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Standard Operating Procedure EAP023, Version 2.5

Collection and Analysis of Dissolved Oxygen (Winkler Method)

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Purpose of this document

The 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.

Washington State Department of Ecology

Environmental Assessment Program

Standard Operating Procedures for the Collection and Analysis of Dissolved Oxygen (Winkler Method)

Version 2.5

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EAP023

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Signatures on File

This SOP is a harmonized version combining SOPs EAP023 and EAP035, which were both dissolved oxygen SOPs.

Please note that the Washington State Department of 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 the Department of 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	Version	Summary of changes	Sections	Reviser(s)
6/21/2006	1.1	Editorial; formatting	all	Bill Kammin
11/2006		Editorial, formatting	all	Bill Ward
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2/2/2016	2.4	Updated waste treatment method, made minor edits, and recertified	6, 9	Bill Ward
4/4/2016	2.4	Recertified	all	Bill Kammin
12/12/2016	2.5	Cover page and footer, Recertified	all	Bill Kammin

Environmental Assessment Program

Standard Operating Procedure for the Collection and Analysis of Dissolved Oxygen (Winkler Method)

1.0 Purpose and Scope

1.1 This document is the Environmental Assessment Program (EAP) Standard Operating Procedure (SOP) for field collection and laboratory procedures used to determine the concentration of dissolved oxygen (DO) in water samples. The samples are analyzed using the Winkler Method (Azide-Modification), SM 21st Edition, 2005 (See attachment A for chemical reaction details). The volume, in mL, of sodium thiosulfate used to analyze a 200mL sample with this method is equal to the DO concentration in mg/L.

1.2 In general, the concentration of DO in water varies in response to changes in atmospheric pressure and water temperature. The higher the atmospheric pressure, the higher the oxygen solubility in water and the higher the potential DO concentration. The opposite is true with temperature, where the higher the temperature, the lower the solubility and saturation concentration of oxygen in water. DO is one of the major factors that determines the types of biological communities that inhabit an aquatic system. The addition of organic or inorganic material that exerts an oxygen demand through respiration and biodegradation lowers the DO concentration and can facilitate the growth of nuisance organisms.

2.0 Applicability

2.1 This SOP is intended for freshwater monitoring.

3.0 Definitions

3.1 Ecology – Washington State Department of Ecology.

3.2 EAP – Environmental Assessment Program.

3.3 EIM – Environmental Information Management System. A searchable database developed and maintained by the Washington State Department of Ecology.

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

3.5 Field Logbook – A weather resistant logbook containing "Rite in the Rain" ® writing paper used to document any and all field activities, sample data, methods and observations for each and all collection sites.

3.6 MQO's – Measurement Quality Objectives

3.7 MSDS – Material Safety Data Sheets provides both workers and emergency personnel with the proper procedures for handling or working with a particular substance. MSDS's include information such as physical data (melting point, boiling point, flash point, etc.), toxicity, health effects, first aid, reactivity, storage, disposal, protective equipment and spill/leak procedures.

3.8 QA – Quality Assurance

4.0 Personnel Qualifications/Responsibilities

4.1 Field operations require training specified in EAP's Field Safety Manual such as First Aid, CPR, and Defensive Driving.

4.2 Boat operations require that staff meet specific training requirements as described in EAP's Field Safety Manual, such as an EAP Boating Course and an approved Boating Safety Course.

4.3 Because the procedure requires the use of hazardous materials, training is required as per the Ecology Chemical Hygiene Plan and Hazardous Material Handling Plan (Section 1) (Ecology, 2006), 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.

