**pH (Electrometric)**

WWTP Laboratory \_\_\_\_\_\_\_\_\_\_\_\_\_\_

Update this procedure to reflect your practices and your instrument instructions

1. Scope and Application

At a given temperature, the intensity of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. This method determines the pH of a sample electrometrically using a combination electrode.

1. Summary of Method: The pH of a sample is determined electrometrically by using a calibrated pH meter and immersing pH electrode and temperature probes into the sample of interest. The resulting pH value is recorded.
2. Interferences
   1. The pH measurement is temperature dependent, and significant error results if the temperatures of the buffers and samples differ appreciably. Using ATC (Automatic Temperature Compensation) equipment will help reduce this drift.
   2. The pH electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.
   3. Sodium error can be an issue at pH levels greater than 12 s.u.
   4. Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by rinsing with distilled water. An additional treatment with a 1M hydrochloric acid solution may be necessary to remove any remaining film. Follow the manufacturer’s instructions for maintenance and care.
3. Safety, Waste Management and Pollution Prevention

As with any potentially toxic or dangerous substance, care should be taken when handling acids and effluents. Proper personal protection such as gloves, apron or lab coat, and eye protection are suggested. Any further precautions are at the discretion of the laboratory personnel or the supervisor.

1. Equipment and Supplies
   1. pH meter - Orion® SA520, SA720 or StarA214
   2. Combination pH electrode probe - Orion® 91-04 or 8165BN
   3. Automatic Temperature Control (ATC) probe
2. Reagents and Standards
   1. Standard Buffers (available commercially)

pH 4.00 NIST Traceable

pH 7.00 NIST Traceable (from 2 different sources or lot numbers)

pH 10.00 NIST Traceable

* 1. Electrode filling solution (3 M KCl)
  2. 0.1 N HCl

1. Sample Collection, Preservation, Shipping, Handling and Storage: Analyze samples for pH as soon as practical, preferably within 15 minutes of collection.
2. Quality Control
   1. Daily Calibration with at least 2 buffers, use buffers to bracket the sample pH (4 and 7, or 7 and 10, or all). The buffer read back results should not differ by more than 0.1 units.
   2. pH meter and probes need to be calibrated on the same day samples are analyzed, use fresh buffers and document the results on the benchsheet.
3. Maintenance pH Electrode
   * + 1. Renew pH 4.0 s.u. buffer storage solution monthly.
       2. Clean the pH probe and replace internal filling solution weekly.
       3. Clean the pH probe by soaking the end of the probe in 0.1 N HCl for 30 minutes.
       4. Replace the probe’s internal filling solution.
       5. Drain by placing the probe straight up and down on a paper towel. Press down on the probe while holding the probe at the very top. Old filling solution will drain from the tip.
       6. Internally rinse and drain the probe twice with new filling solution.
       7. Fill probe with fresh filling solution through the injection hole.
       8. Rinse the probe with Type I water and return to storage solution.
       9. Record maintenance in the appropriate logbook.
4. Method Calibration and Standardization

Orion Star A214 pH meter

* 1. Autocalibration is to be used only with at least two of the following: pH 4.0, 7.0, 10.0 s.u. NIST traceable standard buffer solutions. Use only fresh buffers and ensure the lot numbers of the buffers are recorded in the appropriate logbook.
  2. Turn on the meter and ensure the meter is in pH mode.
  3. In the measurement mode, press f1 (cal).
  4. Rinse the pH and ATC probes with reagent water.
  5. Immerse the probes into the first buffer (e.g. pH 7.0 s.u.). Mix the buffer gently with the probes. Press f3 (start).
  6. Wait for the pH value on the meter to stabilize and stop flashing. Press f2 (accept).
  7. Press f2 (next) to proceed to the next buffer.
  8. Remove the probes from the first buffer and rinse with water.
  9. Immerse the probes into the second buffer solution (i.e. pH 4.00 for samples expected in the pH 4-7 range or pH 10.0 for samples expected in the pH 7-10 range). Gently mix the buffer with the probes. Press f3 (start).
  10. Wait for the pH value on the meter to stabilize and stop flashing. Press f2 (accept).
  11. Press f3 (cal done) to save and end the calibration.
  12. Remove the probes from the buffer solution and rinse with water. Store the probes in pH 4 buffer solution.
  13. The meter will display the calibration summary including the slope. The slope should be 92 – 102%. Record the slope in the appropriate logbook/benchsheet.
  14. If slope is outside these parameters, then change the pH probe’s internal filling solution and/or obtain new, fresh standard buffer solutions and recalibrate the meter.
  15. Press f1 (meas).
  16. The meter is now calibrated and ready for use. If a second source pH 7.00 s.u. buffer check is analyzed the results need to be within 6.95-7.05.

1. Procedure
   1. Calibrate the pH meter before the first use each day.
   2. Rinse the probe water.
   3. Immerse the probes in the sample.
   4. Gently stir the sample with the probes.
   5. Wait for the reading to stabilize (10 - 45 seconds), then note and record the pH. If the reading does not stabilize to within 0.1 s.u. follow the instructions for cleaning the electrode.
   6. Remove the probes from the sample and rinse with water. Store the probes in pH 4 buffer solution when not in use.
   7. The pH is read directly from the meter. Record sample results to the nearest 0.01 s.u.
2. References
   1. Standard Method 4500-H+, pH Value. In *Standard Methods for the Examination of Water and Wastewater*, 22 nd edition (2011 editorial revision).