AUTOMATED DETERMINATION OF FLUORIDE USING THE PC-TITRATE INSTRUMENTATION

1. SCOPE AND APPLICATION

1.1. Fluoride analysis is performed on drinking, surface, ground, effluents, influents, and saline waters. The method detection limit (MDL) is 0.025 mg F/L and the practical quantitation limit (PQL) is 0.10 mg F/L. The calibration range is 0.10 – 10.0 mg F/L. Higher concentrations may be measured by sample dilution.

1.2. Tests covered by this SOP are W-F and W-F-F.

2. SUMMARY OF THE METHOD

2.1. This SOP is based on Standard Methods 4500-F^- C-2011.

2.2. This is an automated method. The sample is mixed with an equal amount of TISAB buffer (10 ml sample + 10 mL TISAB). The fluoride concentration is determined potentiometrically using a fluoride electrode PCE-80-FL1001. The PC-Titrate software is used for data acquisition and process control.

2.3. Sample pH must be between 5 and 9. Si^{4+} Al^{3+} and Fe^{3+} interfere by forming complexes with fluoride. The TISAB buffer complexes the above ions and adjusts the pH. The TISAB buffer may not complex all the interferences in salt waters. Run salt samples with a conductivity between 10,000 and 20,000 µmhos/cm at a 1:2 dilution and greater than 20,000 µmhos/cm at a 1:5 dilution. For salt samples that are close to 10,000 µmhos/cm or are suspect samples, use the handheld conductivity meter or the PC-Titrate to estimate conductivity value before choosing the appropriate dilution. All diluted salt samples should also be run undiluted for comparison.

2.4. Sample Preservation and Holding Time: Sample preservation is not required. Fluoride samples must be analyzed within 28 days of collection to avoid qualification.

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
Fluoride Ion Selective Electrode	ManTech	PCE-80-FL1001
Analytical Balance	Mettler Toledo	MS204TS/0
Adjustable Pipette, 10–100 µL	Eppendorf/Fisher	Research Plus, 3123000047
Adjustable Pipette, 100–1000 µL	Eppendorf/Fisher	Research Plus, 3123000063
Adjustable Pipette, 1–10 mL	Eppendorf/Fisher	Research Plus, 3123000080
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

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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
Pipette tips, Eppendorf, 200 µL	Fisher (SR)	05-403-41
Pipette tips, Eppendorf, 1000 µL	Fisher (SR)	05-403-43
Pipette tips, Eppendorf, 10 mL	Fisher (SR)	05-403-116
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
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. A Certificate of Analysis (CoA) for each purchased reagent and standard is 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.

Note: The volumes prepared for the reagents and standards may be altered by the analyst as necessary. The final concentrations of the constituents of a standard or reagent must not be changed.

4.1. Chemicals:

	Chemical	Alias	Manufacturer[1]	Catalog Number	Purity	Storage
4.1.1.	100 mg F/L Stock Standard	Fluoride Standard	Ricca	3171-32	ACS, ≥99%	Room Temp

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4.1.2.	TISAB Buffer	Total Ionic Strength Adjustment Buffer	Fisher Chemical (SR)	SB175-4	See CoA	Room Temp
4.1.3.	Minerals QC CRM	ALTQC	NSI Lab Solutions	QCI-136	See CoA	Fridge after opening
4.1.4.	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 sample ALTQC (4.1.3.) is prepared following the supplier's instructions, if needed. Standard can be stored at room temp, but is generally stored in the refrigerator. The concentration is provided by the manufacturer. There is not a recommended holding time by the manufacturer, but standard is given a 28-day holding time upon opening.

4.3. Working Standards:

100 mg F/L Stock Standard (4.1.1.) See table
DI Water (4.1.4.) to 1000 mL

Prepare standards by pipetting the specified amounts of 100 mg F/L stock standard, as shown in the table below, into 1 L volumetric flasks, and fill to volume with DI-water.

Holding time, 28 days.

Standard Concentration (mg F/L)	QC Standard, Alias	Final Volume (mL)	Vol of Fluoride Stock (4.1.1.) added (mL)
0.1	Cal Standard 1, PQCK2	1000	1
0.2	Cal Standard 2	1000	2
0.5	Cal Standard 3, CHCK3	1000	5
1.0	Cal Standard 4, CHCK1	1000	10
10.0	Cal Standard 5	1000	100

4.4. Continuing Calibration Verifications (CCVs) – Start with CHCK1 and run either CHCK3 or CHCK1 for the remainder of the run. As a general guideline both standards should be used on each analytical run in an alternating manner.

