Region 4 **U.S. Environmental Protection Agency** **Laboratory Services and Applied Science Division** **Athens, Georgia**	
Operating Procedure	
Title: Field pH Measurement	ID: LSASDPROC-100-R5
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Purpose

This document describes procedures, methods and considerations to be used and observed when conducting field pH measurements in aqueous phase environmental media, including groundwater, surface water and certain wastewaters.

Scope/Application

The procedures contained in this document are to be used by field personnel when measuring the pH of aqueous phase environmental media in the field. On the occasion that LSASD field personnel determine that any of the procedures described in this section cannot be used to obtain pH measurements of the media being sampled, and that another method must be used to obtain said measurements, the variant instrument and/or measurement procedure will be documented in the field logbook and subsequent investigation report, along with a description of the circumstances requiring its use. Mention of trade names or commercial products in this operating procedure does not constitute endorsement or recommendation for use.

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1 General Information

1.1 Documentation/Verification

This procedure was prepared by persons deemed technically competent by LSASD management, based on their knowledge, skills and abilities and has been tested in practice and reviewed in print by a subject matter expert. The official copy of this procedure resides on LSASD's local area network (LAN). The Document Control Coordinator is responsible for ensuring that the most recent version of the procedure is placed on LSASD's LAN and for maintaining records of review conducted prior to its issuance.

1.2 General Precautions

1.2.1 Safety

Proper safety precautions must be observed when conducting field pH measurements. Refer to the LSASD Safety, Health and Environmental Management Program Procedures and Policy Manual (Most Recent Version) and any pertinent site-specific Health and Safety Plans (HASPs) for guidelines on safety precautions. These guidelines, however, should only be used to complement the judgment of an experienced professional. Address chemicals that pose specific toxicity or safety concerns and follow any other relevant requirements, as appropriate.

1.2.2 Procedural Precautions

All field pH measurements pertinent to the sampling event should be recorded in the field logbook for the event. All records, including a unique, traceable identifier for the instrument, such as a property number or serial number, should be entered according to the procedures outlined in the LSASD Operating Procedure for Logbooks (LSASDPROC-010) and the LSASD Operating Procedure for Equipment Inventory and Management, (LSASDPROC-108). Care should be taken not to contaminate standards and samples and verify the expiration date of all standards prior to use. All meters should be calibrated, operated and maintained according to the manufacturer's specifications.

2 Quality Control

All pH meters will be maintained and operated in accordance with the manufacturer's instructions and the LSASD Operating Procedure for Equipment Inventory and Management (LSASDPROC-108). Before a meter is taken to the field, it will be properly calibrated or verified, according to Section 3.2 of this procedure, to ensure it is operating properly. These calibration and verification checks will be documented and maintained in a logbook.

The ambient temperature in the immediate vicinity of the meter should be measured and recorded in the field logbook to ensure the instrument is operated within the manufacturer's specified range of operating temperatures, although this is typically not necessary for ecological studies. For instruments that are deployed for *in-situ* measurements, the temperature of the medium being monitored should be measured and recorded in the logbook prior to deployment. *In-situ monitoring equipment may be utilized in unattended deployments where autonomous logging may preclude temperature measurement prior to deployment. Because in-situ instrumentation generally has a wide range of operating temperatures, the field investigator may utilize professional judgment in determining if the operating environment is suitable for unattended deployment.*

If at any time during a field investigation, it appears that the environmental conditions could jeopardize the quality of the measurement results, the measurements will be stopped. This will be documented in the field logbook.

3 Field pH Measurement Procedures

3.1 General

pH is defined as the negative logarithm of the effective hydrogen-ion concentration. The ion selective pH electrode measures the difference in potentials between the two sides in a glass electrode. The circuit is closed through internal solutions of the electrode and the external solution that is being measured and the pH meter. As the electrode is immersed in the test solution the glass bulb senses the positive charged hydrogen ions as millivolts (mV). The pH meter measures the difference between an internal electrode and a reference electrode. This mV reading is then read by the meter and is displayed in pH units. For routine work, a pH meter accurate and reproducible to within 0.2 Standard Units (S.U.) is suitable. For NPDES compliance monitoring, the pH meter should be accurate and reproducible to within 0.1 S.U. Both meters should have a range of 0 to 14 S.U. and be equipped with a temperature-compensation adjustment. Modern pH meters usually have a protective housing around the glass bulb but are sensitive scientific instruments and should be handled with care. Most pH electrodes last from one to two years, depending on the deployment environment and if proper storage solution was used during periods of inactivity.

