic sulfate, which then acts as an oxidizing agent to liberate free iodine from the alkali-iodide. The iodine, which is stoichiometrically equivalent to the dissolved oxygen in the sample, is then titrated with a standard solution of sodium thiosulfate. The titration end point is determined visually with a starch indicator.

Steps:

- Prepare and run standards.
- Prepare and run blanks.
- Prepare and run samples.

6.1 Analysis Preparation and Dosimat set-up.

6.1.1 Samples must be at room temperature for titration. **Remove** any stored samples from refrigerator at least **3 hours before titration**, keeping samples in dark conditions.

6.1.2 This is an analytical chemistry technique. The glassware, equipment, sample bottles, pipettes, stir bars, and buret tip must be kept scrupulously clean. Thoroughly rinse the glassware with clean hot water after every analysis. Clean every three months using Liqui-Nox® and water. Clean the dosimat as needed.

Figure 1 Dosimat with DO flask on stir plate, beakers for each reagent, pipettes, deionized water in squeeze bottle, desk lamp, laboratory gloves, and Kimwipes.

6.1.3 **Turn on** the Dosimat using the red POWER switch in back.

6.1.4 **Gently lift** the amber bottle of thiosulfate. **Shake** and then replace in the Dosimat..**Turn the dispense speed knob** (labeled dv/dt) to 10. Using the hand control button, flush out the buret with 15-20 ml of thiosulfate to remove air bubbles from the Dosimat line and buret. Be sure there are **no bubbles** in the buret or moving bubbles in the line leading to the buret tip.

6.1.5 **Reduce** the dispense speed to 1.

6.1.6 **Press** the CLEAR button.

6.1.7 **Rinse** the buret tip with deionized (DI) water. Turn the stirrer on.

6.1.8 **Prepare reagents. Decant** small amounts of the reagents for running standards and blanks into smaller beakers. Always shake the reagent before pouring.

6.1.9 Never pipette reagents straight out of the reagent bottle. Always decant a small amount into a clean vessel and pipette out of that. Never pour remaining reagents back into the reagent bottle. Dispose of them as you would a titrated sample, standard or blank.

6.2 Prepare and Run Standards

6.2.1 Pipetting Tips:

- Draw reagent from the smaller beaker.
- Hold the pipette straight up and down, never angled.
- Dispense straight into the sample bottle. Do not put the tip of the pipette against the wall of the sample bottle.

6.2.2 **Fill** a clean standard sample bottle about 3/4's full of DI water.

6.2.3 **Add** a clean stir bar and turn stirrer on, setting speed as appropriate to size of stir bar. For a small stir bar, the best speed setting is 4.5. **Leave stirrer running during entire titration** of each sample to ensure complete mixing.

6.2.4 **Rinse** the inside of the sample bottle with DI water after each of the next chemical addition steps to rinse down any reagent that may have splashed onto the side.

6.2.5 **Pipette 1 ml 10 N H_2SO_4** into flask, rinse and mix well.

6.2.6 **Pipette 1 ml of 8 N NaOH-NaI-azide** solution slowly. Rinse and mix well. If sample is not clear, discard and start again.

6.2.7 **Pipette 10 ml of the 0.01 N KIO_3** standard into flask, rinse and mix well.

6.2.8 **Pipette 1 ml of starch** aqueous solution into flask, rinse and mix well.

6.2.9 **Rinse** inside of flask well with DI water to ensure no chemical residue has adhered to the sides of the flask.

6.2.10 **Position** the sample bottle on the stirrer; making sure the burette tip is under the surface of the sample.

6.2.11 **Make sure** that the Dosimat reads 0.000 ml (press **CLEAR** to zero).

6.2.12 **Titrate** sample to the endpoint by dispensing thiosulfate in the sample using the thumb button.

Titration Tips:

- **Titrate slowly**! Speeding it up will risk missing the endpoint and make it harder to match two samples within +/- 0.001 ml.
- **Acclimate your eyes** to endpoint. The endpoint is achieved when all color is gone. Watch the vortex in the upper half of the bottle. The endpoint is a subtle difference between clear and sparkling clear.