5.0 Equipment, Reagents, and Supplies

5.1 <u>For Sampling</u>

5.1.1 DO Sampler (based on design presented in Figure 4500-0:1 of the 20th Edition of Standard Methods), 1 L Funnel-Tube Sampler, or Kemmerer/Van Dorn Samplers

5.1.2 Sampling rope
5.1.3 DO box
5.1.4 Plastic gloves
5.1.5 300 mL BOD bottles
5.1.6 Glass BOD stoppers
5.1.7 Plastic BOD bottle caps
5.8.1 Safety goggles or glasses
5.1.8 250 mL plastic wash bottle
5.1.9 Deionized water (DI water)
5.1.10 3 mL graduated disposable transfer pipettes
5.1.11 Manganous sulfate monohydrate reagent, (see Attachment D for MSDS) ***Caution* this chemical is a skin and eye irritant and may be harmful if inhaled or swallowed.**
5.1.12 Alkali-iodine-azide reagent, (see Attachment E for MSDS) ***Danger* this chemical is corrosive and may cause eye or skin burns or internal damage if inhaled or swallowed.**
5.1.13 Field Logbook or Field Data Report Form (see Attachment B.)

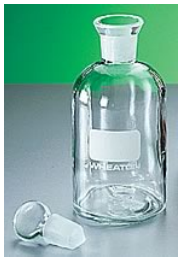

Figure 1. 300mL BOD bottle with glass stopper.

5.2 For Analysis

5.2.1 Nitrile gloves
5.2.2 Plastic apron
5.2.3 Face shield
5.2.4 25 mL graduated burette, w/3-way stopcock
5.2.5 10 mL volumetric burette, w/3-way stopcock or glass volumetric pipette
5.2.6 500 mL Erlenmeyer flask
5.2.7 Magnetic stirrer
5.2.8 Magnetic stir bar
5.2.9 203 mL volumetric flask
5.2.10 Concentrated sulfuric acid (95-98%) ***Danger* this chemical is a strong acid and may cause eye or skin burns or internal damage if inhaled or swallowed.**
https://www.cdc.gov/niosh/npg/npgd0577.html
5.2.11 Aqueous starch solution preserved with salicylic acid (must be kept in refrigerator and discarded if older than nine months)
5.2.12 Sodium thiosulfate (0.025 M), purchased at this concentration, (see Attachment F for MSDS)
5.2.13 Potassium bi-iodate (0.025 M), purchased at this concentration, (see Attachment G for MSDS)

5.3 Sample Containers

5.3.1 The normal container for dissolved oxygen samples is a 300 mL glass biological oxygen demand (BOD) bottle, with a narrow and flared mouth and a tapered and pointed ground glass stopper.

5.3.2 The bottles, stoppers, and bottle caps should be cleaned and rinsed with tap water after every use and stored in a manner to prevent dust and other materials from contaminating them.

5.3.3 Check bottle numbers before sampling to ensure that all numbers are unique (no duplications) to avoid confusion in data processing.

6.0 Summary of Procedure

6.1 EAP Wet Lab Preparation

6.1.1 The wet labs located at the EAP Western Operations Center (OC), the Eastern Regional Office Operations Center (EROC), and the Central Regional Office (CRO) are maintained by all lab users. Please do your part to keep it clean, tidy and safe. Titration chemicals and equipment are maintained by the current lab room coordinator/s at each facility. Bottles and preservatives for each vehicle or for each project are maintained by the vehicle custodian and/or project officer.

6.1.2 The appropriate EAP lab room coordinator should be contacted immediately if lab supplies or chemicals are running low or might be contaminated or expired so that fresh supplies/chemicals can be ordered. The project officer should check all equipment and reagents before sampling and notify others involved in the project of the status of the DO lab and other equipment. The project officer is also responsible to coordinate with lab room coordinator for the replacement/repair of DO equipment and/or chemicals.

6.2 Field Preparation

6.2.1 Prepare DO Box:

6.2.1.1 Use clear 125 mL or 250mL capped bottles (Figure 2) for field reagent storage (Manganous sulfate monohydrate and alkali-iodide-azide) in the DO Box to reduce the contamination potential and to be able to see if they have gone bad. These volumes also ensure that the reagents are

essentially fresh when used and refilled on a regular basis. Discard reagents that have been stored in the DO Box longer than a year.

