*Name of Facility*

Standard Operating Procedure

for the Analysis of

pH

in Non-Aqueous Waste

Method: SW-846 9045 D

Effective Date:

Supervisor Signature Date

Supervisor Name (print)

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*Blue text is replaceable instructional language to be customized for your facility.*

1. **Summary of Method**

***Note: If sample measurement is for 503 regulation, VAR: Option 6 or Option 12, refer to those Approved Procedures and SOPs.***

* 1. This method is an electrometric procedure used to measure the 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.
  2. pH is a method-defined parameter (MDP). MDPs are physical or chemical properties of materials determined with specific methods used to evaluate whether the materials comply with certain RCRA Subtitle C regulations. MDPs can only be determined by the methods prescribed in RCRA regulations because the methods are part of the regulations. These methods must be followed exactly as written, or the resulting data cannot be used to ensure regulatory compliance.
  3. The sample is mixed with reagent water, and the pH of the resulting aqueous solution is determined electrometrically using (select what you are using) *either a glass electrode in combination with a reference potential or a combination electrode*. The measuring device is calibrated using a series of standard solutions of known pH.
  4. *State what type of samples are analyzed (e.g., wastewater effluent, ground water monitoring well, etc.) and permit limits, if applicable.*
  5. *State what your working range is, e.g., 2 to 12 S.U. This is based on the buffers you use.*

1. **Definitions**
   1. Calibration buffer: Standard of known pH used during the calibration of the pH meter.
   2. Calibration check buffer: Standard of known pH analyzed after calibration of the meter to check the calibration acceptability.
   3. *If needed: Post-analysis calibration verification: A calibration check buffer is analyzed at the end of the sampling day to verify the calibration is still valid.*
   4. Reporting range: The pH range which can be reported determined by the highest and lowest buffer analyzed in the calibration and/or calibration check.
   5. S.U.: Standard Units, pH units
   6. NC WW/GW LCB: North Carolina Wastewater/Groundwater Laboratory Certification Branch
   7. *Add any other applicable acronyms used by your facility*
2. **Safety and Waste Handling**
   1. *Items that would be included in this section are things such as:*

* *Precautionary measures, including sampling site safety (list here and at the critical steps in the procedure)*
* *Personal protective equipment (e.g., gloves, eye protection, lab coat, work in a hood, etc.)*
* *Hazardous chemicals/reagents*
* *Storage and disposal of samples and reagents*
* *Reference to Chemical Hygiene Plan, if applicable*
* *Location of Safety Data Sheets (SDS)*

1. **Apparatus, Equipment and Reagents**

*Note: Include storage conditions. It is recommended catalog numbers also be included*

* 1. Beaker, 50 ml
  2. Magnetic stirrer and Teflon-coated stirring bar
  3. Analytical balance capable of weighing 0.1 gram
  4. *List your pH instrument with make and model*
  5. *Electrode type and model*
  6. *Include electrolyte solution if applicable*
  7. Reagent water
  8. Calibration buffer- *state the value of the buffers (state if purchased or prepared- if prepared, how are they made)*

Note: High pH buffers stored with headspace or those not tightly capped could deteriorate prior to expiration date.

* 1. Calibration check buffer- *state the value of the buffer (state if purchased or prepared- if prepared, how is it made)*
  2. Chemical containers are dated when received and when opened.
  3. The date received, date opened (in use), vendor, lot number and expiration date of reagents is documented on a traceability log OR on the benchsheet.

1. **Interferences**
   1. The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or moderate (<0.1 molar solution) salinity.
   2. Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10 S.U., 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 S.U., may give incorrectly high pH measurements.
   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. Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference should be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source of temperature effects is the change of pH due to changes in the sample as the temperature changes. This error is sample-dependent and cannot be controlled. It should, therefore, be noted by reporting both the pH and temperature at the time of analysis.
2. **Sample Collection, Preservation and Holding Time**
   1. *State what containers samples are collected in. Samples must be collected in glass, polyethylene or fluoropolymer containers.*
   2. There is no preservation requirement for pH.
   3. *Because of potential changes from microbial activity, or shift in chemical equilibrium, sample pH should be measured as soon as possible upon receipt at the laboratory. Per guidance in the Frequent Question section on the EPA SW-846 website, the holding time of "Analyze as soon as possible" is not clearly defined for SW-846 but is only recommended as a qualitative goal. In 2007, the definition for “immediately" was established as 15 minutes for the NPDES Program (40 CFR 136, Table II), however, that does not apply to the RCRA program and SW-846. Even though SW-846 Method 9045D is an MDP method and must be followed prescriptively, Section 6.0 of Method 9045D on holding time is not prescriptive. The method authors recognized changes in pH begin as soon as a sample is put into a container and specified that samples should be analyzed as soon as possible. If they meant to analyze by an exact time, the method authors would have put that time into the method. Instead, they left it up to the user to do what is feasible as soon as possible.*

