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SW-846 Method 9045D– Soil and Waste pH

Access to this SOP shall be available within the laboratory for reference purposes; the official copy of this SOP resides on the official Georgia EPD website at https://epd.georgia.gov/about-us/epd-laboratory-operations. Printed copies of this SOP will contain a watermark indicating the copy is an uncontrolled copy.

1 Scope and Application

1.1 This method is an electrometric procedure for measuring pH in soils and waste samples. Wastes may be solids, sludges, or non-aqueous liquids. If water is present, it must constitute less than 20% of the total volume of the sample.

1.2 Restricted Procedure
This procedure is restricted to use by an analyst experienced in the operation of an approved pH meter. Additionally, the analyst must complete the requirements of the GAEPD Initial Demonstration of Analyst Proficiency prior to the analysis of actual samples. Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GAEPD Chemical Hygiene Plan for additional information regarding chemicals required by this method.

2 Definitions

2.1 Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Plan (see SOP reference 13.5) for Quality Control Definitions.

2.2 Primary Source (PS) – A standard that is used to make up the calibration points of a curve.

2.3 Second Source (SS) – A standard made from a manufacturer other than that of the primary source.

2.4 Initial Calibration Verification (ICV) – An ICV is a second source standard that is used to verify the correctness of the primary source calibration curve. The ICV is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve.

2.5 Continuing Calibration Check (CCC) or Continuing Calibration Verification (CCV) – A standard used to verify that the response of the instrument has not changed since initial calibration.

2.6 LCS (Laboratory Control Sample) and LCSD (Laboratory Control Sample Duplicate) are prepared by spiking laboratory reagent water, Ottawa sand or air sampling device with the target analyte or compound. They are used to validate the analytical batch with respect to accuracy and precision. In this method, the CCC results are used for LCS/LCSD for Labworks purposes.

3 Interferences

3.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH of <1, may give incorrectly high pH measurements

3.2 Temperature fluctuations will cause measurement errors.

3.3 Errors will occur when the electrodes become coated. If an electrode becomes coated with an oily material that will not rinse free, the electrode can (1) be cleaned with an ultrasonic bath, or (2) be washed with detergent, rinsed several times with water, placed in 1:10 HCl so that the lower third of the electrode is submerged, and then thoroughly rinsed with water, or (3) be cleaned per the manufacturer's instructions.

4 Safety

4.1 Refer to Laboratory Safety/Chemical Hygiene Plan & Fire Safety Plan, online revision.

5 Apparatus and Equipment

5.1 Sample Container: Samples are collected in plastic or glass containers that are thoroughly cleaned or rinsed.

5.2 50 mL glass beakers.

5.3 pH meter -Thermo Scientific™ Orion™ 3-Star Benchtop pH Meter or other approved pH meter with pH electrode and reference electrode with automatic temperature compensation.

5.4 pH probe - Thermo Scientific™ Orion™ Triode™ 3-in-1 pH/ATC Probe Thermo Scientific™ 9157BNMD Catalog No.13-642-252 or equivalent.

5.4.1 Note: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

5.5 Stir plate and stir bar.

5.6 Class A graduated cylinders, and pipettes

5.7 Balance: analytical, capable of accurately weighing to the nearest 0.1g.

5.8 Thermometer and/or temperature sensor for automatic compensation.

6 Reagents

6.1 <u>Reagent Water:</u>

6.1.1 Purified water which does not contain any measurable quantities of target analytes or interfering compounds for each compound of interest (Deionized, HPLC, Milli-Q water, or equivalent. Milli-Q water has a resistivity of 18.2[MΩ·cm]@ 25ºC and a TOC of 50 ug/L or less).

6.2 <u>Calibration Standards:</u>

6.2.1 The calibration standards are buffer solutions at the following concentrations: 4.00, 7.00, and 10.0. These buffer solutions are certified, commercially prepared and purchased.

6.2.2 Additional checks may be performed using other buffer values if samples are outside the 4.00 to 10.0 range.

6.2.2.1 Use calibration standards 2.00, 4.00 and 7.00 for samples with pH values less than 4.00.

6.2.2.2 Use calibration standards 7.00, 10.0 and 12.0 for samples with pH values above 10.0.

6.2.3 All sample results must be bracketed by valid calibration levels.

6.2.4 The purchased buffers are stable until the expiration date on the bottle or within 6 months of opening date, whichever is sooner.

6.3 <u>Initial Calibration Verification Standard (ICV):</u>

6.3.1 A 7.00 buffer solution from an alternate source is used to verify the initial calibration of the measurement system.

6.3.2 The ICV value must be within 0.1 pH units of the true value, or the calibration must be repeated.

6.3.3. A different lot from the same vendor as the calibration standards is also acceptable.

6.3.4 The purchased buffer is stable until the expiration date on the bottle or within 6 months of opening date, whichever is sooner.