6.2.1.2 Store the 3 mL graduated disposable transfer pipettes used to dispense these reagents in a manner to prevent reagent contamination or cross-contamination. One easy and simple method is to drill a hole in the center of the bottle, just barely larger than the diameter of the pipette, which allows the designated pipette to be inserted for filling and storage purposes (Figure 2).

Figure 2. Reagent containers with holes for pipette filling and storage.

6.2.1.3 The supersaturated alkali-iodide-azide solution is chemically unstable and, when contaminated with dirt or other impurities, can form a colored (not white) precipitate that makes it difficult to pipette. Standard Methods indicates that the white turbidity in the azide solution is acceptable (APHA, 2005). Always stir any turbid solution with the pipette before reagent extraction.

6.2.1.4 Label reagents and pipettes to avoid cross contamination. The manganous sulfate solution is typically labeled with the number “1” and the azide solution is typically labeled with the number “2” (Figure 2).

6.2.2 Record the BOD bottle number, date, time, and sampling location in a Field Logbook or Field Data Report Form.

6.2.3 Selecting an Appropriate Sampling Device.

6.2.3.1 The American Public Health Association (APHA) type 'DO sampler' (Figure 3a) is used to collect samples from a bridge or from the stream bank through the use of a rope.

6.2.3.2 The Kemmerer (Figure 3b) and Van Dorn (Figure 3d) samplers are often used to collect samples at depth in lakes or deeper rivers.

6.2.3.3 The 'Funnel-Tube Sampler' (Figure 3c) is typically used to collect samples in shallow, wade-able streams.

Figure 3a. APHA type DO sampler

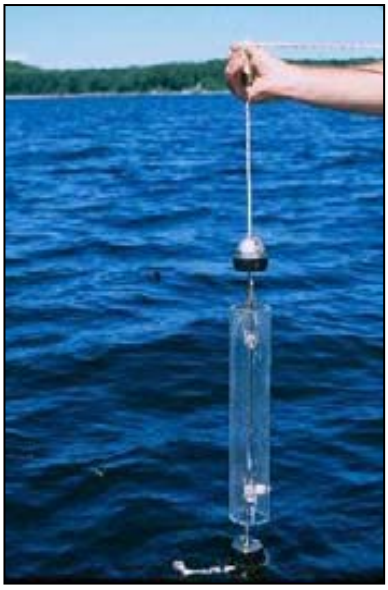

Figure 3b. Kemmerer Sampler

Figure 3c. Funnel-Tube surface sampler

Figure 3d. Van Dorn sampler

6.3 Sample Collection

6.3.1 **DO sampler method.** This method is typically used to collect samples from a bridge or from the stream bank through the use of a rope.

6.3.1.1 Rinse the sampler, top, and filler tubes with stream, tap water, or DI water.

6.3.1.2 Place the BOD bottle into the sampler. Orient the lid of the sampler to insure the filler tube is inserted into the BOD bottle and the lid is secure[1].

6.3.1.3 Attach the sampling rope to sampler.

6.3.1.4 Put on a high-visibility safety vest and move to a well-mixed location, such as the main part of the channel where a representative sample may be collected.

6.3.1.5 Carefully lower the sampler to the water surface, taking care to not dislodge any bridge debris onto it. Allow the bottom of the sampler to touch the water surface. Then raise the sampler off the water for a few moments to allow any debris from the bottom of the sampler to drop off and float away. Finally, rapidly lower the sampler about 0.5 meters to submerge it. ***Note: This minimizes the sampling of surface film and any debris from the bottom of the sampler.***

6.3.1.6 Retrieve the sampler when the bubbles from the vent tube stop (bottle is full). If a swift current carries the sampler downstream before it can completely fill, then pull the sampler from the water, allow it to swing upstream, and drop it back into the water. This action may need to be repeated a few times until the BOD bottle fills.

6.3.1.7 Retrieve the sampler, taking care not to dislodge bridge debris into it.

6.3.1.8 Set the sampler down and carefully remove the top.

6.3.1.9 Insert stopper and remove the BOD bottle.

6.3.2 **1L Funnel-Tube Sampler Method.** This method is typically used to collect a sample from a small or shallow stream.

