MANUAL DETERMINATION OF pH

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1. SCOPE AND APPLICATION

This method describes the procedure for measuring the pH of water, soil, and waste samples. This method is applicable to drinking, surface, ground and saline waters and effluents and influents. Solid and waste sample pH can also be analyzed. The tests covered by this SOP are W-PH and S-PH. The pH of water samples may also be determined with the automated PC-Titrate instrument (see DEP SOP NU-056).

2. SUMMARY OF THE METHOD

2.1. This method is based on Standard Methods 4500-H+ B-2000 and EPA 9045D.

2.2. Sample pH is measured electrometrically.

2.3. Samples for pH determination are stored on ice or in a refrigerator at ≤ 6 °C (not frozen). Since pH is a field parameter for aqueous samples, they are expired upon receipt in the laboratory and must be qualified. The holding time for solid and waste samples is 14 days, chilled to ≤ 6 °C (see DEP SOP FS 1000).

2.4. Interferences may be the result of salts of weak organic and inorganic acids present in large amounts, such as oil or grease. If oil or grease is present in the sample, rinse the probe with ample amounts of deionized (DI) water.

3. EQUIPMENT AND SUPPLIES

3.1. Instrumentation

Instrument ID	Component	Manufacturer	Model
pH Meter 2	pH meter	Fisher Scientific	accumet AE150 pH benchtop meter & stand
	pH electrode	Fisher Scientific	Double junction gel pH electrode
	ATC probe	Fisher Scientific	ATC temperature probe (90 mm length)

3.2 Equipment

Equipment	Manufacturer/Vendor[1]	Model/Catalog Number
Stir Bars, Assorted	Fisher Scientific (SR)	14-513-58; 14-511-65
Graduated Cylinder, Class A, 50 mL	Fisher Scientific (SR)	08-553A
Glass Beaker, 50 mL	Fisher Scientific (SR)	02-540G
Glass Beaker, 100 mL	Fisher Scientific	02-540H
Spatula	Fisher Scientific	14-357Q
Electrode Storage Bottle	Fisher Scientific	13-641-42

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Analytical Balance	Mettler Toledo	XSR105 Dual Range
Or Equivalent		
[1]Note: (SR) designates equipment is typically ordered through the in-house stockroom		

3.3 Supplies/Consumables

Supplies/Consumables	Vendor[1]	Catalog Number
Sample Beakers, Polystyrene, 50 mL	Fisher Scientific (SR)	08-732-122
Kimwipes, Assorted	Fisher Scientific (SR)	06-666A; 06-666C
Or Equivalent		
1Note: (SR) designates supply is typically ordered through the in-house stockroom		

4. REAGENTS AND STANDARDS

Note: Before running samples, please read the safety notes in the safety/hazardous waste section of this SOP and the MSDS for the chemicals used in this analysis.

Note: Standards must be documented in the Laboratory Information Management System (LIMS) 'Standard Preparation Tracker' module. Unique ID numbers for each standard are generated in the module and documented in the run sheet submitted with each analysis folder. If available, a Certificate of Analysis for each standard is maintained in the CertificatesofAnalysis folder at \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\RunData\MetaData\pH\. All containers holding standards must be labeled with their unique ID and expiration date.

4.1 Chemicals and Standards

	Chemical	Alias	Manufacturer [1]	Catalog Number	Purity	Expiration [2]	Storage
4.1.1	pH 1.0 Buffer	1 Buffer	Fisher Scientific	SB140-500	N/A	See CoA	Room Temp
4.1.2	pH 2.0 Buffer	2 Buffer	Fisher Scientific	SB96-500	N/A	See CoA	Room Temp
4.1.3	pH 4.0 Buffer	4 Buffer	Fisher Chemical (SR)	SB101-500	N/A	See CoA	Room Temp
4.1.4	pH 7.0 Buffer	7 Buffer	Fisher Chemical (SR)	SB107-500	N/A	See CoA	Room Temp
4.1.5	pH 10.0 Buffer	10 Buffer	Fisher Chemical (SR)	SB115-500	N/A	See CoA	Room Temp
4.1.6	pH 12.0 Buffer	12 Buffer	LabChem	LC125602	N/A	See bottle	Room Temp
4.1.7	pH 13.0 Buffer	13 Buffer	LabChem	LC125651	N/A	See bottle	Room Temp
4.1.8	pH 5.0 Buffer	ALTQC, 5 Buffer	SPEX CertiPrep	PHBUFF5500	N/A	See bottle	Room Temp
4.1.9	Deionized (DI) Water	H_2O	In house	N/A	N/A	Daily	N/A