6.2.13 **Record** endpoint.

6.2.14 **Remove** sample bottle and dispense a few drops of thiosulfate through the burette tip to flush out any sample residue.

6.2.15 **Pour** sample into waste bucket.

6.2.16 **Rinse** down the burette tip with deionized water.

6.2.17 **Press** CLEAR to zero the Dosimat.

6.2.18 **Run 5 standards**; at least 3 must agree to ± 0.001 ml., 2 of them in succession.

6.3 Prepare and Run Blanks.

6.3.1 **Fill** a standard sample bottle ¾ full of distilled water.

6.3.2 **Add** a clean stir bar and turn stirrer on, leaving on for the entire titration.

6.3.3 **Pipette 1 ml 10 N H_2SO_4** into flask, rinse and mix well.

6.3.4 **Pipette slowly 1 ml of 8 N NaOH-NaI** into flask. Rinse and mix well. If sample is not clear, discard and start again.

6.3.5 **Pipette 1 ml 3 M $MnCl_2$** into flask. Rinse and mix well.

6.3.6 **Pipette 1 ml of the 0.01 N KIO_3** standard into flask, rinse and mix well.

6.3.7 **Pipette 1 ml of starch** aqueous solution into flask, rinse and mix well.

6.3.8 **Rinse** inside of flask well with DI water to ensure no chemical residue has adhered to the inside of the flask.

6.3.9 **Position** the sample bottle on the stirrer, making sure the burette tip is under the surface of the sample.

6.3.10 **Make sure** that the Dosimat reads 0.000 ml (press **CLEAR** to zero).

6.3.11 **Titrate** sample to the endpoint. **Titrate slowly**. Remember this is only 1/10th as strong as the standard.

6.3.12 **Record** endpoint #1; this is Blank1.

6.3.13 **Add 1 ml more of KIO_3 standard** to the flask for Blank 2. **Do not clear** the Dosimat!

6.3.14 **Titrate** to the second endpoint.

6.3.15 **Calculate Blank 2** by first subtracting Endpoint 1 from Endpoint 2.

Endpoint 2 – Endpoint 1 = Blank 2

6.3.16 **Record** Blank 2

6.3.17 **Subtract** Blank 2 from Blank 1 to calculate the Correction Blank:

Blank 1 – Blank 2 = Correction Blank

The Correction Blank must be ± 0.001.

If the Correction Blank is greater than **± 0.001,** there is a problem. Possible problems are reagents (age, condition), the Dosimat set up or the preparation of the blank, e.g. pipetting error. Stop analysis and do not proceed with sample analyses until the issue has been resolved.

6.3.18 **Pour** blank sample into bucket for neutralization after analysis.

6.4 Run Samples.

6.4.1 **Check** for any air bubbles in the sample bottle. If bubbles are present, **record** this as a comment on the log sheet.

6.4.2 Carefully **remove** the cap and **rinse** the stopper into the sample bottle.

6.4.3 **Add** a clean stir bar.

6.4.4 **Pipette 1 ml of 10 H_2SO_4** into flask and begin stirring making sure it is well mixed.

6.4.5 **Pipette 1 ml of starch** aqueous solution into flask.

6.4.6 **Position** the sample bottle on the stirrer, making sure the buret tip is under the surface of the sample.

6.4.7 **Rinse** inside of flask well with DI water to ensure no chemical residue has adhered to the inside of the flask.

6.4.8 **Make sure** that the Dosimat reads 0.000 ml (press **CLEAR** to zero).

6.4.9 **Titrate** sample to the endpoint by dispensing thiosulfate in the sample using the thumb button. **Titrate slowly**! Watch the vortex in the upper half of the bottle. The endpoint is achieved when all color is gone. The endpoint is a subtle difference between clear and sparkling clear.

6.4.10 **Record** endpoint.

