

Washington State Department of Ecology

Environmental Assessment Program

Standard Operating Procedures for the Collection and Analysis of Conductivity Samples

Version 2.1

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EAP032

Signatures on File

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This SOP is a harmonized version combining SOPs EAP032 and EAP10, which were both SOPs for conducting sampling and analysis.

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	Rev number	Summary of changes	Sections	Reviser(s)
4/9/2007	1.1	Editorial; formatting	All	Bill Ward
4/17/2007		Comments	All	Dave Hallock
4/27/2007	1.2	Edits based on comments	All	Bill Ward
5/15/2007		Editorial	All	Bill Kammin
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6/7/07	1.3	Edits based on comments	All	Bill Ward
6/13/07	1.3	Final edits (removed draft, added EAP number)	All	Bill Kammin
6/14/2007	1.3	Attachment incorporation		Bill Kammin
10/14/2010	1.4	Minor revisions	5 & 8	Bill Ward
11/21/2010	2.0	Harmonized with EAP SOP#010	all	Bill Ward; Nuri Mathieu
2/2/2011	2.1	Incorporate reviewer comments	all	Bill Ward; Nuri Mathieu

Environmental Assessment Program

Standard Operating Procedure for the Collection and Analysis of Conductivity Samples

1.0 Purpose and Scope

- 1.1 This document is the Environmental Assessment Program (EAP), Environmental Monitoring and Trends Section, Freshwater Monitoring Unit (FMU), Standard Operating Procedure (SOP) for the field collection and analysis of conductivity samples. In addition, this method covers the 'Direct In-Situ Method' (Section 6.2.4) used in wadeable streams for Total Maximum Daily Load and other special studies.
- 1.2 The procedures cover meter calibration, sample collection, sample measurement, and quality assurance/quality control. The conductivity meter sample measurement methods follow those described in Standard Methods 2510 B (APHA, 2005).

2.0 Applicability

- 2.1 This SOP is intended for freshwater monitoring. Marine waters measurements or samples should be taken as specified in a Quality Assurance project Plan.

3.0 Definitions

- 3.1 Conductivity –A measure of the ability of water to carry an electrical current. It is dependent upon the concentrations and types of dissolved ions and the water temperature. In general, a greater concentration of ions in the water will lead to a larger conductivity value.
- 3.2 EAP – Environmental Assessment Program.
- 3.3 Ecology – Washington State Department of Ecology.
- 3.4 EIM – Environmental Information Management System. A searchable database developed and maintained by the Washington State Department of Ecology.
- 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 μmhos – micro mhos ($\text{mho} = 1/\text{ohm} = 1 \text{ Siemens}$) per centimeter
- 3.7 MQO's – Measurement Quality Objectives
- 3.8 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.

3.9 Run – Scheduled sampling day(s).

4.0 Personnel Qualifications/Responsibilities

4.1 Field operations require training specified in EAP's Field Safety Manual (Ecology, 2006) 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) (WA State Department of 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 and Supplies

5.1 DO Sampler (based on design in Figure 4500-0:1 of the 20th Edition of Standard Methods).

5.2 Sampling ropes (1 @ 10 ft., 1 @ 35 ft. and 2 @ 55 ft.)

5.3 Extension pole with three prong clamp.

5.4 Field Logbook or Field Data Report Form
(see attachment A for form)

5.5 Conductivity meter with a non-linear function and a 4-cell probe

5.6 Two – 100 mL one-shot 100 μ mhos/cm conductivity standards.

5.7 Deionized water (DI water)

5.8 Meter Calibration Log Form (see attachment B)

6.0 Summary of Procedure

6.1 Meter Calibration.

6.1.1 Soak the conductivity probe in a container of tap water for at least 30 minutes (overnight is better) before calibrating.

6.1.2 Clean the conductivity probe cells with a Q-Tip.



Figure 1. Example of a non-linear Conductivity meter with 4-cell probe.