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4.1.10	accumet pH Electrode Storage Solution, Fisherbrand		Fisher Scientific	15-200-900	N/A	N/A	Room Temp
4.1.11	Hydrochloric Acid	HCl	Fisher Chemical (SR)	A144S-212	36.5 to 38.0% (w/w), Certified ACS Plus	5 years (*)	Room Temp
Or Equivalent [1]**Note:** (SR) designates chemical is typically ordered through the in-house stockroom [2]**Note:** (*) designates manufacturer's suggested retest date. No expiration date given.							

5. SAMPLE ANALYSIS/QUANTITATION

Allow the samples to come to room temperature prior to measuring the pH. The pH meter will perform automatic temperature compensation when used with the temperature probe. If the probe is not used, all samples should be measured at a temperature ± 2 °C from the buffer temperature. Also, if the pH of the sample is > 11, the temperature of measurement must be 25 ± 1 °C (a water bath may be used to facilitate this).

Create and print a new pH run sheet. The template is located at: \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\RawData\pH\. See Appendix A for an example including the cover page. See section 7.1. for the file naming convention.

5.1. Set-Up of pH Meter:

Note: EXTREME CAUTION MUST BE TAKEN WITH THE ELECTRODE AT ALL TIMES. The electrode is extremely sensitive and should NOT be pushed to the bottom of the beakers with force of any kind. Also, care should be taken not to allow the electrode to be struck by one of the stir bars.

5.1.1. Look at the back of the meter for the channel adapter connections. The pH electrode should be connected to the INPUT connector. The temperature probe should be connected to the ATC connector.

5.1.2. The Buffer set used is "USA". This is checked by using the meter setup mode and going into P3.0: Select buffer set (bUF).

5.2. Calibration:

Note: Perform an initial pH test of the samples using the appropriate pH paper in order to determine the three pH buffers needed to calibrate the pH meter. The normal calibration is 4.0, 7.0 and 10.0. The pH buffers used for calibration should be close to the sample pH. For example, if the initial pH is < 4.0, use buffers 2.0, 4.0 and 7.0. If the initial pH is >10, use buffers 7.0, 10.0 and 12.0. The correct calibration range MUST be used for

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each sample. Therefore, more than one calibration may need to be performed depending on the pH of the samples.

5.2.1. Pour approximately 40 mL of the buffers needed into three separate beakers appropriately labeled. Add a stir bar.

5.2.2. Rinse the pH electrode and ATC probe with lots of fresh DI water as well as submerging probes into a clean beaker filled with DI water. Rinse again with the DI wash bottle and gently blot dry with a Kimwipe. Do not wipe, as this may cause a buildup of electrostatic charge. Place the pH 7.0 buffer on the stir plate and lower the probes into it with care.

5.2.3. Turn the stir plate on to a low steady speed. Press the CAL/MEAS key to start the calibration. Immerse the electrode in 2 inches of buffer without touching the bottom of the beaker. Wait for the pH meter to show READY to the left of the pH meter, which means its stabilized. Once stable, press the ENTER key to accept that calibration point. Once the measurement is completed, record the measured value of the buffer on the pH run sheet and in the maintenance book.

5.2.4. Repeat steps 5.2.2. - 5.2.3. for the next two buffers in the sequence and record the pH of each buffer and the final calibration slope. The calibration slope is viewed in the meter setup mode via P2.0: View Electrode Diagnosis Program. In pH measurement mode, press the ENTER key to go to P2.2 and view the slope's percentage.

5.2.5. When calibration is complete, the pH meter will automatically return to measurement mode.

Note: Calibration should be completed once daily before use.

5.2.6. Immediately after the calibration, repeat the measurement of the three calibration standards in reverse order. Record the result and temperature on the pH run sheet. This is used to evaluate the relative error of the calibration. **The measured values should be within 0.05 pH units of the buffer solution value**.

5.2.7. Next, measure the AltQC standard (4.2.), usually from a different supplier. Since the calibration buffers are usually from *Fisher Scientific*, the AltQC standard should be from a different vendor such as *Ricca Chemical* or *Inorganic Ventures.* Make sure the AltQC standard has a pH within the calibration range. Record the result and temperature on the pH run sheet. **The measured value should be within 0.1 pH units if manufacturer acceptance limits are not available.**

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5.3. Aqueous Sample Analysis:

Note: Allow the samples to come to room temperature prior to measuring the pH.