6.3.2.1 Rinse the funnel in the stream.

6.3.2.2 Invert the funnel or orient the open end of the funnel upstream and slowly submerge it until it and the funnel tubing completely fills, avoiding any entrainment of air bubbles.

[1] The lid should be secured with bailing wire or string when sampling a stream with high velocity.

6.3.2.3 Pinch the funnel tubing about six inches from the end and remove the funnel, top end first, from the water.

6.3.2.4 Insert the end of the funnel tubing to the bottom of the BOD bottle. Let go of the tubing to allow the water to overfill the bottle (Figure 3c). Withdraw the tubing from the bottle just before the funnel has emptied. This step avoids any aeration of the sample with bubbles from the final discharge of the funnel.

6.3.2.5 Insert stopper into BOD bottle.

6.3.3 **Kemmerer or Van Dorn Method.** This method is typically used to collect samples from lake depths.

6.3.3.1 Rinse the sampler with water, attach the sampling rope, and set the sampler trigger mechanism.

6.3.3.2 Lower the sampler to the desired depth and trip the trigger.

6.3.3.3 Insert the end of the sampler tubing into the bottom of a BOD bottle, open the top of the sampler or the air inlet valve, and over fill the bottle with more than two times its volume prior to quickly removing the tubing. Do not use any samples that were aerated by the final discharge from the sampler.

6.3.3.4 Insert stopper into BOD bottle.

6.4 Field Processing

6.4.1 Wear chemical resistant gloves and eye protection to prevent reagents from getting on hands and in eyes. Hold sample away from body and mix carefully to avoid getting reagents on shoes or clothing.

6.4.2 If necessary, tap the side of the BOD bottle to dislodge air bubbles clinging to the inside

6.4.3 Insert a glass stopper in the BOD bottle and tip it to discard the displaced water.

6.4.4 Remove the stopper and fix the sample by adding two milliliters of manganous sulfate reagent followed by two milliliters of alkaline-azide reagent using the disposable pipettes reserved for each reagent. Gently add these reagents while holding tip of the pipette just above the water (avoids splashing and entraining air bubbles in the reagent stream).

6.4.5 Replace the stopper and mix the contents by inverting the bottle a few times.

6.4.6 Add a few milliliters of deionized water around the stopper to form a water seal, and cover the bottle top with a plastic BOD bottle cap. Then rinse the exterior of bottle with deionized water to prevent DO contamination box with reagent.

6.4.7 Place the fixed sample into the DO box. Samples need to be analyzed with in four days.

6.5 Laboratory Analysis *Note: Save all Winkler chemical waste resulting from any analysis in a pail or bucket for treatment (See 6.5.6 Winkler Waste Treatment and Disposal Methods).*

6.5.1 Initial Cleaning Procedure:

6.5.1.1 Put on a plastic apron and Nitrile gloves.

6.5.1.2 Thoroughly rinse the flask and stir bar with deionized water.

6.5.1.3 Check, and if necessary, fill the Potassium bi-iodate dispenser and starch squirt bottle.

6.5.1.4 Fill the Sodium thiosulfate reservoir and leave the cap loose.

6.5.1.5 Open the volumetric burette stopcock to a fill position.

6.5.1.6 Raise and lower the sodium thiosulfate storage bottle reservoir above and below the volumetric burette a few times to flush the burette and mix the sodium thiosulfate in the reservoir.

6.5.1.7 Clamp the reservoir onto the workstation lab-frame above the volumetric burette.

6.5.1.8 Use the volumetric burette stopcock to fill the burette and get rid of any air in the burette around the stopcock.

6.5.2 Titration Procedure:

6.5.2.1 Remove the plastic cap from the BOD bottle.

6.5.2.2 Pour off the water seal and invert the bottle several times to mix the floc.

6.5.2.3 Allow the floc to settle to the lower half of the bottle.

6.5.2.4 Put on the face shield.

6.5.2.5 Remove the bottle-top sulfuric acid dispenser from the acid storage cabinet. The dispenser should already be pre-set to dispense 2 mL of acid.