5. SAMPLE ANALYSIS/QUANTITATION (SEE DEP SOP NU-033)

Note: Allow the samples and standards to come to room temperature prior to analysis.

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.

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

5.1. Calibration – A multi-level calibration using standards of 0.1, 0.2, 0.5, 1.0, 10 mg F/L must be carried out daily. A calibration can be set up with the samples in the run or as a separate run from the rest of the samples. A DI water rinse should be inserted immediately after the last calibration standard. See 5.2.3. for an example run sequence.

5.2. Analysis of samples:

5.2.1. Set up the run sequence in the timetable of the PC-Titrate software (refer to DEP SOP NU-060 for details).

5.2.2. Pour or filter 45 – 47 mL of sample into a clean 50 mL correctly labeled polypropylene centrifuge tube. If Fluoride is the only test being conducted, 25 – 30 mL of sample can be used. Load the sample onto the autosampler.

Note: Samples are not required to be filtered by the method but should be filtered when necessary to prevent contamination. Samples should be filtered if they are turbid or contain obvious particulates. Filtered samples are identified on the backlog or bench sheet with an F.

5.2.3. Quality control samples analyzed on each run are the calibration standards, ALTQC, PQCK2, CCVs, LFBs, matrix spike, and blanks (DI water).

A method blank (MBLK), LFB, matrix spike and a randomly selected duplicate sample or matrix spike are analyzed for every 20 samples.

Matrix spikes (spike code _N1) at 0.4 mg F/L are prepared by adding 100 µL of 100 mg F/L stock solution (4.1.1.) to 25 mL total volume of sample (only 25 mL is necessary for the matrix spikes and the LFB because the only analysis performed on these aliquots is Fluoride).

The LFB is prepared following the same procedure as the matrix spikes except DI water is substituted for the sample. After every 20 cups and at the end of the run, a CCV (4.4.) and a blank are analyzed (refer to DEP SOP NU-038 for details on quality control).

Example Run Sequence

Rinse – Tap water
Rinse – DI water
Standard-1 (0.1mg F/L)
Standard-2 (0.2mg F/L)
Standard-3 (0.5mg F/L)
Standard-4 (1.0mg F/L)
Standard-5 (10 mg F/L)
Rinse – DI water
MDL (blank)
PQCK2 (PQL level- Standard 1)
ALTQC (4.1.3., in range of 0.1 to 1 mg F/L)

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ALTQC (4.1.3., in range above 1 mg F/L, filtered)
CHCK1 (4.3.)
Blank – DI water
MBLK – Method blank- filtered DI water
LFB_N1
Sample
Sample_Duplicate (dup)/or matrix spike _N1
Sample_N1
Samples batched (max. 20 per batch)
CHCK 1 or **CHCK 3**
Blank

Note: This sequence may vary if other tests (alkalinity, conductivity, and/or pH) are run simultaneously.

Note: If it is suspected the run will go over 24 hours, another PQCK2 (4.3.) should be added later in the run.

Note: The ALTQC must be filtered if any samples in the analytical batch are filtered. The MBLK must be filtered if any samples in the prep batch are filtered. Filtered QC is identified on the bench sheet with an F.

5.3. Calculations/Interpretation:

5.3.1. Calculations – The instrument software calculates fluoride concentration results from the raw data (mV) collected during the analysis using the linear equation corresponding to the appropriate segment of the calibration curve found on the calibration report.

5.3.2. The QC Manager program will calculate the percent recoveries of the CCVs, matrix spikes and quality control sample. It will also calculate the relative percent difference (RPD) for the sample and spike duplicate results.

5.3.3. See Section 7 for QC acceptance limits.

5.3.4. 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, etc.), see supervisor for further instruction.

5.3.5. For general calculations including RPDs, spike recoveries, and QC statistics (UCL and LCL for LFB's, matrix spikes and RPD) see Sections 5.9 of the FDEP Quality Manual.

6. DATA ARCHIVAL

6.1. 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:

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\\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\Archive\PC-TITRATE.

6.2. A tab delimited text file for each run must be exported by the analyst 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 auto-titrator, and # is 1 or 2 which indicates what instrument was used (e.g., fluoride and conductivity run = 160206FC-A1). This file is used by QC manager for data processing and uploading into LIMS.

6.3. 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., ALK, W-COND, and/or W-F), filename/s (YYMMDDN-A#), and initials of the analyst.

6.4. 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.

