AUTOMATED PC-TITRATE INSTRUMENT OPERATING PROCEDURE

1. SCOPE AND APPLICATION

This Standard Operating Procedure provides a generic guideline for routine operation and maintenance of the PC-Titrate instrument – an automated instrument capable of testing for pH, Conductivity, Alkalinity, and Fluoride simultaneously or in any combination. The instrument is used to analyze aqueous samples with the following Test IDs - W-PH, ALKALINITY, W-COND, W-COND-F, W-F and W-F-F. This document complements related DEP SOPs listed as follows:

- **NU-056**: Automated Determination of pH
- **NU-057**: Automated Determination of Alkalinity
- **NU-058**: Automated Determination of Conductivity
- **NU-059**: Automated Determination of Fluoride

2. INSTRUMENT DESCRIPTION

There are two similar systems in-house. The major differences are the type of autosampler and conductivity meters present and the addition of a Titrasip module to one of the systems.

The instrumentation used are Man-Sci PC-Titrate systems consisting of six major components including a ***Gilson Mega or AutoMax 197*** autosampler, a ***Burivar I/2*** buret driver module for accurately delivering titrant, a ***TitraDose*** pump module for delivering TISAB, one or two ***TitraSip*** modules for titration, and a ***PC-Titrate*** interface module for interfacing the system with an IBM compatible PC for data collection and control, and a conductivity meter. The second ***TitraSip*** module is a RapidDuo system which is allows for the analysis of multiple parameters on a single sample in 3 minutes or less.

There are three electrodes used with each system. A conductivity electrode is mounted on the robotic arm of the autosampler. It measures the conductivity of the sample in the sample vial before portions of the sample are pumped into the titration vessel. Two other electrodes, a pH probe and Fluoride probe, are installed in the titration vessel. The measurement of pH, alkalinity and fluoride takes place in that cell. TISAB buffer and acid titrant are delivered from their respective reservoirs to the titration vessel automatically as needed.

2.1. Gilson Autosamplers:

2.1.1. Gilson Mega 215 Autosampler (Instrument 2) - The Gilson Mega 215 Liquid Handler is a robotic XYZ autosampler. It is

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fitted with two 60-position trays and one 59-position tray, for a total of 179 positions. Each of the trays has a designated position on the autosampler base. They are labeled on the front as 'Left front', 'Center front' and 'Right front', respectively. If for any reason a sample tray is removed from the base, it needs to be put back as indicated by the label. The sample trays accommodate 50 mL polypropylene (PP) centrifuge tubes as sample vials. The autosampler should be recognized as ***Mega autosampler 215 179×50 mL*** in the *PC-Titrate* control software.

2.1.2. AutoMax 197 Autosampler (Instrument 1) - The AutoMax 197 is a robotic XYZ autosampler. It is fitted with one 87-position tray and one 110-position tray, which totals 197 positions. Each of the trays has a designated position on the autosampler base. The tray with 87-positions has to be on the far left because it must be placed around the rinse cup. The sample trays accommodate 50 mL PP centrifuge tubes as sample vials. The autosampler should be recognized as ***AutoMax 197 tube sampler - 197x50 mL – Block for Stirrer, Electrode, 3 needles, steel temp probe.GTY*** in the *PC-Titrate* control software.

2.2. Burivar I/2 Buret Module - The Burivar I/2 is a single buret module designed for use with interchangeable valves and syringes. This unit comes with a SGE 25 mL syringe. It is made and tested for use with this buret. This facilitates using a complete buret setup, which includes the valve, syringe, titrant bottle, and holder for different titrants. This unit is used to deliver titrant (0.02 N H_2SO_4) from its storage bottle to the titration vessel for the alkalinity test.

2.3. Titra-Dose Pump - Module - The Titra-Dose pump has been designed for pumping liquids when precision and accuracy are a major consideration. The unit that came with this system is designed to be used for aqueous viscous liquids. This specific unit is used for delivering TISAB buffer from its storage bottle to the titration vessel for the determination of Fluoride.