6.5.2.6 Remove the glass stopper of the BOD bottle. Dispense 2 mL of the acid into the DO sample and put the acid bottle back into the cabinet. *Note: Concentrated sulfuric acid is a very dangerous chemical and should be handled very carefully. Never add water to it and always immediately dispose of gloves that get any acid on them.*

6.5.2.7 Re-stopper the BOD bottle and invert it several times over the sink until the precipitate has completely dissolved. The sample should typically have a clear orange or yellow color. If some floc remains in BOD bottle, then invert the bottle several times to mix the floc and allow 5-6 minutes for the precipitate to dissolve. If the floc still has not dissolved then add a few drops of sulfuric acid from the sulfuric acid dispenser until floc completely dissolves.

6.5.2.8 Slide a magnetic stir bar into an empty 500 mL Erlenmeyer flask.

6.5.2.9 Fill a 203 mL volumetric flask[2] with the DO sample, transfer the sample to the Erlenmeyer flask, and set the flask in the sink.

6.5.2.10 Refill the volumetric burette with sodium thiosulfate. Make sure the sodium thiosulfate escapes from the top nipple.

6.5.2.11 Place the Erlenmeyer flask containing the sample on the magnetic stirrer and turn on the stirrer to the lowest setting.

6.5.2.12 Titrate the sample with the Sodium thiosulfate from the volumetric burette until it turns to a pale yellow color.

6.5.2.13 Squirt 1 to 2 mL of the starch solution into the sample. *Note: the addition of the starch solution earlier than this can cause a less distinct titration endpoint.*

6.5.2.14 Continue the titration process by adding the sodium thiosulfate by quickly twisting the burette stopcock past the discharge point or by slowly adding

[2] This is a slight modification of azide modification method presented in SM 20th Edition, 1998, which calls for the addition of 1 mL of manganous sulfate and alkali-iodine azide instead of 2 mL. The excess reagents are accounted for by using 203mL volumetric flasks rather than 201mL flasks.

individual drops until the purple color of the sample disappears. This is the titration end point[3] and it should be sharp and distinct[4]. Care should be taken to avoid an end point overrun.

6.5.2.15 Check the titration end point of any sample that was possibly overrun by adding a drop of bi-iodate from a 3 mL graduated disposable transfer pipette to the titrated sample. If the end point is correct, a faint purple color should reappear. If more than one drop of bi-iodate is required to get a faint purple color, then the end point was overrun. Do a Back-Titration (see 6.4.3 – Back-Titration) to correct the titration volume of the sample.

6.5.2.16 Record the titration result or corrected titration result in the proper column on the Field Data Report Form or in the field notes as mg/L of DO[5]. If the value is between the 0.1 mL marks on the burette, round the even numbers down and the odd numbers up (e.g., 10.25 to 10.2 and 10.35 to 10.4).

6.5.3 Back-Titration Procedure

6.5.3.1 Back-titrate an overrun end point sample using bi-iodate drops from a 3 mL graduated disposable transfer pipette (1 drop = 0.05 mg/L). Correct the final value[6] if the back-titration requires fewer than or equal to 8 drops and record the result without qualification[7]. If the back-titration requires more than 8 drops but less than or equal to 20, correct the final value and record the result with a "J" qualification (20 drops are equivalent to 1 mg/L). If the back-titration requires more than 20 drops, do not record a result, but make a comment on the Field Data Report Form indicating the titration error[8].

6.5.3.2 If a graduated burette or pipette is available, then carefully back-titrate to the overrun end point sample using a measured quantity of bi-iodate and subtract the amount used to correct the final result.

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[3]The volume of sodium thiosulfate used to titrate 203 mL of a sample equals the DO of the sample in mg/L.