6.5. 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.

6.6. 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.

6.7. 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.

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

7.1. The calibration is acceptable if the slope between the 1 mg/L and the 10 mg/L standard is between 56.2 and 60.9 mV/decade.

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7.2. The relative error of the calibration is also evaluated by analyzing a PQL standard (PQCK2, 4.3.) and a mid-level standard (CHCK1, 4.3.) following the calibration, but before samples are analyzed. Acceptable limits for the recovery of the PQL check (PQCK2, 4.3.) are 70 – 130%. Acceptable limits for the recovery of the mid-level standard are 90 – 110%.

7.3. Acceptable limits for the recovery of the ALTQC (4.1.3.) are 85 – 115% unless the manufacturer's certified limits are more stringent, in which case, the more stringent limits are used.

7.4. Acceptable limits for the recovery of the CCVs (4.4.) are 90 – 110%.

7.5. Acceptable limits for the recovery of the LFBs and matrix spikes (5.2.3.) are established from the upper and lower control limits (UCL and LCL) calculated in the QC Statistics module in LIMS. The limits are evaluated regularly and updated at least annually. The QC Statistics Calculation Reports are archived annually with the PC-Titrate instrument validation data on the Chemistry drive: \\floridadep\data\labs\Lab5\Chemistry\Inorganic\Nutrient\Validations\PC Titrate\QC Stats Limits.

7.6. The matrix spike or sample duplicate analyses should have an RPD that is less than the upper control limit calculated in the QC statistics module. See Section 7.5. for evaluation and archival information.

7.7. All blanks (MDL, MBLKs, and bracketing blanks) should be < 0.025 and > -0.025 mg F/L. (See Section 5.2.3.)

7.8. 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.

7.9. Annual MDL and PQL verification is required using statistics tracker, (see DEP SOP NU-043). Method blank (MBLK) and PQCK2 data is collected and utilized for the ongoing MDL and PQL verification. Acceptance limits for the PQL verification using PQCK2 are 70 – 130%.

8. SAFETY/HAZARDOUS WASTE MANAGEMENT

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

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

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

8.4. Dispose of excess samples by flushing them down the sink with plenty of water.

9. MAINTENANCE

9.1. Refer to DEP SOP NU-060 section 5.

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10. 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.

10.1. Standard Methods Online, 4500-F^- C-2011.

10.2. Automatic PC-Titrate Instrument Operations Manual.

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

10.4. DEP SOP NU-033, Summary of Analysis Procedures for the General Chemistry and Nutrients Workgroups.

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

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

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

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

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

10.10. Quality Manual, Bureau of Laboratories, FDEP.

10.11. Laboratory Health and Safety Plan.

Appendix of Significant Changes

02/19/2008 Section 4: Spike solution prepared from a different stock than the calibration standard.

04/28/2008 Reference method changed from EPA 340.2 to SM 4500-F- C.

04/27/2009 Changed dilution requirements for saltwater samples in section 2.3.

06/21/2010 MDL changed from 0.050 mg/l to 0.035 mg/l due to the new matrix spike calculation procedure.

03/30/2012 Section 2.3: Dilution requirements for salt samples was modified, Section 4: Requirement that the spike solution be prepared from a different stock than the calibration standard was removed, and Section 7.1: CCV recovery limit was changed.

04/02/2015 Data archival information was clarified in Section 6. Clarified acceptance limit for the ALTQC. Control limits for LFBs, matrix spikes, and RPDs are calculated based on QC statistics (Section 7 and 5.3.5.).

02/04/2016 File paths and web addresses were updated.

02/21/2018 Certificate of Analyses storage location updated to network drive.

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08/16/2018	Fluoride Ion Electrode Manual, Mantech-Inc. Fluoride Electrode acceptance limits
12/10/2019	Sample and TISAB buffer volumes added to Section 2. Method validation file path was added in Section 6. MDL/PQL verification requirement added in Section 7.
12/29/2020	In Section 3, the instrumentation, equipment, and supplies were updated and inputted into table format. In Section 4, chemicals were updated and inputted into table format. Preparation procedures for reagents and standards were reformatted.
01/18/2022	Added statement about the evaluation of relative error of the calibration. Made the higher check (CHCK1) required to be run first as a mid-level calibration check, rather than the option of CHCK1 or CHCK3.
11/01/2022	MDL changed from 0.035 mg F/L to 0.025 mg F/L after annual MDL verification.
07/14/2023	Updated data drive file path links.
10/01/2024	Updated data drive file path links.

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