2.4. TitraSip Titration - Module - The TitraSip module has been designed for use with the PC–Titrate Autosampler System. The function of the TitraSip unit is two-fold. Firstly, it must work in conjunction with the autosampler to draw a sample, located on the autosampler rack, into the titration vessel. Secondly, when the titration is complete, it must dispose of the sample and carry out a thorough rinse of the titration vessel as well as the sample lines. The TitraSip is designed for use with aqueous based solutions. It is not designed to function with viscous, non-aqueous, corrosive, or dirty sample solutions.

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2.5. PC-Titrate Interface Module - The PC-Titrate Interface module is the heart of the PC-Titrate hardware system. The main purpose of this module is to facilitate communication between the PC-Titrate software and the hardware or modules in the system. The communication between the interface and the computer is a bi-directional RS232 link. Communication between the interface and the devices connected to the interface are one of three different types; analogue, digital I/O, or serial. All of the modules discussed in this SOP are connected to the interface module.

2.6. Auto-ranging Conductivity Meter – The Model 4510 is a general-purpose conductivity meter with auto range from 0.01µS to 199.9mS with the current conductivity probe. The conductivity readings are automatically temperature compensated over the range of 0 to 100 °C. The reference temperature has been set to 25 °C. The default conductivity coefficient for temperature compensation is 1.91 % per °C; which is adequate for most routine determinations.

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

Note: Before preparing 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: All reagent and standard preparations must be documented in the Laboratory Information Management System (LIMS) 'Standard Preparation Tracker' module. Unique ID numbers for each reagent or standard are generated in the module and documented in the Reagent and Standard logsheet (NU-RGTSTD, found on the Nutrients drive at: \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\REAGENT_PREP\PC Titrate\) submitted with each analysis folder. All containers holding standards or reagents must be labeled with their unique ID and expiration date. If available, a certificate of analysis for each purchased reagent is also maintained in the REAGENT_PREP folder for PC Titrate analyses. Certificates of Analysis for purchased standards and the TISAB buffer are kept in a binder in C307.

Note: Please see NU-056, NU-057, NU-058, and NU-059 for reagent and standard prep information specific to each PC-Titrate analysis.

3.1. Water - In house de-ionized (DI) water is used for rinsing the autosampler home well, liquid transfer line and the titration cell.

3.2. TISAB Buffer - TISAB buffer from Fisher Scientific (Fisher SB175-4) is used to complex cations such as $Si^{4+,}$ Al^{3+} and Fe^{3+}, which will interfere with the determination of fluoride, and to adjust the pH of the solution to between 5 to 9. The expiration date is determined by the manufacturer.

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3.3. Sulfuric Acid Standard - 0.02 N Certified H_2SO_4 Standard is purchased from Fisher Scientific (SA226-4). If the certified standard is not available, use the following procedure; to a 1L volumetric flask add approximately 500 mL DI water. Pipette 555.6 µL of H_2SO_4 into the flask. Dilute to the mark. Invert the flask at least 8 times to mix.

4. INSTRUMENT OPERATION AND SOFTWARE INITIATION

45 to 50 mL of each sample is poured into properly labeled 50 mL PP centrifuge tubes. Load all the sample tubes onto the autosampler.

4.1. Pre-run Check list:

- DI Water Reservoir (for all tests) - check to see whether there is enough water in the tank. Refill the tank if necessary.
- TISAB Buffer Reservoir (for fluoride determination) - check the level of the TISAB buffer in the storage bottle. Refill the bottle as needed.
- Sulfuric Acid Standard Reservoir (for alkalinity determination) - check the amount of the standard in the storage bottle. Add more as necessary.
- Burette/Syringe (for alkalinity determination) - check the burette or syringe on Burivar I/2 Buret Module for any bubbles. Invoke a degas procedure if bubbles are present. For details on degas procedure, please refer to 5.1.
- Electrodes (for alkalinity and fluoride determination) - check the electrolyte level in the electrodes (pH and fluoride). Refill the electrodes with proper electrolyte as needed. Refer to section 5.2. – 5.4. for details on electrode maintenance.
- Sample tubes - All caps must be removed from the centrifuge tubes or damage to the conductivity probe and sample needle will occur. Inspect the shape of all the centrifuge tubes. Discard seriously distorted or deformed tubes to prevent any possible malfunction of the autosampler.