[4] If the end point was not sharp and distinct or the sample contains purple flakes, then replace the starch solution (it may have gone bad – this is rare). Record the result with a "J" qualification to indicate the result is an estimate and note that the starch was bad and was replaced on the Field Logbook or Field Data Report Form.

[5] The mL of Sodium thiosulfate used to analyze a 200mL sample with this method is equal to the DO concentration in mg/L.

[6] The corrected final value is the final value - (number of drops used x 0.05 mg/L). For example, if 8 drops were used and the final value was 10.3 mg/L, then the corrected final value is 9.9 mg/L (10.3 mg/L - (8 x 0.05 mg/L or 0.4 mg/L)).

[7] Justification: Our MQOs specify 0.2 mg/L; 8 drops is equivalent to 0.4 mg/L which leaves a generous allowed error of 50% for miscounting, imprecise drop size, etc. to still be within MQOs.

[8] Justification: Results with a potential error of 50% of 1 mg/L, or 0.5 mg/L, should not be recorded at all.

6.5.4 Sodium Thiosulfate Normality Check. The test is done to verify the strength of the Sodium Thiosulfate solution and get a data correction factor. The normality check result should almost always be 10.0 mL if the Sodium Thiosulfate has been stored properly (a 9.95 or 10.05 result is considered a 10.0 result). The result should also be very similar to those that others have recently recorded in the Titration Log.

6.5.4.1 After the first sample has been titrated to its end point, add exactly 10 mL of the bi-iodate standard using a 10 mL volumetric burette w/3-way stopcock or glass volumetric pipette, rinse the inside wall of flask with starch solution, and re-titrate.

6.5.4.2 Repeat this procedure mid-way through the batch of samples to be titrated.

6.5.4.3 Record the volume of the sodium thiosulfate needed for each normality check on the field note book or worksheet and on the titration log located next to the titration station (The average of the two normality checks is used as a correction factor for the field data). *Note: These normality checks should be very close, within 0.2 mL. If they are not, then do at least two more until you have three consecutive results (within 0.2 mL of each other) to use to calculate a correction factor*.

6.5.4.4 If you get less than a 9.95 mL result, then repeat the normality check but do the following first:

6.5.4.4.1 Eliminate air from the tip of the Potassium Biiodate bottle-top dispenser to ensure it gives you 10.0 mL,

6.5.4.4.2 Gently dispense the Potassium Biiodate into the titrated solution in the bottom of the Erlenmeyer flask and avoid getting any on the inside flask wall,

6.5.4.4.3 Rinse the inside flask wall with starch solution to ensure that all of the Potassium Biiodate is in the titrated solution, and

6.5.4.4.4 Eliminate Sodium Thiosulfate drops/residue from the outside of the refillable burette tip and tube connection.

6.5.5 Correcting Titration End Point Results with Normality Check (NC) Results

6.5.5.1 Divide the average of the two or more normality check results into 10 to get the correction factor ($10/NC_{avg.}$) and then multiply the final result by the correction factor (CF) to get the corrected final result ($DO_{final} \times CF$).

6.5.5.2 For example, if the average of the normality checks was 9.9 mL and the sample titration result was 11.5 mL, then:

6.5.5.3 Correction Factor Multiplier = ($10/NC_{avg.}$) = (10/9.9 mL) = 1.01_{CF}

6.5.5.4 Corrected Final Result = ($DO_{final} \times CF$) = (11.5 mL x 1.01_{CF}) = 11.6 mL

6.5.5.5 *Note: The corrected final result is the volume in mL of sodium thiosulfate used to titrate a 200mL sample. This volume is equivalent to the concentration of DO in mg/L.*

6.5.6 Waste Treatment Procedures

Follow procedure depicted in Figure 4 below, record final pH on the Winkler Waste Treatment Record (Attachment C), and rinse the treated waste down the drain with copious amounts of tap water.

Figure 4. Winkler Waste Treatment.

6.5.7 Clean Up Procedure

6.5.7.1 Move the sodium thiosulfate reservoir back to its storage area on the counter.

6.5.7.2 Open the volumetric burette stopcock to a fill position (this allows the thiosulfate in the volumetric burette to return to the reservoir).