3.2 Instrument Calibration

Many brands of instruments are commercially available for the measurement of pH incorporating a wide variety of technologies. The manufacturer's instruction manual should be consulted for specific procedures regarding their calibration, maintenance and use. Calibration of any measurement instrument must be conducted and/or verified prior to each use or on a daily basis, whichever is most appropriate. At a minimum, a two-point calibration should be conducted to ensure the accuracy of the meter. The following are basic guidelines for calibration/verification and are provided as an example (procedure may vary based on the instrument used):

1. Verify the meter's internal temperature sensor (thermistor) against a National Institute of Standards and Technology (NIST) traceable thermometer and note any differences between the thermistor and the NIST-traceable thermometer in the logbook. If the temperatures do not agree within ± 4°C, the unit or probe must be repaired or replaced. Alternatively, if the meter can be used in a manual temperature compensation mode, the NIST-traceable thermometer may be used for temperature readings and the necessary corrections applied. Check and record the temperatures of the standards and the samples.

2. If the pH range of the sample is not known, the pH of the sample to be tested should be estimated either from historical data or by using a four-color pH indicator paper or equivalent. Using this information, calibrate the pH meter with the buffers that bracket the expected pH range. Buffer solutions are commonly pH 4, 7 and 10. It may be possible to configure the pH meter so that it can be standardized with buffers other than those in the default configuration. Note that buffer values are temperature specific (reading true at 25°C) and be sure to input the correct buffer calibration value for the given temperature in step 3 below. Some pH probes are capable of Automatic Temperature Compensation (ATC) and will recognize the correct temperate corrected value of the calibration standard.

3. Immerse the probe in the required buffer solutions and record pre-cal values (pH 7 buffer is typically the first cal point). Then re-immerse the probe to calibrate to the correct pH buffer value, also recording the post-cal value. Rinse the probe with de-ionized water and blot dry or otherwise remove excess rinse water between the different buffer solutions. Record the buffer values and temperatures used to calibrate the meter.

4. Rinse the probe with de-ionized water, blot dry or otherwise remove excess rinse water and immerse it into the appropriate buffer and read as a measurement. If the meter reads within ± 0.2 S.U. of the known value of the buffer (for general applications such as ecological studies) or ± 0.1 S.U. (for regulatory applications such as NPDES or drinking water programs), record the value indicated by the meter. If the meter is outside of the acceptable accuracy range, it should be recalibrated. If it is still outside of the acceptable accuracy range after the second calibration, the electrode and/or meter should be replaced.

5. Once the meter has been properly calibrated and verified (steps 1-4 above), it is ready for use. Rinse the probe with de-ionized water and store it according to manufacturer's recommendations. Certain instruments may require being left on until all measurements are performed and the results are recorded. When collecting measurements from grab samples, certain instrument manufacturers recommend that an intermediate check(s) be performed by periodically checking the meter against a known calibration buffers if used for extended periods (> 4 hrs).

6. Unless the manufacturer indicates that the meter maintains its calibration after being turned off, meters must be re-calibrated if they are turned off during their period of use.

   Note: If multi-parameter sondes are used, calibrate according to the manufacturer's specifications and procedural directions. Calibration procedures for sondes for *in-situ* monitoring may in some cases be different than those for field pH meters using open probes. Those procedures are documented in LSASD's SOP listed as: LSASDPROC-111-R4, In-Situ

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3.3 Field Measurement Procedures

Measurements in the field may occur under several conditions, requiring various specific procedures. A pH probe should never be placed in an analytical sample to avoid cross-contamination, only sample aliquots should be used as a surrogate for sample pH measurements. Use of the word *sample* below implies that a sample aliquot has been collected.

3.3.1 Grab Sample Measurements

These procedures should be followed when conducting field pH measurements of grab sample:

1. Collect a sample. If the meter's thermistor is to be used for the temperature of record for the measurement activity, the temperature should be read as soon as the reading stabilizes and prior to measuring the pH.

   Note 1a: When the pH meter response is slow, unstable, or non-reproducible, it may be necessary to check the conductivity. If the conductivity is lower than 20 to 30 µmhos/cm, it is permissible to add 1 ml of 1M potassium chloride solution per 100 ml of sample to improve response time for the probe. Recheck the pH and record.

   Note 1b: If the pH measurements are to be used for RCRA regulatory purposes and when the pH approaches the alkaline end (pH ≥ 11.0) of the scale, the pH measurements should be made by a qualified analyst using laboratory quality equipment to control the sample at 25°C ± 1°C.

2. Immerse the lower part of the probe in the sample. Typically, in the field, the pH probe is not kept away from container bottom or sides during calibration, or during field readings in an overtopping cell, as it is not practical. End of day readings are also performed the same way. Allow ample time for the probe to equilibrate with the sample.

3. While suspending the probe in the sample container, record the pH.

4. Rinse the probe with de-ionized water and replace end cap if applicable. For longer term storage, place probe in the manufacturer's recommended storage solution.