5.3.1. Pour 40 mL of sample into a 50 mL beaker. Add a stir bar. Record the volume of sample on the pH run sheet.

5.3.2. Rinse the probe with ample DI water and blot dry with a Kimwipe. Place the probe into the sample beaker while in measurement mode. Once the sample is stable the value will have READY next to it. The pH of the sample will be displayed. Record the result and temperature on the pH run sheet.

5.3.3. Repeat steps 5.3.1. - 5.3.2. for each sample.

5.4. Solid and Non-Aqueous Waste Sample Analysis:

Note: Depending on the nature of the samples, the weights/volumes used in this procedure may be varied. Refer to EPA method 9045D for further details.

5.4.1. Weigh 40 g of the sample in a 100 mL beaker.

Sample weighing procedure:

- Before the sample portion is weighed out, the sample must be thoroughly homogenized using a clean stainless-steel spatula
- Check the maintenance book of the balance to confirm that the balance calibration was checked on the day you intend to use it. If it was not done, perform balance calibration checks (see DEP SOP CM-011 for detailed instructions). Record the Balance ID on the pH run sheet cover page.
- Place a clean, dry 100 mL beaker onto an analytical balance and tare the balance so that it reads 0.0000 g. Using a clean stainless-steel spatula, carefully transfer enough homogenized sample to the beaker to yield 40 g of material. Record the actual weight under "Sample Weight (g)" on the pH run sheet.

Add 40 mL of DI water. Record the volume of water added on the pH run sheet. Add a stir bar and stir for 5 minutes. Allow suspension to settle for 1 hour (solids) or 15 minutes (non-aqueous wastes) and decant off aqueous phase into a 50 mL beaker. Filtration or centrifugation may be used if necessary to separate the liquid phase for analysis. Add a stir bar.

5.4.2. Rinse the probes with ample DI water and blot dry with a Kimwipe. Place the probe into the aqueous layer of the sample in the beaker. The pH of

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the sample will be displayed. Record the result and temperature on the pH run sheet.

5.4.3. Repeat steps 5.4.1. - 5.4.2. for each sample.

5.4.4. Enter the results into the "Export template_Soil pH.xls" spreadsheet located at \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\RawData\pH\ and save the results as a tab-delimited text (.txt) file (see section 7.1. for file naming convention). The saved text file is ready to be uploaded to the LIMS QC Manager program. **Report the sample pH results to one decimal place and report the temperature with all sample results using the appropriate comment in QC Manager.**

6. MAINTENANCE

6.1. When not in use, cover the tip of the pH electrode with the protective storage bottle containing storage solution. When removing storage bottle, ensure that you unscrew the cap from bottle to not damage the probe while removing the storage bottle.

6.2. For general cleaning, rinse off any salt buildup with DI water. If the electrode is in need of a more extensive external cleaning, it can be soaked in a 0.1 M HCL solution stirring moderately for half an hour. If it is suspected that the glass bulb has dehydrated, immersing it in storage solution for one to two hours can rehydrate it. If this fails, follow the pH electrode rejuvenation procedure in the manual.

7. DATA ARCHIVAL AND ASSESSMENT

7.1. The raw data is archived in paper format. A report folder is created for each analytical run. Occasionally more than one run may be in one folder. The folder is labeled with the test (W-PH or S-PH), filename/s, and initials of the analyst. The file should follow the following naming convention: YYMMDDSPH# or YYMMDDWPH#, where YY represents the year, MM the month, DD day of analysis, S is for soil or waste, W is for water, and the number represents the 1st, 2nd, etc. run of the day. An example is "150427SPH1".

7.2. Each report folder should contain the following items - the run sheets(s) including cover page with standards unique IDs, and a copy of the data and QC assessments uploaded from QC Manager to LIMS at the time of test authorization.

7.3. The report folders are on file with the nutrients and general chemistry supervisory personnel. Periodically, the files are moved to the State Records Center for long time storage according to DEP SOP LB-006.

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7.4. Excel transfer files for upload to QC manager are stored in electronic format in: \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\RawData\pH\

8. QUALITY CONTROL/DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES (SEE DEP SOPS NU-038 AND NU-043)

8.1. Following the calibration and before samples are analyzed, a repeat measurement of the three calibration standards is taken. The measured values should be within 0.05 pH units of the buffer solution value. This will be used to evaluate the relative error of the calibration.