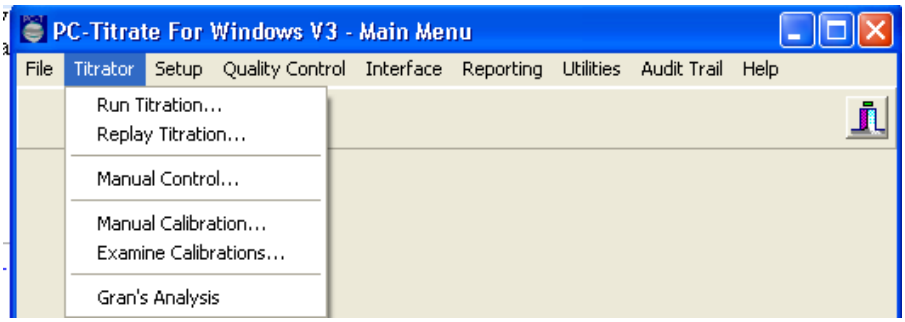
4.2. Start the PC-Titrate Software:

The information provided below is an outline of general operation of the system, which applies to all tests for this instrumentation. For details on

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the operation and configuration of the software, please refer to the PC-Titration Plus System Operator's Manual and PC-Titrate Software Manual

Log in - On the desktop of the computer, find the PC-TITRATE icon. Double click on the icon to start the PC-Titrate software.



Compile Time Table - Chose "Titrator" from the menu. Then chose "Run Titration". Once the new window has opened, choose a saved time table or create a new one. The time table will be presented to the operator either as a blank table (run sample without any template) or as a table with some fields preset (run from template). In the case of a blank table, the operator needs to fill all necessary fields. The meanings of fields that are necessary to start a run are as follows:

Schedule - Double click in this field and choose an analysis.

Order Number - Use the 'Auto Generate Order-Number' button to generate this number

Sample Name - Enter sample ID in this field.

Volume - The software enters the correct sample volume by default when alkalinity is scheduled to be analyzed (10 mL for Instrument 1 and 20 mL for Instrument 2. Volume is left blank by default if alkalinity is not scheduled for analysis.

To add more rows to the table use the 'Add x Rows…' button located at lower part of the same window or right click the mouse at any point on the table and then choose to add one or multiple rows.

If a template is used, enter the correct sample IDs in the Sample Name field and check to make sure the correct schedule is set for each sample. The length of the time table has to be tailored to the specific run. Delete any extra rows from the table and save the modified template. The file name should use the format YYMMDDN-A# where YY is the year, MM

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is the month, DD is the day, N is the first letter of the test/s conducted, A is autotitrator, and # is 1 or 2 which indicates what instrument was used (ex. Fluoride and Conductivity run = 120206FC-A1).

It is important to remember that at the end of any run sequence, including the preset calibration methods, a storage solution has to be added to the sequence, although this solution does not appear on any time table. The system will automatically go to the sample position immediately after the last sample in the run sequence to transfer storage solution to properly store the electrode. The storage solution is prepared by diluting the pH 4 buffer 1:2 and adding 1 mL of 0.2 ppm or 0.5 ppm fluoride standard. Make sure the 50 ml PP centrifuge tube is filled to 40-45 ml.

Once the time table has been set, pressing the 'Start' button located in the top right of the same window will start the run.

