AUTOMATED DETERMINATION OF pH USING THE PC-TITRATE INSTRUMENTATION

1. SCOPE AND APPLICATION

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. 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™.

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. PC-Titrate™ instrument with a pH electrode

3.2. Graduated cylinder (Class A; 50 mL)

3.3. Polypropylene (PP) centrifuge tubes (50 mL) for samples

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 \\FLDEP1\DEAR\LABS\Lab3\Chem_Data\Inorganic\Nutrients\Reagent_Prep\PCTitrate. Follow preparation and labelling instructions in DEP SOP NU-042. Certificates of Analysis for purchased standards are maintained in the STANDARDS subfolder within the REAGENT_PREP folder for PC-Titrate analyses on the Nutrients drive. All

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containers holding standards or reagents must be labeled with their unique ID and expiration date.

4.1. Buffer solutions at pH 4.0, 7.0 and 10.0 (purchased from Fisher). The expiration date is provided by the manufacturer.

4.2. Alternate standard (AltQC) pH buffer purchased from a different vendor than the one used for the calibration standards or a certified standard purchased from Inorganic Ventures (pH value differs for each lot #). The expiration date is provided by the manufacturer.

4.3. 4 N KCl Fill Solution for probe (or solution specified by probe manufacturer). The expiration date is provided by the manufacturer.

5. SAMPLE PRESERVATION AND HOLDING TIME

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

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. A DI water sample has to be inserted immediately after the last calibration standard.

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

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 – Shake 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 (4.1.)
Rinse – DI water
ALTQC (4.2.)
pH4 (4.1.)
pH7 (4.1.)
pH10 (4.1.)
Blank- DI water
Batched samples with one sample run in duplicate (sample ID_D) for each batch of max. 20 samples
pH4
pH7
pH10
Blank- 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.

7. MAINTENANCE

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.

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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. At the beginning of every week, the raw data is moved to the network drive by the analyst for archiving in the PCT BACKUP SYSTEM 1 (for PC-Titrate 1) or PCT BACKUP SYSTEM 2 (for PC-Titrate 2) folder located at: \\FLDEP1\DEAR\\Labs\Lab3\Chem_Data\Inorganic\Nutrients\PC-TITRATE.

8.2. A tab delimited text file for each run must be exported to the network drive: \\FLDEP1\DEAR\LABS\Lab3\Chem_Data\Inorganic\Nutrients\PC-Titrate or \\FLDEP1\DEAR\LABS\Lab3\Chem_Data\Inorganic\Nutrients\PC-Titrate\PC-Titrate 2, 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.

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 \\FLDEP1\DEAR\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.

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

9.1. At the start of the run analyze the AltQC (4.2.) sample and check the result falls within the supplier's acceptance limits.

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

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

9.2.2. 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.

9.3. 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.

9.4. 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.

9.5. Calibration - The calibration standards (4.7.) are 4.0, 7.0, and 10.0 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 manufacturers instructions and are documented on the Calibration Report. The instrument will not proceed with sample analysis if the criteria are not met.

10. SAFETY/HAZARDOUS WASTE MANAGEMENT

10.1. Review the laboratory Health and Safety Plan (accessible on the intranet at https://www.fldepnet.org/content/dear/bureau-laboratories-health-and-safety-plan).

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 $\leq$ 2 or $\geq$ 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

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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.

11.10. Laboratory Health and Safety Plan.

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.

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Section 9:Acceptance criteria for quality control measures were updated.

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