***Therefore, the laboratory must set and adhere to a holding time based on agreement with the data receiving agency. This must be stated in the SOP.***

1. **Calibration**
   1. The pH meter must be calibrated daily with a minimum of two points that bracket the expected pH of samples. The calibration must be performed prior to sample analysis and the date and time documented.
   2. *If a separate pH calibration log is maintained state:* Document the instrument ID on the calibration log*.*
   3. The meter is calibrated using the following buffers: *(state here)*
   4. Place the buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar.
   5. Use a new portion of standard buffer for each calibration and discard any used buffer portions. Do not pour any unused portions back into the original bottle.
   6. *Include the manufacturer’s directions for calibration and operation. e.g., buttons to push, opening the electrolyte filling hole, maintaining electrolyte solution level, etc. Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. For corrosivity characterization, the calibration of the pH meter should include a buffer of pH 2 for acidic wastes and a pH 12 buffer for caustic wastes; also, for corrosivity characterization, the sample must be measured at 25 ± 1 °C if the pH of the waste is above 12.0. Various instrument designs may involve use of a dial, to "balance" or "standardize", or a slope adjustment, as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.*
   7. After calibration, analyze a calibration check buffer *(state the value of the buffer here)* and document both the true value and the observed value.
   8. The calibration check buffer must read within ± 0.1 S.U. to be acceptable. If the buffer does not read within ± 0.1 S.U., corrective actions must be taken before any samples are analyzed. See Section 14 of this SOP for corrective action options.
2. **Procedure**
   1. **Sample Preparation and Measurement of Soils**
      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 min. Additional dilutions are allowed if working with hygroscopic soils and salts or other problematic matrices.
      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.
      3. Lower the electrodes just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. For combination electrodes, immerse just below the suspension.
      4. If the sample temperature differs by more than 2 °C from the buffer solution, the measured pH values must be corrected. Report the results as "soil pH measured in water at xx °C" where "xx °C" is the temperature at which the test was conducted.
      5. If performing analyses at multiple site locations, a post-analysis calibration verification using the check standard buffer must be analyzed at the end of the run. The post-analysis check standard buffer must read within ± 0.1 S.U. of the true value or corrective action must be taken. See Section 15 of this SOP for corrective action options.
   2. **Sample Preparation and Measurement of Waste Materials**
      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 min. Additional dilutions are allowed if working with hygroscopic wastes and salts or other problematic matrices.
      2. Let the waste suspension stand for about 15 min to allow most of the suspended waste to settle out from the suspension or filter or centrifuge off aqueous phase for pH measurement.

NOTE: 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.

NOTE: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned (Section 3.3) if it becomes coated with an oily material.

* + 1. Lower the electrodes just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. For combination electrodes, immerse just below the suspension.
    2. If the sample temperature differs by more than 2 °C from the buffer solution, the measured pH values must be corrected. Report the results as "soil pH measured in water at xx °C" where " xx °C" is the temperature at which the test was conducted.
    3. *This section is for analysts who are taking measurements at multiple sites and the meter is transported by vehicle after calibration. If samples from multiple sites are brought into the lab to analyze, a post-analysis verification is NOT required. Delete if not applicable.* When the meter is transported by vehicle to another location after calibration, a post-analysis calibration verification using the calibration check buffer must be analyzed at the end of the run. The post-analysis check standard buffer must read within ± 0.1 S.U. of the true value or corrective action must be taken. See Section 14 of this SOP for corrective action options.

1. **Documentation**

The following must be documented in indelible ink whenever sample analysis is performed.