3.3.2 Overtopping Cell Measurements

Often during groundwater sampling, an overtopping cell may be used with purge water constantly flowing through the cell during purging. These procedures should be followed when conducting field pH measurements using an overtopping cell:

1. Immerse the bottom portion of the probe in the open-top container being used for purge water

flow-through. Allow it to equilibrate with the purge water and stabilize until the meter indicates that it is ready for readings. Readings may be recorded at certain timed intervals in the field, prior to collecting the sample for laboratory analysis.

2. When finished at one sampling station during the day and moving to the next, the protective end cap should be placed on the probe until ready for use again.

3.3.3 *In-Situ* Measurements

These procedures should be followed when conducting *in-situ* field pH measurements:

1. Place the probe/sonde into the media to be measured and allow the pH and temperature readings to stabilize. Once the readings have stabilized, record the measurements in the logbook.

2. When deploying meters for extended periods of time, ensure the measurement location is representative of average media conditions.

   Note: If multi-parameter sondes are used for pH measurement, procedures such as for depth profiling of pH, may be different than for pH meters with open probes. Those procedures are documented in LSASD's SOP listed as: LSASDPROC-111-R4, In-Situ Water Quality Monitoring.

3.3.4 Sample Preservation Verification

When verifying the pH for sample preservation in a field sample collected for laboratory analysis, this procedure should be followed:

1. Pour a small amount of sample from bottle over a pH strip to determine if the sample has been preserved to the specified pH range; meters are not needed. Be sure to properly dispose of used pH strips, as contaminant level is likely unknown.

3.4 Operational Check

Even though it is not necessary to re-calibrate pH meters at regular intervals during the day, depending on the instrument, it may be appropriate to occasionally perform operational checks to determine if site conditions, such as an increase in temperature, have impacted the meter's performance. If an operational check is warranted, the following procedure should be followed to ensure that the performance of the meter has not changed.

1. While in use, periodically check the pH by rinsing the probe with de-ionized water, blot dry or

otherwise remove excess rinse water and immerse it into the appropriate buffer solution. If the measured pH differs by ≥ 0.2 S.U. or 0.1 S.U. (depending on the application) from the buffer solution, the meter must be re-calibrated.

A post-operation instrument verification check will be performed using the appropriate buffer(s) at the end of the day or after all measurements have been taken for a particular period of operation. These measurements must be recorded in the field logbook.

References

LSASD Operating Procedure for Equipment Inventory and Management, LSASDPROC-108, Most Recent Version

LSASD Operating Procedure for Logbooks, LSASDPROC-010, Most Recent Version

United States Environmental Protection Agency (US EPA). 2001. Environmental Investigations Standard Operating Procedures and Quality Assurance Manual. Region 4 Science and Ecosystem Support Division (LSASD Athens, GA

USEPA. Safety, Health and Environmental Management Program Procedures and Policy Manual. Region 4 LSASD, Athens, GA, Most Recent Version.

Revision History

The top row of this table shows the most recent changes to this controlled document. For previous revision history information, archived versions of this document are maintained by the LSASD Document Control Coordinator on the LSASD local area network (LAN).

History	Effective Date
LSASDPROC-100-R5, *Field pH Measurement,* replaces SESDPROC-100-R4 **General:** Corrected any typographical, grammatical, and/or editorial errors. Updated document format and naming convention. Replaced SESD and FSB with LSASD and ASB throughout due to Agency Re-alignment. Added language to Section 3.2 to specify that pH readings are temperature dependent and include steps for entering the current temperature when calibrating meters. Included language for documenting pre cal and post calibration readings. Section 3.3- clarified that pH meters should not be placed in samples to prevent contamination. Added Section 3.3.2 for performing pH measurement using overtopping cells. Added language for long term storage of probes to Section 3.3.1.3 Updated References	July 23, 2020
LSASDPROC-100-R4, *Field pH Measurement,* replaces LSASDPROC-100-R3 **General:** Corrected any typographical, grammatical, and/or editorial errors. **Title Page:** Changed the Field Quality Manager from Bobby Lewis to Hunter Johnson. Updated cover page to represent LSASD reorganization. John Deatrick was not listed as the Chief of the Field Services Branch	December 16, 2016
LSASDPROC-100-R3, *Field pH Measurement,* replaces LSASDPROC-100-R2	January 29, 2013
LSASDPROC-100-R2, *Field pH Measurement,* replaces LSASDPROC-100-R1	June 13, 2008
LSASD-100-R1, *Field pH Measurement*, replaces LSASDPROC-100-R0	November 1, 2007
LSASDPROC-100-R0, *Field pH Measurement*, Original Issue	February 05, 2007