AUTOMATED DETERMINATION OF pH USING THE PC-TITRATE INSTRUMENTATION

1. SCOPE AND APPLICATION

1.1. This method is used for determining the pH of water samples with the automated PC-Titrate instrument. The method is applicable to drinking, surface, ground, and saline waters as well as effluents and influents.

1.2. The test covered by this SOP is W-PH.

2. SUMMARY OF THE METHOD

2.1. This method, based on Standard Methods 4500-H+ B-2011, is used for determining the pH of water samples with an automatic titration instrument – PC-Titrate™. It is not certified by the National Environmental Laboratory Accreditation Program (NELAP).

2.2. Samples are handled automatically by the robotic autosampler and the pH is measured electrometrically.

2.3. Interferences: If oil or grease is present in the sample it may coat the electrode causing false readings. If this happens, rinse the probe with ample amounts of deionized (DI) water.

3. EQUIPMENT AND SUPPLIES

3.1. Instrumentation: See NU-060 for the components of the PC-Titrate instrument.

3.2. Equipment:

Equipment	Manufacturer/Vendor[1]	Model/Catalog Number
pH Electrode	ManTech	PCE-80-PH1200D
Volumetric Flask, Class A, Assorted	Fisher (SR)	10-212B; 10-210-5D; 10-212E; 10-212-5L; 10-208M
Graduated Cylinder, Class A, Assorted	Fisher (SR)	08-553A; 08-548D
Glass Beaker, Assorted	Fisher (SR)	02-540E; 02-540G; 02-540K; 02-555-20E
Or Equivalent		
[1]**Note:** (SR) designates equipment is typically ordered through the in-house stockroom		

3.3. Consumables and frequently replaced supplies:

Supplies/Consumables	Vendor[1]	Catalog Number
Electrode filling solution	Fisher	50-633-682
Lithium Grease	Fisher	NC0484446
Centrifuge Tubes, Polypropylene, 50 mL	Fisher (SR)	05-538-68, 05-53855A
Sample Beakers, Polypropylene, Assorted	Fisher (SR)	08-732-119; 08-732-120; 08-732-122
Syringe, Polypropylene	Fisher (SR)	B303134
Syringe Filters, Polypropylene, 25mm (0.45 µm pore size)	Fisher (SR)	05-713-404A
Pipet, Transfer, Polyethylene, 7mL	Fisher (SR)	13-711-7M

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Parafilm	Fisher (SR)	13-374-12
Or Equivalent [1]**Note:** (SR) designates supply is typically ordered through the in-house stockroom		

4. REAGENTS AND STANDARDS (SEE DEP SOPS NU-041 and NU-042)

Note: Before preparing reagents or standards, or 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: Standard preparations 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 reagent and standard logsheet (NU-RGTSTD) submitted with each analysis folder. The reagent and standard logsheet (NU-RGTSTD) template is located at \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\RunData\MetaData\Auto-T\Forms\. Follow preparation and labelling instructions in DEP SOP NU-042. Certificates of Analysis (CoA) for purchased standards are maintained in the CertificatesofAnalysis subfolder within the Auto-T folder on the Nutrients drive. All containers holding standards or reagents must be labeled with their unique ID and expiration date.

4.1. Chemicals:

	Chemical	Alias	Manufacturer[1]	Catalog Number	Purity	Storage
4.1.1.	pH 5.00 Buffer	ALTQC, pH 5 Buffer Standard	SPEX CertiPrep	PHBUFF5500	See CoA	Room Temp
4.1.2.	pH 4.00 Buffer	4 Buffer	Fisher Chemical (SR)	SB101-500	ACS, ≥99%	Room Temp
4.1.3.	pH 7.00 Buffer	7 Buffer	Fisher Chemical (SR)	SB107-500	ACS, ≥99%	Room Temp
4.1.4.	pH 10.00 Buffer	10 Buffer	Fisher Chemical (SR)	SB115-500	ACS, ≥99%	Room Temp
4.1.5.	DI Water	H_2O	In house	N/A	N/A	N/A
Or Equivalent [1]**Note:** (SR) designates chemical is typically ordered through the in-house stockroom						

Deionized water is replaced daily. All other purchased chemicals are given the expiration date from the CoA and/or chemical container. If there is not an expiration date listed, the expiration date is designated by following the protocol in SOPs NU-041 and NU-042.