* 1. Date and time of sample collection
  2. Date and time of sample analysis to verify the xx-minute (laboratory established) holding time is met
  3. Weight of sample and volume of water added
  4. Permitted facility name or permit number, and sample site (ID or location)
  5. Collector’s/analyst’s name or initials
  6. Instrument identification (serial number preferred)
  7. Parameter analyzed
  8. Method reference (refer to Certified Parameters Listing (CPL) for correct method description)
  9. Meter calibration and meter calibration time(s)
  10. True values of buffers used for calibration
  11. True value for the calibration check buffer
  12. Value obtained for the calibration check buffer (verification of ± 0.1 S.U.)
  13. Delete if not applicable: True value and value obtained for the post analysis calibration verification(s)
  14. Delete if not applicable: Indication of when the post analysis calibration verification was performed (e.g., time of analysis, end of day analysis, etc.)
  15. Quality control assessments (i.e., evaluation of acceptance criteria)
  16. Units of measure
  17. Temperature of sample during pH measurement
  18. Final value to be reported
  19. Traceability for chemicals, reagents, standards and consumables
  20. Data qualifier(s), where applicable
  21. Equipment maintenance (recommended)

1. **Proficiency Testing (PT) Procedures**
   1. Analysis of a blind (PT) Sample is not required for this parameter.

1. **Reporting**
   1. *State who is transcribing the data and whether anyone peer reviews (checks) it. Peer review is recommended, but if that is not possible, it is recommended that the employee rechecks their own transcription for errors after a certain amount of time has passed.*
   2. *State how the data is documented on the benchsheet. It is recommended to be documented to the one-hundredths (0.01 S.U.).*
   3. *State significant figures used to report and describe the rounding procedure.*
2. **Quality Assurance and Quality Control**
   1. The calibration check buffer must read within ±0.1 S.U. of the true value to be acceptable. If the buffer does not read within ±0.1 S.U., corrective actions must be taken before any samples are analyzed. (See Section 14 for corrective actions)
   2. *(if applicable)* The post-analysis calibration check buffer(s) must read within ±0.1 S.U of the true value or corrective action must be taken per Section 14 of this SOP.
   3. All documentation errors shall be corrected by drawing a single line through the error so that the original entry remains legible. Entries shall not be obliterated by erasures or markings. Wite-Out®, correction tape, or similar products designed to obliterate documentation are not to be used; instead the correction shall be written adjacent to the error. The correction shall be initialed by the responsible individual and the date of change documented. All manual data and log entries shall be written in indelible ink.
3. **Preventative Maintenance**
   1. *State if a maintenance log or record is maintained. Could include items like replacing the electrode solution.*
   2. *State if there is any scheduled timeframe for replacing probes.*
4. **Troubleshooting and Corrective Action**
   1. If the check buffer does not read within ± 0.1 S.U. of the true value, first try pouring a new aliquot of the check buffer and reading it again. If it still does not read within ± 0.1 S.U., the meter must be recalibrated.
   2. (*use if applicable*) If the post-analysis check standard buffer(s) do not read within ± 0.1 S.U., corrective actions must be taken. If recalibration is necessary, all samples analyzed since the last acceptable calibration verification must be reanalyzed, if possible. If samples cannot be reanalyzed, the data must be qualified.
   3. Possible corrective actions include: check the meter calibration procedure, refer to the trouble shooting section in the instrument manual and check the buffers. If, after recalibration, the check buffer does not read within ± 0.1 S.U., the meter and/or probe operation may be suspect and may require servicing. Also refer to ‘Troubleshooting the pH electrode’ published by Hach (Appendix 1). *If the laboratory does not have a back-up meter/electrode, or another meter/electrode cannot be procured, it is recommended that the lab report the measured pH results with a qualifier that indicates the value is estimated.*
5. **Employee Training**

Employee training must be documented and kept on file.

* 1. *Include required education, training, experience and/or demonstrated skills*
  2. Employee must have read and acknowledged understanding of this SOP *– may also include reading the Approved Procedure for the Analysis of pH*
  3. *Employee must obtain acceptable results on Proficiency Testing samples or other demonstrations of proficiency (e.g., Initial Demonstration of Capability (IDOC), side-by-side comparison with established analyst, etc.) before analyzing compliance samples for reporting.* *Specify how proficiency is demonstrated and how the results are evaluated.*

1. **References**
   1. EPA SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods; 3rd Edition, Method 9045D, Revision 4, November 2004, Soil and Waste pH
   2. 15A NCAC 02H .0800.
   3. *Troubleshooting the pH electrode,* Hach.
   4. SW-846 pH Calibration Verification Policy
2. **Revision History**

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| --- | --- | --- |
| Type: Review or Revision | Date | Summary of Changes Made if Revision |
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Appendix 1: Troubleshooting the pH electrode (from Hach)

Problems with a pH electrode can be frustrating. The most common problems for electrodes are: **reference electrode fouling**, **a dirty or aging sensor**, and/or **bad buffers**.