- 6.1.3 Hold the cable end of the probe, rinse the other end of the probe with DI water, and flick the water off the probe with a quick downward jerking movement a few times. *Note: avoid striking the probe on the sink edge or counter.*
- 6.1.4 Set the probe into a freshly opened one-shot 100 µmhos/cm conductivity standard bottle. *Note: the conductivity standard is easily contaminated. Keep it tightly capped and avoid diluting it with DI or stream sample water. The accuracy of freshly opened standard lasts for up to 5 days. For this reason, large containers of standard are not recommended.*
- 6.1.5 Check the meter settings to ensure the meter reads in the non-linear function (nLF) mode for temperature compensation and the reference temperature setting is 25°C¹.
- 6.1.6 Adjust the cell constant to calibrate the meter according to the meter instruction manual.
- 6.1.7 Record the conductivity standard concentration, the meter I.D. number, the initial and final cell constants, and any other required information on the Meter Calibration Log Form (see Attachment B for form).
- 6.1.8 Store the conductivity probe in DI water or stream sample water while collecting samples. (Do not store with the pH probe).

6.2 Sample Collection.

- 6.2.1 **DO sampler method.** This method is typically used to collect stream samples from a bridge or from the stream bank through the use of a rope.
 - 6.2.1.1 Rinse a dedicated 1 L pH and conductivity grab sample bottle (marked with red permanent ink) with DI water and secure it in the DO sampler bottle holder location.
 - 6.2.1.2 Put on a high visibility safety vest and carry the needed sampling gear to a well mixed location such as the main part of the channel where a representative stream sample may be collected.
 - 6.2.1.3 Attach the sampling rope to the DO sampler, remove the bottle cap to the 1 L pH and conductivity grab sample bottle, and set the cap aside where it can remain clean.
 - 6.2.1.4 Carefully lower the DO 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, and 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. Then 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.*

¹ The nLF setting works best for measuring low ionic strength natural waters and the temperature reference setting adjusts results to equivalent conductivities at 25°C to facilitate data comparison.

- 6.2.1.5 Retrieve the sampler taking care not to dislodge bridge debris into it.
- 6.2.1.6 Replace the bottle cap.
- 6.2.1.7 Return to the van with all the sampling gear.
- 6.2.2 **Hand Dip Method.** This method is typically used to collect samples within reach of the water surface (when standing in or near the stream or lake, or from small boat).
 - 6.2.2.1 Move to a well mixed location such as the deepest part of the active channel or another location where a representative sample may be collected. *Note: Do not contaminate the sample location by wading upstream of it or collect a sample from an eddy that had been waded.*
 - 6.2.2.2 Grab the base of the pH and conductivity grab sample bottle with one hand and remove the bottle cap. Then invert the bottle, reach upstream, and plunge the bottle into the water about 15 cm (6 inches), and tip the bottle mouth up toward the water surface. Allow the bottle to fill and then take it out of the water. *Note: If sampling from a boat or in still water, plunge the bottle into the water, and move it away from the boat while tipping it to avoid contamination.*
- 6.2.3 **Extension Pole Method.** This method is typically used to reach a more representative or undisturbed sample location from the stream bank or when wading in a lake or slow moving stream.
 - 6.2.3.1 Secure the pH and conductivity grab sample bottle in the extension pole clamp.
 - 6.2.3.2 Move to a location where a representative sample may be reached with the pole.
 - 6.2.3.3 Remove the cap from the bottle and place it where contamination can be avoided.
 - 6.2.3.4 Position the bottle just over the desired sample location.
 - 6.2.3.5 Invert the bottle and in one quick motion plunge the mouth of the bottle into the water about 15 cm (6 inches) and then tip the bottle mouth toward the water surface. Wait until the bottle has filled and then take it out of the water.
- 6.2.4 **Direct In-Situ Method.** This method is primarily used in Total Maximum Daily Load and other special studies to measure conductivity in shallow wadeable streams and occasionally used to measure it in larger streams and lakes.
 - 6.2.4.1 Freshwater measurements should be taken from an undisturbed representative location, such as the thalweg of a stream (deepest and fastest portion), in the middle of the water column (at least several inches above the stream bed and below the surface), and, for rivers and streams, where water is visibly flowing in the downstream direction.

6.2.4.2 Rinse the conductivity probe directly in the waterbody with a swirling motion, turn on the meter, and then allow it to stabilize. Record the result following section 6.3.4 of this SOP.