4.2. A certified quality control standard (ALTQC, 4.1.1.) is analyzed following the supplier's instructions. The concentration is provided by the manufacturer.

4.3. Buffer solutions at pH 4.00, 7.00, and 10.00 (4.1.2., 4.1.3., and 4.1.4.) are used as calibration standards.

5. SAMPLE PRESERVATION AND HOLDING TIME

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5.1. Samples for pH determination are stored on ice or in a refrigerator at ≤ 6 °C (not frozen). pH is a field parameter that is considered expired upon receipt in the laboratory and must be qualified.

6. SAMPLE ANALYSIS/QUANTITATION

Note: This SOP should be used in conjunction with DEP SOP NU-060 – Automated PC Titrate Instrument Operating Procedure, which gives a more detailed description of the instrumentation.

IMPORTANT – All sample tubes must have their caps removed prior to operation of the instrument or the probe will be damaged.

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

6.1. Calibration:

6.1.1. Prior to calibration, check the level of filling solution in the pH probe and refill as needed.

6.1.2. Pour approximately 45 mL of buffers 4.0, 7.0 and 10.0 into three separate PP centrifuge tubes appropriately labeled.

6.1.3. The multi-level calibration with pH 4.0, 7.0 and 10.0 buffers may be carried out either independently on a daily basis or together with other samples in each run.

6.1.4. If the calibration does not comply with the manufacturers specifications the instrument will not continue to perform sample pH analysis.

6.1.5. Following the calibration and before samples are analyzed, a repeat measurement of the three calibration standards is taken. This is used to evaluate the relative error of the calibration.

6.2. Analysis of samples:

6.2.1. Start-up of the PC-Titrate Software – Log in to the PC-Titrate software; choose the appropriate method (pH only or any combo with pH test included if the run involves multiple tests). Set up the run sequence in the timetable of the PC-Titrate software (refer to DEP SOP NU-060 for details).

6.2.2. Loading samples – Invert samples and pour 45-47 mL of sample or standard into a 50 mL PP centrifuge tube. Load the sample tubes onto the autosampler in the correct sequence. It is recommended to run DI water at the very beginning as a rinse to clean up the system and condition the probe.

Example Run Sequence

Rinse – Tap water
Rinse – DI water
pH CAL – 4.00, 7.00, and 10.00 pH buffers (4.1.2., 4.1.3., 4.1.4.)

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pH CAL Check – 10.00, 7.00, 4.00 pH buffers (relative error check)
Rinse – DI water
BLK – DI Water
ALTQC (4.1.1.)
pH CCV Check – 4.00, 7.00, and 10.00 pH buffers every 20 cups
BLK – DI water
Batched samples with one sample run in duplicate (sample ID_D) for each batch of max. 20 samples
BLK – DI Water
pH CCV Check – 4.00, 7.00, and 10.00 pH buffers every 20 cups
BLK – DI Water

6.2.3. Click on the START button.

6.3. Calculations – The instrument software calculates pH results from the raw data (mV) collected during the analysis using the equation found on the calibration report.

6.4. Cleaning and reusing PP centrifuge tubes – The PP centrifuge tubes can be reused by washing them in the Lancer-2 Dishwasher, using Program 8. The tubes then are air-dried and can be reused. For routine maintenance and start-up of the dishwashers, please refer to SOP NU-046.

7. MAINTENANCE

7.1. Always keep the probe in water or buffer when not in use. For further details on maintenance of the instrument and the probe refer to DEP SOP NU-060 and related hardware manuals.

8. DATA ARCHIVAL

8.1. All analytical results are automatically saved in the database of the instrument software. Raw data is retrievable with the 'HISTORICAL DATA' function of PC-Titrate software.

8.2. A tab delimited text file for each run must be exported to the network drive: \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\RawData\Automatic Titrators\PC-Titrate1\ or \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\RawData\Automatic Titrators\PC-Titrate2\., depending on which instrument is used. The file is stored in the analysis year subfolder for the instrument used. The file name should use the format YYMMDDN-A# where YY is the year, MM is the month, DD is the day, N is the first letter of the test/s conducted, A is autotitrator, and # is 1 (for PC-Titrate 1) or 2 (for PC-Titrate 2) which indicates what instrument was used (e.g., conductivity and pH run = 120206CP-A1). This file is used by QC manager for data processing and uploading into LIMS.

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8.3 Method validation data is on file with the supervisor. Digital copy is also stored on the network, under an appropriate sub-folder in \\floridadep\data\labs\Lab5\Chemistry\Inorganic\Nutrient\Validations\PC Titrate.

