*Name of Facility*

Standard Operating Procedure

for the analysis of pH,

Electrometric

Method: SM 4500 H+ B-2011

Effective Date:

Supervisor Signature: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ Date:\_\_\_\_\_\_\_\_\_\_

Supervisor Name (print):\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

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Appendix 1: Troubleshooting the pH Electrode Pg. x

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

1. Summary of Method
   1. The pH of a sample is analyzed with a calibrated pH meter equipped with temperature-compensation adjustment.
   2. *State what type of samples are analyzed, e.g., wastewater effluent, ground water monitoring well, etc.*
   3. *State what your working range is, e.g., 4 to 10 S.U. This is based on the buffers you use*
2. Definitions
   1. Calibration buffer: Standard used during the calibration of the pH meter.

* 1. Calibration check buffer: Standard analyzed after calibration of the meter to check the calibration acceptability.
  2. *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.*

* 1. Reporting range: The pH range which can be reported determined by the highest and lowest buffer analyzed in the calibration and/or calibration check.
  2. S.U.: Standard Units, pH units
  3. NC WW/GW LC: North Carolina Wastewater Groundwater Laboratory Certification
  4. *Add any other applicable acronyms used by your facility*

1. 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. *List your pH instrument with make and model*
  2. *Include electrolyte solution if applicable*
  3. Calibration buffer- *state the value of the buffers (state if purchased or prepared- if prepared, how are they made)*
  4. Calibration check buffer- *state the value of the buffer (state if purchased or prepared- if prepared, how is it made)*

1. Interferences
   1. pH measurements are affected by temperature in two ways: mechanical effects that are caused by changes in the properties of the electrodes and chemical effects caused by equilibrium changes. In the first instance, the Nernstian slope increases with increasing temperature and electrodes take time to achieve thermal equilibrium. This can cause long-term drift in pH. Because chemical equilibrium affects pH, standard pH buffers have a specified pH at indicated temperatures.
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. The holding time for pH is 15 minutes.
   3. There is no preservation requirement for pH.
   4. *State where the sample is analyzed e.g., in the stream, immediately at the sampling site, in the lab within holding time, etc.*
3. Calibration
   1. The pH meter must be calibrated daily before compliance sample analysis and the time documented.
   2. 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.
   3. The meter is calibrated using the following buffers: *(state here)*
   4. Standards shall be gently stirred during measurement*.* The pH sensing portion and the reference junction must be completely immersed.
   5. *Include the manufacturer’s directions for calibration and operation. e.g., buttons to push, opening the electrolyte filling hole, correct electrolyte solution level, steps to eliminate cross contamination, etc.*

* 1. *If a separate pH calibration log is maintained, state the following:* Document the instrument ID on the calibration log.
  2. After calibration, a check standard buffer *(state the value of the buffer here)* is analyzed and documented.

1. Procedure
   1. Samples shall be gently stirred during measurement*.* The pH sensing portion and the reference junction must be completely immersed.

* 1. *State what step the analyst is taking to eliminate cross contamination between measurements (e.g., rinsing and blotting the electrode dry, dipping the electrode in stream multiple times, etc.).*
  2. *State how the data is recorded on the benchsheet in terms of significant figures. It is recommended to be recorded to the one-hundredths (0.01 S.U.).*
  3. *This section is for analysts who are taking measurements at multiple sites, for example, effluent and downstream. If samples from multiple sites are brought into the lab to analyze, a post-analysis verification is NOT required. Delete if not applicable.* When analyzing samples at multiple locations, a post-analysis calibration verification using the calibration check buffer must be analyzed at the end of the run.