Many analysts do not realize that the condition of the electrode can be readily determined. The best way to determine its condition is to place the electrode into [pH 7.0 buffer](http://www.hach.com/hc/search.product.details.invoker/PackagingCode=2283561/NewLinkLabel=www.hach.com/PREVIOUS_BREADCRUMB_ID=HcTrainingHcHTTCUpdatevnohtml/SESSIONID%7CBE5Ua3dNemN5TkNabmRXVnpkRmxUUlVWR01USXdOUT09Q1RNeA==%7C). Select the mV mode on the pH meter and observe the millivolt value.

First, a mV value should reach reasonable stability within a minute at room temperature. Consider the electrode value stable if the mV reading is not changing by more than a couple of mV in a 15-30 second period. If the values are not stable, there is a strong possibility that the reference junction of the electrode is clogged or the reference electrolyte is contaminated. In most cases the electrolyte is not diffusing out of the reference electrode at an appropriate rate or concentration. This results in a weak salt bridge between the reference electrode and the H ion sensing electrode.

If the reference electrode can be emptied and refilled, try rinsing it inside and out with DI water and refilling it with fresh reference electrolyte. In some cases you might want to soak the electrode in hot tap water in case the saturated salts of the reference electrolyte have crystallized and clogged the reference junction. The hot water often dissolves the salts thereby freeing the junction for diffusion. If the electrode is a gel type, you might also try the hot water soak. These actions may or may not bring the electrode back to proper functioning. If it continues to cause failure you have little choice other than replacement.

Second, the value of the electrode in a 7.0 pH buffer should be 0 mV ± 30 mV. In a perfect world the value is 0.00. However, electrodes differ with manufacturing, use, and age. The mV difference between the meter reading and 0.0 is the best way to determine the electrode's condition. A good rule of thumb is if the reading is outside of plus or minus 15 mV then try cleaning the electrode according to the manufacturer's instructions. Retest and see if it has improved. Over time an electrode will age and fail regardless of how much you clean it, and will eventually need replacement. At the point where the value is in the 30 mV range and cannot be improved is an indication that you need to replace the electrode with a new one.

Third, record the value in the 7.0 buffer. Rinse and blot dry the electrode and place it in a fresh [4.0 pH buffer](http://www.hach.com/hc/search.product.details.invoker/PackagingCode=2283461/NewLinkLabel=www.hach.com/PREVIOUS_BREADCRUMB_ID=HcTrainingHcHTTCUpdatevnohtml/SESSIONID%7CBE5Ua3dNemN5TkNabmRXVnpkRmxUUlVWR01USXdOUT09Q1RNeA==%7C). After it has stabilized record that value. Subtract the mV value of the 7.0 buffer reading from the 4.0 reading and divide the difference by 3. If the electrode is responding properly the calculated value should be 59 ± 3 mV.

**Example:**  
mV reading in 7.01 Buffer = 5.2 mV  
mV reading in 4.00 Buffer = 179.6 mV  
Delta = 179.6 - 5.2 = 174.4  
174.4 / 3 = 58.1  
  
In this example, the result is well within the 59 ± 3 vM range. Therefore, the electrode is responding as it should.

Obviously all of these tests are assuming you are using [fresh buffers](http://www.hach.com/hc/browse.exploded.category.products/PRODCAT0641/NewLinkLabel=pH+Buffer+Solutions/PREVIOUS_BREADCRUMB_ID=HcTrainingHcHTTCUpdatevnohtml/SESSIONID%7CBE5Ua3dNemN5TkNabmRXVnpkRmxUUlVWR01USXdOUT09Q1RNeA==%7C). Realize that pH 10.0 buffers are unstable. Because of their alkaline pH they quickly absorb CO2 in the air resulting in a pH drop to below 10.0. The pH 10.0 buffers that have been exposed to air for any length of time are questionable. The [pH 7.0 buffer](http://www.hach.com/hc/search.product.details.invoker/PackagingCode=2283561/NewLinkLabel=www.hach.com/PREVIOUS_BREADCRUMB_ID=HcTrainingHcHTTCUpdatevnohtml/SESSIONID%7CBE5Ua3dNemN5TkNabmRXVnpkRmxUUlVWR01USXdOUT09Q1RNeA==%7C) is an ideal medium for microbial growth. If you notice cloudiness or slime in the buffer it should not be used. Never leave beakers of buffer open and exposed to air. Replace them from a fresh source on a daily basis to ensure accurate calibration. Finally, repeat these series of tests on a frequent planned basis and log the changes in the electrode's behavior. This will gain you confidence in your pH values.