6.4.11 **Raise** buret tip and **dispense** a few drops of thiosulfate through the buret tip to flush out any sample residue into the sample bottle.

6.4.12 **Remove** sample bottle.

6.4.13 **Rinse** down the buret tip with deionized water.

6.4.14 **Press CLEAR** to zero the Dosimat.

6.4.15 **Pour** sample into waste bucket for neutralization after all samples have been analyzed.

6.5 Endpoint Recovery or 'Back Titration'

6.5.1 If you miss the endpoint (i.e., you titrate past the point where the sample turns clear), you can recover the endpoint by doing a 'back titration' as follows:

6.5.2 Leave the sample as is on the stirrer with the buret tip in solution.

6.5.3 **Pipette 1 ml of the 0.01 N KIO_3** standard to the flask.

6.5.4 **Titrate** to the endpoint.

6.5.5 **Record** endpoint in the comment column.

6.5.6 **Subtract the volume** of Sodium thiosulfate needed to titrate 1 ml of KIO_3 standard for the blanks from the endpoint (6.3.13.1, 6.3.13.3). This is your 'true' endpoint and can be recorded in the 'buret reading' column of the log sheet.

6.5.7 **Write** "***over-titrated - added 1 ml KIO_3***" in the "Comments" column on the log sheet, followed by the final endpoint reading and volume subtracted used to calculate the "true" endpoint. For example '***over-titrated – added 1 mL KIO_3; (0.955 – 0.050)'***.

6.6 Waste Management and Clean-up

6.6.1 **Neutralize** the Winkler waste from all standards, blanks, and samples: pour the waste into a plastic bucket with an excess amount (about 2 tablespoons) of baking soda. Use a pH strip to ensure that the final pH is near 7.

6.6.2 **Pour** the contents of the bucket down the "dead" sink with copious amounts of water.

6.6.3 **Rinse** all glassware, pipette tips, and small plastic beakers with 3 rinses of hot water and then 3 rinses of DI water.

6.7 Data Documentation, Calculations and Review

6.7.1 Record standards, blanks and sample bottle numbers and associated buret readings during analysis using the form DO Analysis Data Log sheet. Also include related metadata including the lab or field event name, analyst name, analysis date, and any comments.

6.7.2 Data results are entered into EAPMW, the Marine Waters Monitoring database as soon as possible after analysis is done. Alternately, results can be entered into the form 'MW DO Analysis Log.xlsx' for calculation and stored in the appropriate ECY network folder location.

6.7.3 The equations used to calculate concentration results from the titration are sourced from UW Marine Chemistry lab and a modification of Carpenter, 1965 equations, using the obsolete unit mg-at/L.

6.7.3.1 Carpenter, 1965 equation

$$O2\ (ml/l) = \frac{(R - Rblk) * V\,IO_3 * M\,IO_3 * E}{(RStd - Rblk)(Vb - Vreg)} - DOreg$$

R = Sample titration (ml)
Rblk = Blank (ml)
RStd = Volume used to titrate standard (ml)
VIO_3 = Volume of KIO3 standard (ml)
MIO_3 =Molarity of standard KIO3 (mol/l)
E = 5,598 ml O2 /equivalent

Vb = Volume of sample bottle (ml)
Vreg = Volume of reagents (2 ml)
DOreg = oxygen added in reagents

The additional correction for DOreg of 0.0017 ml oxygen added in 1 ml manganese chloride and 1 ml of alkaline iodide has been suggested by Murray, Riley and Wilson (1968).