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 15-minute holding time is met. Alternatively, one time may be documented for collection and analysis with the notation that samples are measured *in situ* or immediately at the sample site.
  3. Facility name, sample site (ID or location) and permit number
  4. Collector’s/analyst’s name or initials
  5. Instrument identification *(serial number preferred)*
  6. Parameter analyzed
  7. Method reference (refer to Certified Parameters Listing (CPL) for correct method description)
  8. Meter calibration and meter calibration time(s)
  9. True values of buffers used for calibration
  10. True value for the calibration check standard buffer
  11. Value obtained for the calibration check standard buffer (verification of ± 0.1 S.U.)
  12. *Delete if not applicable:* True value and value obtained for the post-analysis calibration verification(s)
  13. *Delete if not applicable:* Indication of when the post-analysis calibration verification was performed (e.g., time of analysis, end of day analysis, etc.)
  14. Units of measure
  15. Final value to be reported
  16. Traceability for chemicals, reagents, standards and consumables
  17. Data qualifier(s), where applicable.
  18. Equipment maintenance (recommended)

1. Proficiency Testing Procedures
   1. Analysis of a blind PT Sample is required at least once during every 9-month PT calendar year (January 1- September 30).
      1. A list of approved PT Sample Providers may be found on the NELAC website at <http://nelac-institute.org/content/NEPTP/ptproviders.php>. Check this list yearly to assure the chosen vendor is approved.
      2. A PT Sample can be analyzed as early as January 1 and the graded result must be reported to NC WW/GW LC office from the PT Sample Provider no later than September 30.
   2. PT Samples must be analyzed in accordance with the routine testing, calibration and reporting procedures, unless otherwise specified in the instructions supplied by the PT Sample Provider. **NOTE:** Most PT Sample Providers instruct to report pH results to two decimal places.
      1. PT Samples are logged in and analyzed using the same staff, sample tracking systems, standard operating procedures including the same equipment, reagents, calibration techniques, analytical methods, and the same quality control acceptance criteria.
      2. PT Samples shall not be analyzed with additional quality control. They are not to be replicated beyond what is routine for Compliance Sample analysis.
      3. PT Sample analysis must be documented on the laboratory’s daily benchsheet.

* 1. The PT Sample Provider’s instructions for analyzing the PT Sample must be followed and the practice documented by the analyst. The instruction sheet will be initialed and dated when the PT sample is prepared and retained for 5 years.
  2. The following information must be included when reporting the PT Sample result.
     1. EPA Lab Code: *(enter here so it is easy to retrieve)*
     2. State Lab Certification number: *(enter here so it is easy to retrieve)*
     3. Method description (refer to CPL for current method description):
     4. Mailing address for NC WW/GW LC: 1623 Mail Service Center, Raleigh, NC 27699-16233

1. Reporting
   1. Compliance sample pH data must be reported in tenths only (0.1 S.U.) and in units of S.U.
   2. If more than one pH concentration has been measured on a particular day, these values cannot be averaged due to the logarithmic nature of pH concentrations. All values must be reported on the DMR, either in the daily cell or the comments section. The following convention must be followed when deciding which value to report in the daily cell:
      1. Any value in violation of permit limits must be reported in the daily cell. If multiple samples yielded noncompliant results, the most extreme noncompliant value must be reported in the daily cell.
      2. If all values taken during the day were compliant with the permit limits, the value closest to the bounds of the limit range (high or low) must be reported in the daily cell.
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. *State who is transcribing the data to the DMR 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*
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*
   3. *State any other manufacturer recommended maintenance*
4. Troubleshooting and Corrective Action
   1. If the calibration check buffer does not read within ±0.1 S.U., first try pouring a new aliquot of the calibration 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 calibration check buffer(s) does 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 for expiration or biological growth. If, after recalibration, the calibration check buffer does not read within ±0.1 S.U., the meter and/or probe operation may be suspect and may require servicing. *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 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.*

1. References
   1. Standard Methods, 4500 H+ B-2011.
   2. North Carolina Wastewater/Groundwater Laboratory Certification Approved Procedure for the Analysis of pH, Revision 06/2019.
   3. 15A NCAC 02H .0800.
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.