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Collection and Analysis of pH Samples

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Contact information

For more information contact:

Publications Coordinator
Environmental Assessment Program
P.O. Box 47600, Olympia, WA 98504-7600
Phone: (360) 407-6764

Washington State Department of Ecology - www.ecy.wa.gov

o	Headquarters, Olympia	(360) 407-6000
o	Northwest Regional Office, Bellevue	(425) 649-7000
o	Southwest Regional Office, Olympia	(360) 407-6300
o	Central Regional Office, Union Gap	(509) 575-2490
o	Eastern Regional Office, Spokane	(509) 329-3400

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 pH Samples

Version 1.5

Author - William J. Ward
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Reviewers – Brad Hopkins (2017), Dan Dugger (2013), Casey Clishe (2007)
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QA Approval - William R. Kammin, Ecology Quality Assurance Officer
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Signatures on File

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
5/15/2005		Editorial comments	All	Bill Kammin
5/18/2007		Edits based on comments	All	Bill Ward
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6/7/07	1.3	Edits based on comments	All	Bill Ward
6/13/2007	1.3	Correct footer, title page	All	Bill Kammin
4/10/13		Added new chemical awareness and waste disposal language, and updated procedures. Attached MSDS sheets. Also made minor procedure updates	5, 6, 9	Bill Ward
5/12/14		Editorial comments	All	Dan Dugger, Andy Bookter, Bill Kammin
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8/13/14	1.4	Final edits	All	Olegre, Kammin
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6/26/17	1.5	Recertified	All	Bill Kammin

Environmental Assessment Program

Standard Operating Procedure for the Collection and Analysis of pH Samples

1.0 Purpose and Scope

1.1 This document is the Environmental Assessment Program (EAP) Standard Operating Procedure (SOP) for the field collection and analysis of pH samples. The SOP covers meter calibration, sample collection, sample measurement, and quality assurance/quality control procedures to ensure we have the highest data quality. It is not a substitute for the electrode user manual: calibration, maintenance, storage, and troubleshooting recommendations, or the mandatory training.

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 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 sample sites.

3.5 MQO’s – Measurement Quality Objectives

3.6 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.

3.7 OC – Operations Center. The location of the program field equipment, boats, walk-in cooler and shop (where technicians repair or fabricate the equipment).

3.8 pH – A measure of the acidity or alkalinity of a solution, numerically equal to 7 for neutral solutions, increasing with increasing alkalinity and decreasing with increasing acidity. The pH scale ranges from 0 to 14.

4.0 Personnel Qualifications/Responsibilities

4.1 Field operations require training specified in EAP's Field Safety Manual (Ecology, 2012). The required trainings include: 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, 2011), 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 Bridge Sampler.
5.2 Sampling ropes (1 @ 10 ft., 1 @ 35 ft. and 2 @ 55 ft.).
5.3 Extension pole with a bottle clamp.
5.4 Field Logbook or Field Data Report Form (See Attachment A for example form).
5.5 Refillable pH electrode that is capable of having at least a two point calibration. *Note: Non-refillable (gel-filled) electrodes are not considered reliable enough for our field measurements.*
5.6 QC 7 pH buffer that is from a different manufacturer than the pH 7 calibration buffer.
5.7 pH buffers that bracket the expected range of field measurements (See Attachment B for MSDS sheets). *Note: These buffers are not considered a health hazard.*
5.8 Dedicated pH buffer calibration bottles (125 mL clear bottles) or pouches.
5. 9 pH electrode filling and storage solution. (See Attachment C for MSDS sheet). *Caution: These solutions may cause eye irritation.*
5. 10 Deionized water (DI water) and squirt bottle.
5. 11 Meter Calibration Log Form (See Attachment D for example form).

6.0 Summary of Procedure

6.1 Meter Calibration. *Note: Always store the meter, electrode, pH buffers, and filled DI squirt bottle overnight in a heat-controlled room that is kept between 15-30 °C (59-86°F). Also, all pH electrode calibrations must be done using buffers that are above 15°C (but not warmer than 30°C). Further, always keep the electrode upright (sensor tip down) and the storage bottle about half-full of the filling and storage solution.*

6.1.1 Empty and refill the dedicated pH buffer calibration and QC check bottles with fresh solution at the beginning of each week or when considered contaminated.