6.7.3.2 Ecology Equation

$$O2\ mg\text{-}at/L = \frac{[R - Rblk] * VIO3 * NIO3 * E}{[Rstd - Rblk]*[Vb-Vreg]} - DOreg$$

$$Bottle\ Factor\ (mg\text{-}at/L) = \frac{VIO3 * NIO3 * E}{[Rstd - Rblk]*[Vb-Vreg]}$$

$$Convert\ E:\ 5.598 * 1000\ mL\ O2/equivalent * \frac{1\ mg\text{-}at/L}{11.192\ mL} = \frac{1}{2}\ mg\text{-}at/L \times 1000/eq.$$

$$Bottle\ Factor\ (mg\text{-}at/L) = \frac{(10\ mL)(.01\ eq/L)(1000\ meq/eq)}{[Rstd - Rblk\ mL]*[Vb - 2\ mL][2\ meq/mg\text{-}at]}$$

$$= \frac{50\ mg\text{-}at}{[Rstd - Rblk]*[Vb - 2\ mL]\cdot L}$$

$$O2\ mg\text{-}at/L = \frac{50\ mg\text{-}at * [R - Rblk\ mL]}{[Rstd - Rblk]*[Vb - 2\ mL]\cdot L} - DOreg$$

Final Equation Used for Calculation:

$$O2\ mg/L = \frac{16 * 50\ mg\text{-}at * [R - Rblk\ mL]}{[Rstd - Rblk]*[Vb - 2\ mL]\cdot L} - DOreg$$

R = Sample titration (ml)
Rblk = Correction Blank (ml)
Rstd = Volume used to titrate standard (ml)
VIO3 = Volume of KIO3 standard (10 ml)
NIO3 =Normality of standard KIO3 (mol eq/l = .01 N)
E = 5,598 ml O2 /equivalent
Vb = Volume of sample bottle (ml)
Vreg = Volume of reagents (2 ml)
DOreg = oxygen added in reagents (.0017 as mL or .0016 as mg-at/L)

The factor of 16 is used to convert units of mg-at O_2/liter to mg O_2/liter.

The correction of 0.0016 accounts for the oxygen added in 1 mL $MnCl_2$ and 1 mL NaOH-NaI-azide.

6.7.4 Winkler analysis results are reviewed by an independent Marine Waters Monitoring staff scientist to ensure all steps were followed properly and that results are correctly determined.

7.0 Records Management

7.1 Scan and store paper copies of the laboratory logs in the designated digital and physical file locations. These are 100-year archival files and must be stored and archived according to Ecology Information Management governance.

7.2 Results are entered into EAPMW, the current Marine Monitoring Waters database, which is housed on a secure server at the Department of Enterprise Services and managed by Ecology I.T. staff.

8.0 Quality Control and Quality Assurance

8.1 The method detection limit (MDL) is 0.03 mg/L and the reporting limit (RL) is 0.05 mg/L. The accuracy is 0.04 mg/L and the precision is based on the Dosimat dispensing unit capabilities of 0.001 mg/L.

8.2 Standard and blanks must be run before acidified samples are run. The original Winkler method recommends running 5 standards..

8.3 Standards must be within ± 0.001 of each other before they can be accepted.

8.4 The Correction Blank must be ± 0.001 before it can be accepted.

8.5 If standards and blanks do not meet these MQOs, there is an issue with the analysis. The reagents may be old or contaminated and new reagents should be used instead. There could be air bubbles in the Dosimat plumbing, or dispensing or pipetting errors could be an issue. Speed of titration could also contribute to insufficient mixing and titrating beyond the endpoint. All of these should be considered for solving issues prior to analyzing samples.

8.6 Winkler analysis results are reviewed by an independent Marine Waters Monitoring staff scientist and assessed for meeting MQOs.

9.0 Safety

9.1 Follow general procedures for safety found in the Environmental Assessment Program Safety Manual.

9.2 The 8 N NaOH-NaI-azide and the 10 H_2SO_4 are suspected carcinogens and should be treated with care. Always wear safety glasses, gloves and a lab coat when handling these reagents. In addition, 10 N H_2SO_4 is poisonous and corrosive. The 0.01 N KIO_3 solution is an oxidizer and should always be handled with care.

9.3 The titrated sample is washed down the drain with copious amounts of tap water. The solution is acidic and must be diluted as much as possible to reduce any impact on the wastewater treatment plant.

10.0 References

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