6.4 <u>Reference Filling Solution:</u>

6.4.1 Thermo Scientific™ Orion™ pH Electrode Filling Solution Thermo Scientific™ 900011, Fisher Catalog No. 13-641-686 or equivalent.

6.5 <u>Cleaning Solution:</u>

6.5.1 Markson Labsales ELECTRODE CLEANER SOLUTION DFS Item 62000004-Fisher Catalog No. NC9035712 or equivalent.

7 Sample Collection

7.1 Samples are collected in wide mouth glass or plastic container.

7.2 No chemical preservative is necessary.

7.3 Samples should be placed on ice as soon as possible after collection.

7.4 Samples are stored between 0-6ºC (not frozen) until analysis if necessary.

7.5 No specific holding time is presented in the method; however samples should be analyzed as soon as possible after collection.

8 Calibration

8.1 <u>Calibration Standards</u>

8.1.1 The calibration consists of calibration buffers at the following concentrations: 4.00, 7.00, and 10.0. These buffer solutions are certified, commercially prepared and purchased.

8.1.2 Use calibration standards 2.00, 4.00 and 7.00 for samples with pH values less than 4.00.

8.1.3 Use calibration standards 7.00, 10.0 and 12.0 for samples with pH values greater than 10.0.

8.1.4 The purchased buffers are stable until the expiration date on the bottle or within 1 year of opening date, whichever is sooner.

8.2 <u>Calibration Curve</u>

8.2.1 The pH meter is calibrated daily.

8.2.2 The slope should be between 92 -102%. If it is not, clean the electrode according to manufacturer instructions and recalibrate.

8.2.3 Once the pH meter is calibrated, the calibration standards must be analyzed against the curve and the readings must be within 0.05 pH units of the buffer solution value.

8.3 Calibration Verification

8.3.1 An initial calibration verification standard (ICV) must be analyzed immediately after the calibration standards.

8.3.1.1 The ICV standard must be from an alternate source than the standards used in the calibration of the pH meter.

8.3.2 A Continuing Calibration Check Standard (CCC) must be analyzed every 10 samples and at the end of a sample run.

8.3.2.1 The CCC must be within 0.05 pH units of the expected value

8.3.2.2 If the CCC does not meet acceptance criteria, then all samples affected by out of control CCC are to be rerun.

8.3.2.3 The CCC may be from the same source as the calibration standards.

8.3.2.4 Either the 4.00, 7.00 or 10.0 buffer used for the calibration is also used for the CCC.

8.3.2.5 If the 2.0, 4.0, and 7.00 calibration curve is used, the 4.00 buffer is to be used for the CCC.

8.3.2.6 If the 4.00, 7.00 and 10.0 calibration curve is used, the 7.00 buffer is to used for the CCC.

8.3.2.7 If the 7.00, 10.0 and 12.0 curve is used, the 10.0 buffer is to be used for the CCC.

9 Quality Control

9.1 Refer to Table14.1 for Reporting Limits (RL's), Table 14.2 for Quality Control Acceptance Criteria, and Table 14.3 for Quality Control Procedures associated with this method, and Standard Operating Procedures for control charts and control limits.

9.2 Refer to the GA EPD Laboratory SOP's – Initial Demonstration of Capability SOP 6-001, Rev. 3 or later, or Continuing Demonstration of Capability SOP 6-002, Rev. 2 or later SOPs for training criteria.

9.3 The temperature compensation electrode must be verified at least quarterly using a NIST traceable thermometer. The allowable temperature deviation of the pH electrode temperature sensor compared to a NIST traceable thermometer is ± 2ºC.

9.4 Samples should be analyzed as soon as possible.

9.5 Sample duplicates must be analyzed at a rate of no less than 10% of all samples analyzed over time.

9.5.1 At least one sample duplicate should be analyzed for each batch of 1-9 samples and two sample duplicates analyzed for each batch of 17 samples.

9.6 Every sample requesting pH must have an independent temperature recorded for it on the bench sheet.

9.7 Record manufacturer, serial number, and model number in the maintenance log when pH electrode is replaced and record info on data review checklist.

9.8 All pH acceptance criteria are static (i.e. not based on control charts).

9.9 pH analyses are exempt from the requirement to perform MDL studies.

9.10 Quality control limits are static, but control charts are created and reviewed twice per year for trend monitoring.

10 Procedure

10.1 Remove samples from the cold storage and allow to equilibrate to room temperature prior to sample preparation and/or analysis.