8.4. The raw data is archived in paper format. A report folder is created for each analytical run. A folder may contain more than one analysis (e.g. Alkalinity, and Conductivity, and/or Fluoride) in it if the analyses are part of the same analytical run. The folder is labeled with the test (e.g., W-PH, ALK, W-COND, and/or W-F), filename/s (YYMMDDN-A#), and initials of the analyst.

8.5. Each report folder should contain the following items – general results report, calibration report(s), running list report (bench sheet), reagent and standard logsheet(s), and a copy of the data and QC assessments uploaded from QC Manager to LIMS at the time of test authorization.

8.6. 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.

8.7. The analytical file can be authorized online if necessary by scanning the entire folder into the correct year on the Nutrients drive at \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\RunData\AnalysisFolders\Auto-T\. Once the authorizer has made comments and digitally signed all items of the pdf after reviewal, the QC report from QCM is saved as YYMMDDN-A#_Authorization and digitally signed as well. The signed analytical file and QC report is saved into a folder. The entire contents of this folder is then printed and archived with the original paper format.

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

9.1. The calibration standards (4.3.) are 4.00, 7.00, and 10.00 pH buffers. Every day samples are analyzed a new calibration is performed at the beginning of the analysis. The acceptance criteria are set according to the manufacturer's instructions and are documented on the Calibration Report. The instrument will not proceed with sample analysis if the criteria are not met.

9.2. 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.

9.3. At the start of the run analyze the ALTQC (4.1.1.) sample and check that the result falls within the supplier's acceptance limits.

9.4. For every 20-sample batch analyzed, the following must be included:

9.4.1. A randomly selected sample duplicate, which should differ by no more than 0.1 pH units.

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9.4.2. All buffer solutions at pH 4.0, 7.0, and 10.0 should be analyzed every 20 cups and at the end of each run. The measured values should be within 0.1 units of their true value.

9.5. For general 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.

9.6. If there are any anomalous results (e.g., differing results for multiple analyses of same sample) or any unusual events (spilled sample, cannot locate sample, possible sample switch, etc.) see supervisor for further instructions.

10. SAFETY/HAZARDOUS WASTE MANAGEMENT

10.1. Review the laboratory Health and Safety Plan (accessible at https://floridadep.sharepoint.com/dear/SitePages/Lab%20Health%20and%20Safety.aspx).

10.2. Safety glasses, gloves and lab coats should be worn at all times whilst handling samples and reagents.

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

10.4. Buffers and leftover samples with a pH < 2 or > 12.5 units should be poured into the appropriate corrosivity waste container.

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

11. REFERENCES/DEFINITIONS

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.

11.1. Standard Methods Online, 4500-H+ B-2011.

11.2. Automatic PC-Titrate Instrument Operations Manual.

11.3. Quality Manual, Bureau of Laboratories, FDEP.

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

11.5. DEP SOP NU-041, Reagent Preparation Procedure

11.6. DEP SOP NU-042, Standard Preparation Procedure

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

11.8. DEP SOP NU-060, Automated PC-Titrate Instrument Operating Procedure.

11.9. DEP SOP LB-006, Standard Operating Procedure for Records Maintenance and Storage.

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11.10. Laboratory Health and Safety Plan.

11.11. DEP SOP NU-046, Procedure for TKN/TP Glassware Cleaning

Appendix of Significant Changes

04/28/2008	Reference method changed from EPA 150.1 to SM 4500-H+ B.
04/24/2009	Changed the number of samples between buffer solution checks from every 20 cups to every 10 cups.
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 9.2)
02/03/2015	Data archival information was clarified in Section 8.
02/04/2016	File paths and web addresses were updated.
02/21/2018	Certificate of Analyses storage location updated to network drive.
12/10/2019	Section 6: Clarification on the run sequence was added. Section 9: Acceptance criteria for quality control measures were updated.
01/31/2022	Tables added for instrumentation, equipment, supplies, chemicals, and standards. Calibration and acceptance criteria were updated in sections 6 and 9 so that pH standards will be rerun immediately following the calibration as a means of evaluating the relative error of the calibration.
07/14/2023	Updated ALTQC and data drive file path links.
10/01/2024	Updated data drive file path links.
12/18/2025	Added section 6.4 to describe the cleaning and reusing of PP centrifuge tubes.

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