8.2. Before the samples are run analyze the AltQC (4.2.) and check that the result falls within 0.1 pH units of the true value.

8.3. For every 20 samples analyzed, the following are analyzed:

8.3.1. Sample duplicate. The results should be within 0.1 pH units for waters and 0.2 pH units for soils and wastes.

8.3.2. At the end of each run and after every 20 cups analyzed, there should be two buffers that bracket sample values. If there is a sample(s) that has:

8.3.2.1. pH < 2, use the 1.0 buffer as one of the check standards.

8.3.2.2. pH > 12, use the 13.0 buffer as one of the check standards.

The pH should be within 0.1 pH units of the buffer value.

8.4. For method performance and acceptance criteria for QC measures and corrective action for out-of-control data and contingencies for handling out-of-control or unacceptable data, refer to DEP SOPs NU-038 and NU-043.

9. SAFETY/HAZARDOUS WASTE MANAGEMENT

9.1. Review the Laboratory Health and Safety Plan (accessible on the intranet at https://floridadep.sharepoint.com/dear/SitePages/Lab%20Health%20and%20Safety.aspx).

9.2. Safety glasses, gloves and lab coats should always be worn whilst handling samples and reagents.

9.3. Read the MSDS information for safe reagent and sample handling.

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9.4. Buffers and leftover samples with a pH $\leq$ 2 or $\geq$ 12.5 units should be poured into the appropriate waste container.

9.5. Buffers and leftover samples with a pH value of > 2 and < 12.5 units may be flushed down the sink with water.

10. REFERENCES

For definitions see section 3 of the FDEP Quality Manual. All abbreviations used throughout the document are defined at least once in the document usually at the first time of use.

10.1. Standard Methods Online, 4500–H+ B-2000 and EPA 9045.

10.2. Quality Manual, Bureau of Laboratories, FDEP.

10.3. Laboratory Health and Safety Plan.

10.4. DEP SOP NU-038, Nutrients and General Chemistry: Quality Assurance and Quality Control.

10.5. DEP SOP NU-043, Nutrients and General Chemistry Quality Assurance and Data Authorization Guidelines.

10.6. DEP SOP LB-006, Standard operating procedure for records maintenance and storage.

10.7. DEP SOP CM-011, Gravimetric Analysis: Analytical Weight and Balance Calibration

10.8. DEP SOP NU-056, Automated Determination of pH Using the PC-Titrate Instrumentation (Based on SM 2320 B)

10.9. DEP SOP FS 1000, General Sampling.

10.10. User Manual. Fisher Scientific accumet AE150 pH Benchtop Meter.

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Appendix of Significant Changes

05/01/2009	Changed the number of samples between buffer solution checks from every 10 cups back to every 20 cups. Changed the number of samples in a batch from 10 samples to 20 samples. (See Section 8.2)
04/28/2010	The Calibration of the pH meter was clarified in Section 5.2, the reporting procedure was clarified in Section 7, and the quality control requirements and limits were clarified in Section 8.
04/17/2012	Waste disposal procedure was clarified in Section 9.
04/03/2015	Data archival information was clarified in section 7. Holding time for the S-pH test was specified.
03/14/2018	Updated for new instrumentation procedures.
12/14/2020	pH meter model corrected in Section 3.
12/06/2021	Added tables for instrumentation, equipment, supplies/consumables, and chemicals. Added table of contents.
02/11/2022	Equipment updated with new meter and electrode. Operating instructions updated to fit new model. Statements added about evaluating the relative error of the calibration.
08/25/2023	Updated data drive file path links.
10/01/2024	Updated data drive file path links.

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Appendix A

Example pH Cover Page and Run Sheet

pH (SM 4500-H+ B-2000, and EPA 9045D), DEP SOP NU-026

Manual Determination of pH

Instrument: accumet AE150 pH Benchtop Meter

pH meter Unique ID: **Balance ID:**

Test ID:

File Name:

Analyst:

Date:

Start Time:

End Time:

Buffers used (Unique IDs/stickers) **AltQC (Unique ID/sticker):**

Manual determination of pH NU-026 **File name:** **Analyst Initials and date:**

Sample ID	Sample/Water Volume	Sample Weight (g)	Sample pH	Temp (°C)

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