6.5.7.3 Tighten the reservoir cap and turn the volumetric burette stopcock to a closed position.

6.5.7.4 Thoroughly rinse the used flasks and stir bar(s), and give them a final rinse with deionized water.

6.5.7.5 Return all lab equipment to designated storage locations.

6.5.7.6 Clean counter and give sinks a final rinse.

7.0 Records Management

7.1 All hardcopy documentation of the data such as completed Field Logbook and Field Data Report Forms are kept and maintained by the project lead. These documents are organized in binders or in expanding files. After about six years, hardcopies are boxed and moved to EAP archives.

7.2 Data collected for Ecology's Ambient River and Stream Monitoring Program will be entered into an Access-based database, reviewed and verified following the Quality Control and Quality Assurance procedures (see 8.1 below), uploaded into EIM, and posted on our webpage www.ecy.wa.gov/programs/eap/fw_riv/index.html.

7.3 Data collected for special projects or Total Maximum Daily Load (TMDL) studies will be reviewed, verified, and stored based on the Quality Assurance Project Plan (QAPP) for the project.

8.0 Quality Control and Quality Assurance

8.1 Freshwater Ambient Monitoring Program

8.1.1 The data QA program for field sampling consists of four parts: (1) adherence to the SOP procedures for sample collection, processing, and periodic evaluation of sampling personnel, (2) consistent instrument calibration methods and schedules, (3) titration endpoint verification, and (4) collection and processing of field quality control (QC) samples. Our QA program is described in detail in

https://fortress.wa.gov/ecy/publications/summarypages/0303200.html (Hallock and Ehinger, 2003).

8.1.2 The field QC sample is collected as a duplicate (Sequential) Field Sample. This consists of the collection of an additional sample approximately 15-20 minutes after the initial collection at a station. This sample represents the total variability due to short-term, instream dynamics, sample collection and processing, and laboratory analysis.

8.1.3 A two-tiered system is used to evaluate data quality of individual results based on field QC. The first tier consists of an evaluation of the variability in field duplicates and the reasonableness of the result. Results exceeding pre-set limits are flagged. The second tier QC evaluation is a manual review of the data flagged in the first tier. Data are then coded from 1 through 9 (1 = data meets all QA requirements, 9 = data are unusable). Criteria for assigning codes are discussed in more detail in Hallock and Ehinger (2003). We do not routinely use or distribute data with quality codes greater than 4. *Note: results from highly turbid samples are estimated.*

8.2 Total Maximum Daily Load (TMDL) Studies

8.2.1 The TMDL data QA program for field sampling consists of two parts: (1) adherence to the SOP procedures for sample/data collection and periodic evaluation of sampling personnel and (2) the collection of a field quality control (QC) sample for ten percent of the samples collected for a given study.

8.2.2 The field QC sample is collected as a duplicate field sample. This consists of the collection of an additional sample in either a side by side manner or immediately following the initial sample. This sample represents the total variability due to sample collection and laboratory analysis.

8.2.3 QA/QC procedures will be addressed more thoroughly on a project-by-project basis in the QAPP for the project.

9.0 Safety

9.1 Safety is the primary concern when collecting samples. Since most sample sites are located on highway bridges, road and pass conditions should always be checked before departure (especially in winter). If roadside hazards, weather, accidents, construction, etc. make sample collection dangerous, then skip that station. Note the reason on the Field Data Report Form and notify your supervisor of the hazard when you

return to the office. If the hazard is a permanent condition, relocation of the station may be necessary. Review Ecology's Safety Program Manual (Ecology, 2015) periodically to assist with these safety determinations.

9.2 The proper safety gear (gloves, apron, face shield, etc.) should be worn, as described in the field processing and lab analysis sections above, to avoid exposure to potentially dangerous chemicals.

