USGS District Laboratory, Troy, NY

Soil pH Measurement

Standard Operating Procedure

1. Scope and Application

1.1 Analytes

Soil pH

1.2 Reporting limit

None

1.3 Applicable matrices

This method is used to determine the pH of soils in DI H_2O and $CaCl_2$ solutions.

1.4 Dynamic range

None

2. Summary of Procedure

Each soil sample is weighed out into two separate cups, one for analysis in DI H_2O and one for analysis in a $CaCl_2$ solution. The respective solutions are added and mixed in with a glass stir rod. Each sample then sits for approximately 10 minutes to allow the soil pH to equilibrate in solution. A pH electrode is then calibrated and used to measure the pH of each sample, once in each of the two solutions.

3. Safety Issues

3.1 Chemical Hazards

A. Gloves, safety glasses, and lab coats should be worn when preparing and performing this analysis
B. For proper handling techniques for specific chemicals, consult the appropriate Material Safety Data Sheets (MSDS).

4. Sample Preservation, Containers, Holding Times

4.1 Sample Preservation

Samples are spread on plastic sheets until thoroughly air-dried.

4.2 Containers

Samples are stored in plastic storage bags until analysis.

4.3 Holding Times

There is no holding limit.

5. Reagents and Standards

5.1 General Information

All reagents are commercially purchased and should be stored in the original container. Date the reagent bottles when received and when opened. Note expiration date, if any. No verification of the reagents is necessary.

5.2 Reagents

A. 0.01 M Calcium Chloride
   1. Dissolve 1.47 g of $CaCl_2$ dihydrate, granular into 1,000-mL volumetric flask with about 800 mL of Milli-Q water.
   2. Swirl; fill to the mark with Milli-Q water and mix thoroughly.
   3. Store in the 1,000 mL volumetric flask; label and date.
   4. Prepare as needed.

B. 4.0 M Potassium Chloride saturated with Silver Chloride
   1. Use a commercially purchased 4.0 M potassium chloride (KCl) electrode filling solution saturated with silver chloride (AgCl).

5.3 Standards

A. Buffers
   1. Use commercially purchased pH 4.00 and pH 7.00 buffers.
   2. Replace buffers when the expiration date has passed.

B. Quality Control (QC) Stock Solution for QC Standard, 0.1 N Sulfuric Acid
   1. Use commercially purchased 0.1 N Sulfuric Acid (H_2SO_4).
   2. Replace solution when expiration date has passed.
   3. To avoid contamination, aliquots of stock solution must not be taken directly from the bottle.

C. QC Sample pH 4.44
   1. Pipette 400 µL of QC substock solution (0.1 N H_2SO_4) into a 1,000-mL volumetric flask.
   2. Fill to the mark with Milli-Q water and mix thoroughly.
   3. Store in a polyethylene bottle; label and date.
   4. Prepare as needed.

6. QA/QC Requirements

A. The pH electrode response is verified by ensuring that the electrode potential for pH 7.00 buffer is $^{+}/_{-}$ 30 mV and the electrode potential for pH 4.00 buffer is about 160 mV greater that for pH 7.00 buffer.

B. Quality-control samples are analyzed at the start of the run, after every 10 samples during the run, and at the end of the run.

C. The pH quality-control sample is acceptable if the analyzed value is within 10 percent of the QC range theoretical value (4.40-4.49), when expressed in hydrogen ion concentration.

D. If the QC sample fails the acceptance criteria, the run is stopped and the QC sample is re-run. If the QC sample fails again the run is stopped, the QC sample is remade from the substock, and/or the instrument is re-calibrated. Samples associated with the failed QC sample are re-analyzed.

E. Every analytical run should include twenty-four samples including at least one triplicate to be run as the second, second to last, and a middle sample. If you are running more than forty samples and time permits, run a second triplicate and standard intermixed in the middle.

F. Every analysis is run with a mineral (DCBX99) and/or organic (DCOX99) QC soil sample. The QC soils are composed of an equal parts mixture from

their respective horizons of several soils collected in the Dry Creek watershed in the Catskill Mountains of New York State.

7. Procedure

7.1 Instrumentation

Orion 250A pH Meter
Orion 9157BN Triode pH Electrode

7.2 Set-Up

A. Check the date of QC sample and prepare new if more than four weeks old.
B. Check the date of 0.1 N $CaCl_2$ solution and prepare new if more than one week old.
C. Check the DI water rinse container and fill if close to empty.
D. Brush off any salt deposits on electrode by hand.
E. Uncover fill hole on electrode and check to make sure it is filled with filling solution above the reference junction and will be at least one inch above the sample level on immersion. Fill as necessary to maintain this level.

7.3 Calibration

A. Calibrate the pH probe daily before running any samples.
B. Turn on pH meter and press "2nd" followed by "mode/cal".
C. Rinse electrode first with DI water and then with pH 7 buffer. Place the electrode in pH 7 buffer.
D. Wait for stable display. Verify that screen flashes 7.00. Press "yes"
E. Rinse pH probe first with DI water and then with pH 4 buffer. Put the electrode in pH 4 buffer.
F. Wait for stable display. Verify that screen flashes 4.00. Press "yes"
G. If calibration is successful the slope will flash on screen and be between 92% and 102%
H. Rinse with DI water and analyze first QC sample.
I. If QC sample fails, rerun QC sample, remake QC sample and/or recalibrate.
J. When QC sample falls within accepted values, rinse electrode with DI water and proceed to pH measurement of samples.

7.4 Sample Preparation

A. For each sample, label two sample cups with the respective soil coding. One is for analysis in DI water and one is for analysis in 0.1 N $CaCl_2$.
B. Fill each sample cup with soil sample:
    1. Tare each sample cup before weighing out soil samples.
    2. Weigh and record the weight of each soil sample on pH analysis record sheet.
    3. For mineral soil samples, use 20.00 g of 2 mm sieved, air-dried soil.
    4. For organic soil samples, use 5.00 g of 1mm sieved, air-dried soil.
C. Pipette DI water into soil filled cups:
    1. For mineral soils pipette 20 mL of DI water (1 mL DI water/ 1 g soil) into soil filled cups.

2. For organic soils pipette 25 mL of DI water (5 mL DI water/ 1 g soil) into soil filled cups

D. Repeat with second set of soil samples using 0.1 N $CaCl_2$ in place of the DI water
E. Stir the soil slurry with a glass stir rod until well mixed. Rinse stir rod with DI water between samples to avoid contamination.
F. Let samples stand for 10 minutes.

7.5 Analysis

A. Place electrode into first QC sample. If QC passes record value and rinse electrode with DI water.
B. Continue on with every subsequent sample.
C. Place electrode into sample where the sediment and supernatant meet. Do not submerge the electrode into sediment. Be consistent with your placement of probe throughout analysis.
D. Analyze each sample in the set mixed with the DI water before you begin to analyze the sample set mixed with 0.1 N $CaCl_2$.

8. Archiving requirements

8.1 Data

Analysis forms are entered into a Microsoft Excel spreadsheet which includes sample names, analysis date, sample temperature, pH in DI water and pH in 0.1 N $CaCl_2$.

8.2 Samples

Samples are discarded after all samples have been run and last QC has passed.

9. References

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U.S.G.S. National Water Quality Laboratory, Format for SOP – Laboratory Analytical Method.

10. Key words

Soil pH

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