6.3 Sample Measurement Procedure.

6.3.1 **Direct conductivity grab sample bottle measurement.**

6.3.1.1 Insert probe directly into conductivity grab sample bottle.

6.3.1.2 Turn on the conductivity meter and allow it a few minutes to indicate a stable result.

6.3.1.3 Record the conductivity result on the Field Data Report Form or Field Logbook. *Note: The meter displays results to the nearest tenth and the result needs to be rounded to the nearest whole number. If the tenths digit > 0.5, round up; if it is < .5, round down; and if it is = to 0.5 round to the nearest even number. For example, a result of 103.5 μ mhos rounds to 104 μ mhos and a result of 62.5 μ mhos rounds to 62 μ mhos.*

6.3.2 **Conductivity cup measurement.**

6.3.2.1 Rinse the conductivity measurement cup and probe with DI or sample water.

6.3.2.2 Remove the cap to the conductivity grab sample bottle and gently over fill the conductivity measurement cup with the sample water.

6.3.2.3 Turn on the conductivity meter and allow it a few minutes to indicate a stable result.

6.3.2.4 Record the conductivity result following section 6.3.1.3.

6.4 End of Day QC Procedures.

6.4.1 Check the calibration of the conductivity meter by rinsing the probe with DI water, shake the water off the probe, and set the probe into the recently opened one-shot 100 μ mhos/cm conductivity standard (or another standard that is within the expected range of measured field results). Record a stable result on the Field Data Report Form or Field Logbook. If the result is not within 5 μ mhos/cm of the standard, then troubleshoot the meter² and if possible re-measure all of the samples.

6.4.2 If troubleshooting the meter steps do not work, then review the troubleshooting section in the meter instruction manual to fix the problem. If the problem cannot be fixed, then turn the defective equipment into the Operation Center Technician along with a completed Equipment Problem Report Form.

² Check to make sure that the meter is in the non-linear function (nLF) and the temperature coefficient is 25. Then verify the meter calibration using an unopened conductivity standard (the standard is easily contaminated). If the meter needed to be changed to the non-linear function, temperature reference 25, or be recalibrated, then re-measure all of the samples. If on a run, then re-measure using the TSS sample.

6.5 End of Day or Run Procedures.

6.5.1 If the meter and probe will be used the next day, then store the probe in stream sample or tap water.

6.5.2 If the overnight air temperatures will be below 45 °F, then move the meter, probe stored in DI or stream sample water, and conductivity standard into a heated room (hotel room, regional lab, or operation center).

6.5.3 If the meter and probe will not be used the next day, then rinse the probe with DI water and store the meter and dry probe in a heated room.

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 web page http://www.ecy.wa.gov/programs/eap/fw_riv/rv_main.html.

7.3 Data collected for Total Maximum Daily Load or special project studies will be reviewed, verified, and stored based on the QAPP for the project.

8.0 Quality Control and Quality Assurance Section

8.1 Freshwater Ambient Monitoring Program

8.1.1 The data QA program for field sampling consists of three parts: (1) adherence to the SOP procedures for sample/data collection and periodic evaluation of sampling personnel, (2) consistent instrument calibration methods and schedules, and (3) the collection of one field quality control (QC) sample during each sampling run: either a duplicate field sample or a true process field blank sample. Our QA program is described in detail in www.ecy.wa.gov/biblio/0303200.html (Hallock and Ehinger 2003).

8.1.2 Duplicate (Sequential) Field Sample. This sample is collected approximately 15-20 minutes after the initial sample was collected. This sample represents the total variability due to short-term, in-stream dynamics, and sample collection and measurement.

- 8.1.3 True Process Field Blank Sample. This sample is subject to the sample site collection and processing conditions. The expected value for this analyzed result is less than 3 μ S (micro Siemens).
- 8.1.3.1 Return to the sample site with the cleaned pH and conductivity grab sample bottle and go through the normal sample collection procedure but do not immerse the uncapped bottle or Bridge sampler. Cap the bottle, return to the van, and fill the container with the Lab provided DI water.
- 8.1.3.2 Fill the conductivity measurement cup with water from the pH and conductivity grab sample bottle, allow the conductivity probe to stabilize, and record the measurement.
- 8.1.4 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 data. 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.
- 8.2 Total Maximum Daily Load Monitoring Program
- 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) measurement for ten percent of the samples or measurements collected for a given study.
- 8.2.2 The field QC measurement is taken as a replicate field measurement. This consists of moving several feet upstream of the initial measurement location and repeating the measurement procedure. This sample represents the total variability due to in-situ measurement. Alternately, if available, a second pre-calibrated meter (of the same model) can be used to take a measurement in the same location as the initial measurement.
- 8.2.3 QA/QC procedures will be addressed more thoroughly on a project-by-project basis, as stated 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, 2010) periodically to assist with these safety determinations.