10.2 Remove the pH electrode from the pH ICV storage solution.

10.2.1 Inspect probe and filling solution.

10.2.2 Rinse probe with reagent water.

10.2.3 If filling solution is low or crystals have formed, refer to section 10.8 for maintenance.

10.3 Daily, pour up fresh 4.00, 7.00, and 10.0 buffer solutions into 3 separate 50 ml beakers containing stir bars. Keep buffer solutions covered when not in use.

10.4 Press the POWER button on the meter and wait for the pH numbers to appear and the meter to warm-up. Important: Always assure that the reference electrode with the automatic temperature compensation is plugged in securely to the rear of the pH meter and check the temperature adjustment when monitoring samples.

10.5 Calibration Procedure:

10.5.1 Press calibrate button.

10.5.2 When “CAL 1” appears on screen, place the beaker with 4.00 buffer on stir plate under the electrode, turn stirrer on to stir gently. Immerse the electrode into the 4.00 buffer solution. Allow the reading to stabilize. When the pH symbol stops blinking, the meter is stable.

10.5.3 Before removing the 4.00 buffer solution, press the calibrate button and turn off the stirrer. When the “CAL 2” appears, raise the electrode out of the 4.00 buffer solution, rinse well with reagent water and blot the excess water from the electrode with a tissue.

10.5.4 Place the beaker containing the 7.00 buffer solution on the stir plate, turn on the stirrer to stir gently, immerse the pH electrode into the 7.00 buffer solution and wait for the meter to stabilize and the pH symbol to stop blinking.

10.5.5 Press the calibrate button on the pH meter and wait for “CAL 3” to appear, turn off the stirrer, raise the electrode out of the 7.00 buffer solution, rinse well with reagent water and blot the excess water off of the electrode with a tissue.

10.5.6 Place the beaker containing the 10.0 buffer on the stir plate, turn on the stirrer to gently stir and immerse the electrode into the 10.0 buffer solution.

10.5.7 Allow the meter to stabilize, wait for pH symbol to stop blinking and record the pH reading in the calibration section on the sample bench sheet.

10.5.8 Press the “measure/save/print” button to save the calibration curve and the “SLOPE” reading will appear on the screen. Make sure to record the “SLOPE” reading on the sample bench sheet

10.5.9 The slope should be within 92% - 102%. If not clean the pH electrode according to manufacturer’s instructions and calibrate the meter again following the instructions above.

10.5.10Read the 4.00, 7.00 and 10.0 buffers and record the results on the worksheet. Results must be within ± 0.05pH units.

10.5.11Verify the calibration by checking a second source standard (pH ICV). Record the result on the bench sheet.

10.6 <u>Sample preparation and pH measurement of soils</u>:

10.6.1 To 20 g of soil in a 50 ml beaker, add 20 ml of reagent water, cover, and continuously stir the suspension for 5 minutes. Additional dilutions are allowed if working with hygroscopic soils and salts or other problematic matrices.
10.6.2 Let the soil suspension stand for about 1 hour to allow most of the suspended clay to settle out from the suspension or filter or centrifuge off the aqueous phase for pH measurement.
10.6.3 Adjust the electrode in the clamps of the electrode holder so that it is immersed just below the suspension. Record reading and temperature of sample.
10.6.4 If the sample pH does not fall within the 4.00 to 10.0 range, recalibrate the pH meter with the appropriate buffers that will bracket the sample pH. Then re-read the sample pH, record the reading and temperature of sample. See section 8.1 for appropriate buffers to use for your curve and section 8.3.2 for appropriate CCC buffer to use. Ex: Use CCC 4.00 buffer for low curve and CCC 10.0 buffer for high curve
10.7 <u>Sample preparation and pH measurement of waste materials:</u>
10.7.1 To 20 g of waste sample in a 50 ml beaker, add 20 ml of reagent water, cover, and continuously stir the suspension for 5 minutes. Additional dilutions are allowed if working with hygroscopic wastes and salts or other problematic matrices.
10.7.2 Let the waste suspension stand for about 15 minutes to allow most of the suspended waste to settle out from the suspension or filter or centrifuge off aqueous phase for pH measurement
10.7.3 If the waste is hygroscopic and absorbs all the reagent water, begin the experiment again using 20 g of waste and 40 ml of reagent water.
10.7.4 If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase.
10.7.5 Adjust the electrode in the clamps of the electrode holder so that it is immersed just below the suspension. Record reading and temperature of sample.
10.8 <u>Maintenance</u>
10.8.1 Inspect probe and filling solution daily
10.8.2 Rinse probe with D.I. water.
10.8.3 If solution is low, crystals have formed, or probe becomes coated with an oily material, clean probe with cleaning solution (Section 6.5) then replace filling solution (Section 6.4). Then allow probe to sit in Buffer 7.00 solution for at least one hour for probe to stabilize before recalibrating.
10.8.4 Record maintenance performed in the maintenance logbook.
10.8.5 Probe should be cleaned and filling solution changed weekly or sooner if needed.

