Region 4
U.S. Environmental Protection Agency
Science and Ecosystem Support Division
Athens, Georgia

OPERATING PROCEDURE

Title: **Field pH Measurement**

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Revision History

This table shows changes to this controlled document over time. The most recent version is presented in the top row of the table. Previous versions of the document are maintained by the SESD Document Control Coordinator.

History	Effective Date
SESDPROC-100-R3, *Field pH Measurement*, replaces SESDPROC-100-R2 **General:** Corrected any typographical, grammatical and/or editorial errors. **Cover Page:** The Author was changed from Ron Phelps to Timothy Simpson. The EIB Branch Chief was changed from Antonio Quinones to Danny France. The EAB Branch Chief was changed from Bill Cosgrove to John Deatrick. The Field Quality Manager was changed from Laura Ackerman to Bobby Lewis. **Section 1.2:** Added the following statement: Mention of trade names or commercial products in this operating procedure does not constitute endorsement or recommendation for use. **Section 1.3, last sentence:** Added "and for maintaining records of review conducted prior to its issuance." **Section 1.4:** Added reference to the SHEMP Manual. **Section 1.5.1:** Updated the SHEMP Manual reference to reflect that the most recent version of the Manual will be used. **Section 2:** In the first paragraph, replaced "and" in the second sentence with "or". **Section 3.2:** Replaced the first paragraph with the following language for clarification purposes: "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: In Item #4, the first sentence, replaced "original buffer" to "appropriate buffer".	January 29, 2013

Item #5 was replaced with the following: "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 sample 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). **Section 3.4:** Revised the language to clarify procedures associated with operational checks. Item # 2 was converted to paragraphs 2.	
SESDPROC-100-R2, *Field pH Measurement*, replaces SESDPROC-100-R1 **Cover Page:** Author was changed from Marty Allen to Ron Phelps. **Revision History** Changed Field Quality Manager to Document Control Coordinator. **Section 1.3** Changed Field Quality Manager to Document Control Coordinator. **Section 2** Added requirements for unattended deployment of in-situ monitoring equipment. **Section 3.1 and 3.2, 4** Clarified requirements for routine and NPDES compliance monitoring. **Section 3.2, 2 and 5** Added first sentence for clarification.	June 13, 2008

SESDPROC-100-R1, *Field pH Measurement*, replaces SESDPROC-100-R0 **General** Deleted all references to SOSA. Updated referenced procedures due to changes in title names and/or to reflect most recent version. Replaced "shall" with "will". **Title Page** Changed title for Antonio Quinones from Environmental Investigations Branch to Enforcement and Investigations Branch. Changed Bill Cosgrove's title from Acting Chief to Chief. **Section 1.3** Updated information to reflect that procedure is located on the H: drive of the LAN. **Section 1.4** Alphabetized and revised the referencing style for consistency. **Section 2** Added last paragraph regarding stopping measurements due to environmental conditions. **Section 3.4** Re-phrased procedure #2 for clarity.	November 1, 2007
SESDPROC-100-R0, Field pH Measurement, Original Issue	February 05, 2007

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1 General Information

1.1 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.

1.2 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 SESD 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.

1.3 Documentation/Verification

This procedure was prepared by persons deemed technically competent by SESD 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 SESD's local area network (LAN). The Document Control Coordinator is responsible for ensuring that the most recent version of the procedure is placed on SESD's LAN and for maintaining records of review conducted prior to its issuance.

1.4 References

SESD Operating Procedure for Equipment Inventory and Management, SESDPROC-108, Most Recent Version

SESD Operating Procedure for Logbooks, SESDPROC-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 (SESD), Athens, GA

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

1.5 General Precautions

1.5.1 Safety

Proper safety precautions must be observed when conducting field pH measurements. Refer to the SESD 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.

1.5.2 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 SESD Operating Procedure for Logbooks (SESDPROC-010) and the SESD Operating Procedure for Equipment Inventory and Management, (SESDPROC-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 SESD Operating Procedure for Equipment Inventory and Management (SESDPROC-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 insure the instrument is operated within the manufacturer's specified range of operating temperatures. 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 temperature, 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. For routine work, a pH meter accurate and reproducible to within 0.2 Standard Unit (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.s and be equipped with a temperature-compensation adjustment.

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:

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.

3. Immerse the probe in the first buffer solution and calibrate the meter to read the correct pH. After the initial buffer calibration, calibrate the meter using other buffer solutions, as appropriate. 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 sample. 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 sample 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.

3.3 Sample Measurement Procedures

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

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 1: 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 2: 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 probe in the sample keeping it away from the sides and

bottom of the sample container. Allow ample time for the probe to equilibrate with the sample.

3. While suspending the probe away from the sides and bottom of the sample container, record the pH.

4. Rinse the probe with de-ionized water and store it in the manufacturer's recommended storage solution until the next sample is ready.

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

1. Place the probe 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, insure the measurement location is representative of average media conditions.

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 $\geq$ 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.