10.0 References

- 10.1 APHA, 2005. Standard Methods for the Examination of Water and Wastewater, 21st Edition. Joint publication of the American Public Health Association, American Water Works Association, and Water Environment Federation. www.standardmethods.org/ .
- 10.2 Ecology, 2006. Chemical hygiene plan and hazardous materials management plan. Washington State Department of Ecology. Olympia, WA.
<http://aww.ecology/services/es/Safety/ChemicalHygiene.pdf>
- 10.3 Ecology, 2010. Environmental Assessment Program Safety Manual. Washington State Department of Ecology. Olympia, WA.
<http://aww.ecology/programs/eap/Safety/Safety1.html>
- 10.4 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.
www.ecy.wa.gov/biblio/0303200.html

ATTACHMENT B

Meter Calibration Log Form

Run: _____ Date: _____ Sampler: _____

Meter ID Numbers		Pre-Run Calibration			
Cond.		(a) Thermometer (°C)		Van pressure (Pre-cal.)	
pH		(b) Thermister (°C)		Lab pressure	
pH probe		Correction (a minus b)		Adjusted?	Y/N
Temp.		Was that corr. expected?	Y/N		

DAY 1

Cond Meter	Standard:		Initial Meter Reading:		Initial Cell Const:		Final Cell Const:	
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pH Meter	Slope ^a :		Time:	
	mv @ pH 4/10:		Buffer Temp:	
	mv @ pH 7:		Response Time ^b :	
	True pH	Meter pH	Time	Recal?
QA Check #1		c		Y / N
QA Check #2		c		Y / N
QA Check #3		c		Y / N

pH of buffers at various temperatures					
Temp	pH7	pH9	Temp	pH7	pH9
10	7.01	9.27	20	6.98	9.19
11	7.01	9.26	21	6.98	9.19
12	7.00	9.25	22	6.97	9.18
13	7.00	9.25	23	6.97	9.17
14	7.00	9.24	24	6.97	9.16
15	7.00	9.23	25	6.97	9.16
16	6.99	9.22	26	6.96	9.15
17	6.99	9.22	27	6.96	9.14
18	6.99	9.21	28	6.96	9.13
19	6.98	9.20	29	6.95	9.13

Cond Meter	Standard:		Meter Reading:	^d	Cell Const:		Time:	
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DAY 2

Cond Meter	Standard:		Initial Meter Reading:		Initial Cell Const:		Final Cell Const:	
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pH Meter	Slope ^a :		Time:	
	mv @ pH 4/10:		Buffer Temp:	
	mv @ pH 7:		Response Time ^b :	
	True pH	Meter pH	Time	Recal?
QA Check #1		c		Y / N
QA Check #2		c		Y / N
QA Check #3		c		Y / N

Footnotes:

- ^a If <90%, buffers, probe, or cable may be bad.
- ^b If > 45 seconds try 1) cleaning probe, 2) changing cable, 3) new probe
- ^c If meter pH is >± 0.05 units, recalibrate; if > ± 0.10 units, recalibrate, re-read sample, & "J" data since last calibration.
- ^d If meter conductivity is >± 5µs/cm, recalibrate, re-read sample, & "J" data since last calibration.

Cond Meter	Standard:		Meter Reading:	^d	Cell Const:		Time:	
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DAY 3

Cond Meter	Standard:		Initial Meter Reading:		Initial Cell Const:		Final Cell Const:	
pH Meter					<u>Comments:</u>			
Slope ^a :			Time:					
mv @ pH 4/10:			Buffer Temp:					
mv @ pH 7:			Response Time ^b :					
	True pH	Meter pH	Time	Recal?				
QA Check #1		c		Y / N				
QA Check #2		c		Y / N				
QA Check #3		c		Y / N				
Cond Meter	Standard:		Meter Reading:	d	Cell Const:		Time:	

DAY 4

Cond Meter	Standard:		Initial Meter Reading:		Initial Cell Const:		Final Cell Const:	
pH Meter					<u>Comments:</u>			
Slope ^a :			Time:					
mv @ pH 4/10:			Buffer Temp:					
mv @ pH 7:			Response Time ^b :					
	True pH	Meter pH	Time	Recal?				
QA Check #1		c		Y / N				
QA Check #2		c		Y / N				
QA Check #3		c		Y / N				
Cond Meter	Standard:		Meter Reading:	d	Cell Const:		Time:	