6.2 Non-Hach PHC281 Electrode Calibrations.
6.2.1 Calibrate electrode following the meter instruction manual for a two- or three-point

calibration. Buffers used for a two-point calibration must bracket the expected range of the field measurement results (e.g., 4 and 7 or 7 and 10).

6.2.2 Record the calibration information on the calibration sheet or field log. Then reattach the electrode storage bottle, plug the electrode filling-hole hole, and store the electrode upright.

6.2.3 Hach PHC281 Electrode Calibrations.

6.2.3.1 Clear the junction. Remove the filling-hole cap, and slowly pull the attached electrode soaker bottle down the electrode in half-inch increments until there is a noticeable drop in the volume of the electrode filling solution.

6.2.3.2 Remove the electrode storage bottle and top off the electrode fill chamber with filling solution.

6.2.3.3 Calibrate electrode following the meter instruction manual for a three-point calibration (Note: Hach 4, 7, and 10 buffers must be used).

6.2.3.4 Check the calibration accuracy by reading the QC7 buffer.

6.2.3.5 Record the calibration information on the calibration sheet or field log. Then reattach the electrode storage bottle and store the electrode upright.

6.3 Sample Collection.

6.3.1 Bridge 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.

6.3.1.1 Rinse a dedicated 1 L pH and conductivity grab sample bottle with DI water and secure it in the Bridge Sampler.

6.3.1.2 Put on a high-visibility safety vest and carry the needed sampling gear to a well-mixed sampling location where a representative stream sample may be collected.

6.3.1.3 Attach the sampling rope to the Bridge Sampler, remove the bottle cap, and set the cap aside.

6.3.1.4 Carefully lower the Bridge 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 allow it to submerge about 0.5 meters. *Note: These steps help minimize the sampling of surface film and any debris from the bottom of the sampler.*

6.3.1.5 Retrieve the sampler taking care not to dislodge bridge debris onto it, replace the bottle cap, and return to the van with all the sampling gear.

6.3.2 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).

6.3.2.1 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 has been waded.*

6.3.2.2 Hold the base of the pH and conductivity grab sample bottle with one hand, and remove the bottle cap. Then invert the bottle, reach upstream, plunge the bottle mouth into the water about 15 cm (6 inches), and then tip it up toward the water surface. Remove the filled bottle from the water, replace the cap, and return to the van. *Note: If sampling still water or from a boat, then plunge the bottle opening into the water, and move it upstream or away from the entry location while tipping it upright.*

6.3.3 Extension Pole Method. This method is typically used to reach a more representative or undisturbed sample location from the stream bank or lake shore, or slow moving stream.

6.3.3.1 Secure the pH and conductivity grab sample bottle in the extension pole clamp.

6.3.3.2 Move to a location where a representative sample may be reached with the pole.

6.3.3.3 Remove the cap from the bottle, and place it where contamination will be avoided.

6.3.3.4 Invert the bottle over the desired sample location, plunge the bottle mouth into the water about 15 cm (6 inches), and then tip it toward the water surface. Allow the bottle to fill, remove it from the water, replace the cap, and return to the van.

6.4 Sample Measurement Procedure. *Note: It takes a minimum of three to five minutes to obtain a repeatable and stable pH measurement from a grab sample. Also note: Avoid significant sample temperature changes by keeping the collected sample in the shade by the stream, or closing up the van and turning on air conditioner or heater. (Sample pH can change with temperature).*

6.4.1 Unplug the electrode filling-hole, and remove the electrode storage bottle. Rinse electrode and pH measurement cup with DI or sample water.

6.4.2 Gently fill and overfill the pH measurement cup with the sample water. *Note: excessive agitation of the sample water will affect pH.*

6.4.3 Insert the electrode into the sample, turn on the meter, and gently stir the sample with the electrode a few times during the first two minutes.

6.4.4 Then gently stir the sample with the electrode, push the measurement button, and continue to stir the sample until a stable result is indicated.

6.4.5 Gently stir and re-measure the sample until obtaining consecutive stable readings at about 30 second intervals (within 0.02 pH units).

6.4.5.1 ***Note: If the Hach PHC281 electrode initial measurement is acidic and it becomes progressively more acidic with each measurement, then clear the junction and remeasure the sample. This ensures that the result was not from a plugged junction that caused the electrode to mostly read 6 pH unit filling solution.***

6.4.6 Record the stable pH result on the Field Data Report Form or Field Logbook. If the result is greater than 8.5, then an alkalinity sample should be collected and sent in for lab analysis.