Report and Data Archiving - After the completion of the run, a report window will be automatically presented to the operator. Note the run number and close this window. A printout of the report should be generated by opening the historical report template at the bottom of the main software screen, showing all the data stored in the database. Limit the results by clicking on the define search tab and entering the run number noted earlier (if the run number was not noted it can be found by going to the end of the results page where the current sample results are found). The data must be exported as a text file 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 name should use the format above. The QC manager will use this file to process and upload the final results into LIMS.

5. EQUIPMENT MAINTENANCE

For detailed maintenance and troubleshooting procedures on each of the individual components of the system, please refer to the related chapters in the hardware manuals. Listed below are some routine maintenance practices. Record all maintenance except daily syringe degassing in the maintenance logbook for each instrument.

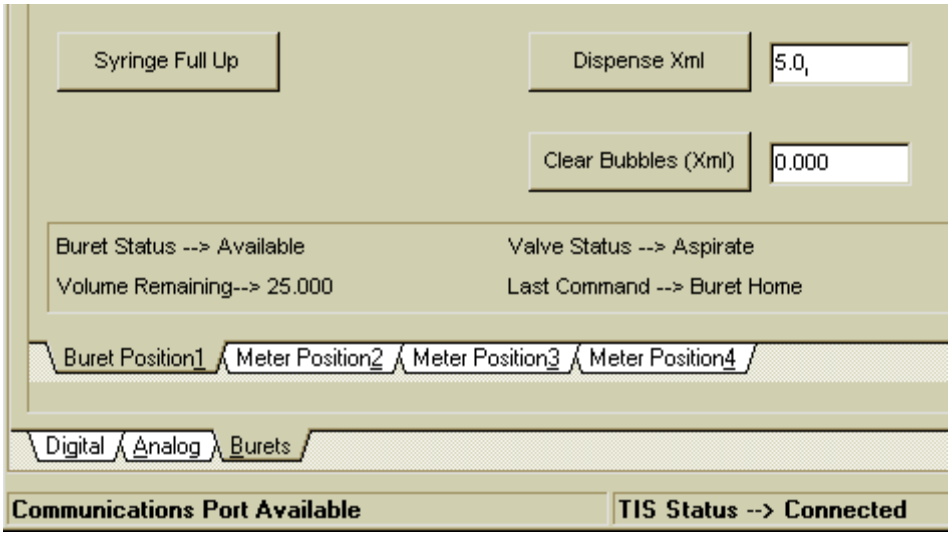
5.1. Daily Maintenance:

5.1.1. Degassing of Syringe on Burivar I/2 Buret Module - Bubbles may accumulate on top of the syringe. The bubbles will introduce titration errors to alkalinity determinations. Follow this procedure

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to expel the bubbles; Launch the manual control panel by following this path: *menu bar* → *Titrator* → *Manual Control* …; find and select the 'Burets' table on the manual control panel; find and select the 'Buret Position1' tab within the 'Burets' frame; select the 'Dispense Xml' button to dispense 5.0 mL of the content of the syringe; select the 'Clear Bubbles' button and follow the instructions.

If the de-bubble procedure is to be conducted after completion of the run sequence or time table, the time table must be saved immediately once it is completed.



5.1.2. Maintenance of pH Electrode - The electrode should be filled with the solution purchased from the manufacturer. Check the level of KCl solution in the electrode daily and refill the solution as needed if the electrolyte level is low. After each run, the electrode has to be stored in the designated storage solution. For extended storage, the electrode should be stored dry.

5.1.3. Maintenance of Fluoride Electrode - The electrode should be filled with the solution purchased from the manufacturer. Check the level of KCl solution in the electrode daily and refill the solution as needed if the electrolyte level is low. After each run, the electrode has to be stored in the designated storage solution. For extended storage, the electrode should be stored dry.

5.1.4. Maintenance of Conductivity Electrode - After each use, the electrode tip should be rinsed in DI water. If there is build-up of solid inside the measurement area of the cell, it should be removed

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very carefully with a cotton swab soaked in a mild solvent, taking care not to touch the metal parts of the inner cell.