9.3 Material Safety Data Sheets (MSDSs) for all chemicals used in EAP field sampling or analytical procedures can be found at the following SharePoint link:
http://teams/sites/EAP/QualityAssurance/ChemicalSafetyDataSheets/Forms/AllItems.aspx
Also, binders containing MSDSs can be found in all field vehicles, vessels, Ecology buildings, or other locations where potentially hazardous chemicals may be handled. EAP staff following Ecology SOPs are required to familiarize themselves with these MSDSs and take the appropriate safety measures for these chemicals.

10.0 References

10.1 APHA (American Public Health Association), 2015. Standard Methods for the Examination of Water and Wastewater-. No: 4500-O C. Winkler Method, Azide Modification, American Public Health Association, 22nd Edition. Washington D.C.

10.2 Ecology, 2011. Chemical hygiene plan and hazardous materials management plan. Washington State Department of Ecology. Olympia, WA.

10.3 Ecology, 2015. Environmental Assessment Program Safety Manual. Washington State Department of Ecology. Olympia, WA.

10.4 Ecology, 2007. Standard Operating Procedures for the Collection and Processing of Stream Samples. Olympia, WA.

10.5 Hallock, D. and W. Ehinger, 2003. Quality Assurance Monitoring Plan: Stream Ambient Water Quality Monitoring. Washington State Department of Ecology, Olympia, WA. 27pp. Publication No. 03-03-200. https://fortress.wa.gov/ecy/publications/summarypages/0303200.html

ATTACHMENT A

The Chemistry of the Winkler Method:

1. $MnSO_4$ (manganous sulfate) + 2 KOH + KI (alkali-iodide) $\longrightarrow$ $Mn(OH)_2 + K_2SO_4$

2. $Mn(OH)_2$ (white precipitate) + $O_2 \longrightarrow MnO(OH)_2$ (brown precipitate)

3. $MnO(OH)_2 + H_2SO_4 \longrightarrow Mn^{+4}(SO_4)_2 + 3H_2O$
   $Mn^{+4}(SO_4)_2$ +2 KI $\longrightarrow$ $Mn^{+2}SO_4 + K_2SO_4 + I_2$ (dark brown/red, free iodine)

4. 2 $Na_2S_2O_3$ (thiosulfate) + $I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

Steps one and two occur simultaneously and result in a brown precipitate. The addition of acid (step 3) produces the iodine that is equivalent to the DO concentration, i.e., the iodine reduced in step 4 is equivalent to the concentration of DO in the sample.

The Winkler method is sensitive to interference from a number of substances. Two of the most common substances that cause interference are nitrite ions (NO_2^-) and ferrous ions (Fe^{+2}). Since nitrite is common in environmental samples, an azide modification that eliminates environmental levels of nitrite is used.

Azide Modification:

5. $2NaN_3 + H_2SO_4 \longrightarrow 2HN_3 + Na_2SO_4$
   $HNO_2 + HN_3 \longrightarrow N_2O + N_2 + H_2$

ATTACHMENT B

FIELD DATA REPORT FORM

DEPARTMENT OF ECOLOGY
State of Washington

FIELD DATA REPORT FORM

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SURVEY ..... SAMPLER ..... PAGE ..... OF

STATION NO.	STATION NAME	TIME	TEMP °C	DO mg/L	DO #	TEMP pH	TRUE pH METER	COND µMHOS/CM	BARO. PRESS. in. Hg	*	STAGE HEIGHT	CHK BAR/ WT LNGTH ADDTN	COMMENTS

WEATHER, etc.:

Relinquished By:	Received By:	Da		Hr		Mn		Comments

* 1 = WWG 2 = Staff 3 = GH 4= Tape Down 5 = Other (Specify above

ATTACHMENT C
WINKLER WASTE RECORD

Winkler Waste Record

Name	Date	Volume	Initial pH	pH after treatment

Measure and record waste volume and initial pH. Then sprinkle in about two tablespoons of Baking Soda per ½ gallon (or one scoop), stir it to mix, wait about five minutes, and then re-measure and record the final pH.