6.4.7 If the pH result equals 6.5 or less or 8.5 or higher, then check calibration of the pH meter using the closest buffer (e.g., 7 or 10). Record the calibration check result on the Field Data Report Form and, if necessary, recalibrate meter, and remeasure the sample.

6.4.8 Rinse electrode with DI water, carefully re-attach the half-filled electrode soaker bottle, plug the filling-hole, and store the electrode upright.

6.5 Troubleshooting Procedure. *Note: Most electrode calibration, calibration drift, field drift, or inaccurate field measurement issues can be caused by a plugged or contaminated electrode junction, cold or low battery, or worn out electrode. If none of the following steps work, then reference the electrode manual.*

6.5.1 Non-Hach PHC281 electrodes.

6.5.1.1 Refer to meter instrument manual and review the troubleshooting section and if necessary perform self-test to identify and fix the problem.

6.5.1.2 Alternately soak the electrode in 10% HCl and household ammonia for a few minutes (**This is not an accepted practice for the Hach electrode**). *Note: Household ammonia vapors can be a problem for the conductivity electrode and can contaminate the Ammonia sample. This electrode cleaning process **must** be done outside the van.*

6.5.1.3 If you cannot fix the electrode issue, then consult with a more experienced coworker to help resolve the problem.

6.5.2 Hach PHC 281 electrode.

6.5.2.1 If the calibration slope is greater than 101 or lower than 97 (usually indicates a bad buffer), then empty and refill one or all the dedicated pH buffer calibration bottles with fresh buffer solution that are the same temperature and at least 15 °C. Return to the calibration procedure (6.2).

6.5.3.2 Electrode cannot be easily calibrated or drifts during field measurements.

6.5.3.2.1 Make sure the electrode filling-hole is open. If it is not, then open it, and return to the calibration or field measurement procedure (6.2 or 6.4).

6.5.3.2.2 If the electrode filling-hole is open, then clear the junction. Remove the filling-hole cap, reattach the electrode soaker bottle, and slowly pull the bottle down the electrode in half-inch increments until there is a noticeable drop in the volume of the electrode filling solution.

6.5.3.2.3 Remove the electrode storage bottle, top off the electrode fill chamber with filling solution, and return to the calibration or field measurement procedure (6.2 or 6.4).

6.6 QC Procedure.

6.6.1 Check the calibration of the pH meter after the first and last station of the day using the 7 QC buffer that is at or above 15°C and record the result on the Field Data Report Form.

6.6.1.1 If the difference between the pH calibration check result and the true QC buffer value is greater than or equal to 0.05 pH units, then recalibrate the meter.

6.6.1.2 If the difference between the pH meter result and the standard is greater than or equal to 0.10 pH units, then recalibrate the meter, re-read the sample, and "J" the data since last calibration check.

6.7 End of Day or Run Procedures.

6.7.1 Plug the electrode filling-hole hole, rinse it with DI water, replace the bottle cap, put the nearly half-filled electrode soaker bottle against the bottom of the electrode, slide the bottle cap down until it contacts the bottle threads, grasp the bottle cap and electrode to keep them from moving, and screw on the soaker bottle (goal is to prevent pushing air bubbles from entering the fill chamber through the junction).

6.7.2 Store the meter, electrode (tip down), calibration buffers, and a filled DI water squirt bottle into a heated room (hotel room, regional lab, or operation center).

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 typically organized in binders or in expanding files. After about six years, hardcopies are boxed and moved to EAP archives.

8.0 Quality Control and Quality Assurance Section

8.1 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 a field quality control (QC) sample during each sampling run. In addition, the alkalinity sample/CO_2 saturation levels comparisons may be done to determine if our measurement sampling methods are biasing the pH results.

8.2 Further data quality control and quality assurance procedures will be addressed thoroughly in each study Quality Assurance Project Plan.

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, 2012) periodically to assist with these safety determinations.

9.2 Waste disposal. Rinse the used pH buffers and the electrode filling/storage solution down the drain with water to reduce any impact on the wastewater treatment system.

10.0 References

10.1 Ecology, 2012. Environmental Assessment Program Safety Manual. Olympia, WA.

10.2 Ecology, 2011. Chemical hygiene plan and hazardous material handling plan. Olympia, WA.