5.1.5. Hardware - Inspect the instrument to insure the pump and buret tips are in the correct locations, with pump tips above the solution level and buret tips submerged. Purge and prime all pumps and be sure all modules are turned on and set to auto.

5.1.6. Chemicals - Ensure all reagents, titrants and rinse water carboys are full and that the waste carboy is empty.

5.2. Bi-weekly Maintenance:

5.2.1. Electrodes - Drain, rinse and refill the pH and Fluoride electrodes with fresh KCl solution.

5.2.2. Rinse Station - Ensure the rinse station is clean, rinsing and draining properly.

5.3. Monthly Maintenance:

Buret Valve - Clean the buret valves by taking it apart and rinsing the pump head and its components with DI water. Dry the pieces with a paper towel and reassemble.

5.4. Semi-Annual Maintenance:

Dosing Pump Heads - Purge all solution from the pump and remove the screws that hold the pump to the front of the instrument. Remove the black hood and pull the pump out. Remove the piece coming out of the back of the pump head (the one with the small silver rod sticking sideways out the end). Run tap water over all pieces and replace the rod, this pieces should turn easily. This should be done every 6 months to ensure proper functioning of the pump.

Note: The flow rate of the pumps needs to be checked anytime the pump head is taken apart.

5.5. Annual Maintenance:

5.5.1. Dosing Pumps - Replace the lip seals and gland washers in the dosing pump head. For detailed instructions consult the maintenance manual.

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5.5.2. Replace all tubing, fittings, tips and pump rollers on pumps and burets - For detailed instructions consult the maintenance manual.

Note: Annual maintenance will be completed as part of the PM if purchased through the instrument company.

6. SAFETY

6.1. The equipment in this system has been designed for use with aqueous liquids only. Failure to use equipment in the manner that it has been designed to operate may cause harm to the equipment and/or the operator.

6.2. Always disconnect power when making adjustments to the liquid handler. Injury may occur if you interfere with the work area of the autosampler while it is running.

6.3. Do not use an extension cord for instrument; it may overheat and cause fire.

6.4. Always keep hands, hair, jewelry, and clothing away from all moving parts such as the robotic arm of the autosampler. To avoid puncture wounds, do not place your hands near the sample needle of the autosampler.

7. REFERENCES/DEFINITIONS/VALIDATION DATA

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. Method validation data is on file with the supervisor.

7.1. PC-Titration Plus System Operator's Manual, customized for FDEP by Man-Tech Associates Inc.

7.2. 215 Liquid Handler User's Guide and AutoMax 197 Autosampler User's Guide, Gilson, Inc.

7.3. QC/PC-Titrate Hardware & Service Manual, Cat. No. PC-1000-218, Man-Tech Associates Inc.

7.4. PC-Titrate Software Manual, Cat. No. PC-1000-212, Man-Tech Associates Inc.

7.5. Model 4310 and Model 4510 Conductivity Meter Operating Manuals.

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7.6. DEP SOP NU-041, Reagent Preparation Procedure.

7.7. DEP SOP NU-042, Standard Preparation Procedure.

7.8. DEP SOP NU-056, Automated Determination of pH using the PC-Titrate Instrumentation.

7.9. DEP SOP NU-057, Automated Determination of Alkalinity using the PC-Titrate Instrumentation.

7.10. DEP SOP NU-058, Automated Determination of Conductivity using the PC-Titrate Instrumentation.

7.11. DEP SOP NU-059, Automated Determination of Fluoride using the PC-Titrate Instrumentation.

Appendix of Significant Changes

02/19/2008 Section 2: Added information about new (second) system.

02/04/2010 Section 2: Added information about the RapidDuo instrumentation.

02/07/2012 Section 2: Added information about the new Autosampler; Section 4: Sample analysis volume and naming convention changed; also edited for clarity.

02/10/2015 Added maintenance schedule details in Section 5, and Standard Prep Tracker information in Section 3.

02/04/2016 The test names W-ALK and W-ALK-F were updated to ALKALINITY in Section 1. File paths and web addresses were updated.

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