11 Calculations

11.1 The pH meter reads directly in pH units. pH is reported to the nearest 0.1 units for samples and 0.01 units for QC.

11 Calculations

11.1 The pH meter reads directly in pH units. pH is reported to the nearest 0.1 unit.

11.2 Quality Control Calculations

11.2.1 Duplicate Difference

$$\text{Duplicate Difference} = \left| R_{\text{sample}} - R_{\text{duplicate}} \right|$$

11.2.1.1 Where:

R_{sample} = pH result of the sample

$R_{\text{duplicate}}$ = pH result of the sample duplicate

Difference of ICV or CCC from Calibration

11.2.2 $$\text{ICV/CCC Difference} = \left| R_{\text{expected}} - R_{\text{actual}} \right|$$

11.2.2.1 Where:

R_{expected} = pH expected for the standard

R_{actual} = pH measured for the standard

12 Waste Management

12.1 Refer to GA EPD Laboratory SOP-EPD Laboratory Waste Management SOP, SOP 6-015, online revision.

12.2 Buffers with a pH less than 5.5 or greater than 10.5 must be neutralized before disposal in a lab sink drain.

12.3 Samples with a pH less than 5.5 or greater than 10.5 must be lab packed in drum.

13 References

13.1 SW-846 Method 9045D (Soil and Waste pH), U.S. EPA Office of Research and Development: Cincinnati, OH, Revision 4. November 2004.

13.2 GA EPD Laboratory SOP's – Initial Demonstration of Capability SOP 6-001, online revision, or Continuing Demonstration of Capability SOP 6-002, online revision.

13.3 GA EPD Laboratory SOP – EPD Laboratory Procedures for Control Charts and Control Limits SOP, SOP 6-025, online revision.

13.4 GA EPD Laboratory SOP-EPD Laboratory Waste Management SOP, SOP 6-015, online revision.

13.5 GA EPD Laboratory – Laboratory Quality Assurance Plan, Rev. online revision.

13.6 GA EPD Laboratory SOP- Laboratory Safety/Chemical Hygiene Plan & Fire Safety Plan, online revision.

14 Reporting Limits (RLs), Precision and Accuracy Criteria, and Quality Control

Approach

Table 14.1 RLs for SW-846 Method 9045D			
Parameter/Method	**Analyte**	**Matrix (Soil and Waste)**	
		RL	**Unit**
SW-846 Method 9045D	Soil and Waste pH	1.0	pH units

Table 14.2 Acceptance Criteria for SW-846 Method 9045D

QC Type	Analyte	CCC(LCS) Accuracy (pH units)	CCC(LCS) Precision (pH units)
CCC(LCS)*	Soil and Waste pH	0.05	0.1
Sample Duplicate	Soil and Waste pH	--	0.1

*LCS/LCSD for this analysis are essentially interchangeable with CCCs, therefore all control limits are static.

Table 14.3 Summary of Calibration and QC Procedures for SW-846 Method 9045D

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
SW-846 Method 9045D	Soil and Waste pH	Initial Calibration	Initial calibration prior to sample analysis	pH slope of 92-102%	Correct problem then repeat initial calibration	
		Initial calibration verification (ICV)	Prior to sample run.	pH value must be within 0.05 pH units of expected value	Correct problem then reanalyze results	
		Initial Demonstration: Demonstrate ability to generate acceptable accuracy and precision using four analysis of a QC check sample, and a blind sample. In addition, the analyst must perform an acceptable calibration.	Once per analyst	QC Acceptance Criteria Table SOP 3-043 and Initial Demonstration SOP (Reference 13.2)	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	

Table 14.3 Summary of Calibration and QC Procedures for SW-846 Method 9045D

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
SW-846 Method 9045D	Soil and Waste pH	Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample(s)	Every 6 months	QC Acceptance Criteria Table SOP 3-043 and Continuing Demonstration of Capability SOP (Reference 13.2)	Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample(s)	
		Sample Duplicate	10% of samples	pH value must be within 0.1 units of expected value.	Evaluate out of control event, reanalyze, or flag data	
		Continuing Calibration Check (CCC) CCCs are used for LCS/LCSD	After every 10 samples and at the end of sample sequence.	pH value must be within 0.05 units of expected value.	Correct problem and reanalyze all samples associated with the out of control CCC.	
		Temperature Compensation Probe Verification	At least quarterly with NIST traceable thermometer	± 2ºC	Correct problem or replace probe	
		Record sample temperature	All samples	NA	Evaluate out of control event, reanalyze data	

Updates to Previous Version:

Section 2
Section 5
Section 6
Section 10
Table 14.3