AUTOMATED DETERMINATION OF FLUORIDE USING THE PC-TITRATE INSTRUMENTATION

1. SCOPE AND APPLICATION

Fluoride analysis is performed on drinking, surface, ground, effluents, influents and saline waters. The method detection limit (MDL) is 0.035 mg F/L and the practical quantitation limit (PQL) is 0.10 mg F/L. The calibration range is 0.1 – 10.0 mg F/L. Higher concentrations may be measured by sample dilution. 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 10000 and 20000 umhos/cm at a 1:2 dilution and greater than 20000 umhos/cm at a 1:5 dilution. For salt samples that are close to 10000 umhos/cm or are suspect samples, use the handheld conductivity meter 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:

Instrument Unique ID	Component	Manufacturer	Model/Catalog Number
PC-TITRATE1	Autosampler	Gilson	AutoMax 197, PC-1000-680
	Burette Module	ManTech	Burivar I/2, PC-1000-1040
	Pump Module	ManTech	TitraRinse/A Pump, PC-1000-408
	Titration Module	ManTech	TitraSip Titration, PC-1300-475
	Titration Module	ManTech	TitraSip Titration, PC-1300-475
	Interface Module	ManTech	Interface Module, PC-1000-102/4
	Conductivity Meter	Jenway	4510 Conductivity Meter, PCA-2000-1015
	Software	ManTech	PC-TITRATE V3

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PC-TITRATE2	Autosampler	Gilson	Mega 215 Autosampler, PC-1000-680
	Burette Module	ManTech	Burivar I/2, PC-1104-00
	Pump Module	ManTech	TitraRinse/A Pump, PC-1000-408
	Titration Module	ManTech	TitraSip Titration, PC1300-475
	Interface Module	ManTech	Interface Module, PC-1000-102/4
	Conductivity Meter	Jenway	4510 Conductivity Meter, PCM-1000-991
	Software	ManTech	PC-TITRATE V3

3.2 Equipment:

Equipment	Manufacturer/Vendor[1]	Model/Catalog Number
pH Electrode	ManTech	PCE-80-PH1200D
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
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, 100 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.

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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. A Certificate of Analysis for each purchased reagent is maintained in the Certificate of Analysis folder within the REAGENT_PREP folder for PC-Titrate analyses on the Nutrients drive. Certificates of Analysis for purchased standards and the TISAB buffer are maintained in the STANDARDS subfolder within the Certificate of Analysis folder for PC-Titrate analyses 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	Expiration[2]	Storage
4.1.1.	100 mg F/L Stock Standard	Fluoride Standard	Ricca	3171-32	ACS, ≥99%	1 year	Room Temp
4.1.2.	TISAB Buffer	Total Ionic Strength Adjustment Buffer	Fisher Chemical (SR)	SB175-4	See COA	1 year	Room Temp
4.1.3.	QC Mineral Standard	ALTQC	Inorganic Ventures	QCP-MIN-500	See COA	See COA	Fridge after opening
4.1.4.	DI Water	H_2O	In house	N/A	N/A	Daily	N/A
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.							

4.2. A certified quality control sample AltQC (4.1.3.) is prepared following the supplier's instructions if needed. Check the manufacturer's expiration date on the bottle or the certificate of analysis for the particular lot number and ensure it does not expire within the next 28 days.

Holding time, 28 days after opening.

4.5. Standards:

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

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Working standards –

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

Dilute with DI water from purchased 100 mg F/L stock (4.1.1) according to the table.

Holding time, 28 days.

4.6. Continuing Calibration Verifications (CCVs) - Either or both of these check standards (CHCK3 and CHCK1) can be used on the run. As a general guideline both standards should be used on each analytical run.

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

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

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 conductivity probe will be damaged.

5.1. Calibration - A multi-level calibration using standards of 10, 1.0, 0.5, 0.2, 0.1 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 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.

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.

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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 (4.6.) 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)
ALTQC (4.1.3., in range above 1 mg F/L)
CHCK1 (4.6.)
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.

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

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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: \\FLDEP1\DEAR\\Labs\Lab3\Chem_Data\Inorganic\Nutrients\PC-TITRATE.

6.2. A tab delimited text file for each run must be exported by the analyst 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 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.

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6.6 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.

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.

7.2 The relative error of the calibration is also evaluated by analyzing a PQL standard (PQCK2, 4.5.) and a mid-level standard (CHCK1, 4.5.) following the calibration, but before samples are analyzed. Acceptable limits for the recovery of the PQL check (PQCK2, 4.5.) 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 (4.6.) 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 PCTitrate instrument validation data on the Chemistry drive: \\FLDEP1\DEAR\Labs\Lab5\Chemistry\Inorganic\Nutrient\Validations\PC Titrate\QC Stats.

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 < 0.035 and > -0.035 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 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 on the intranet at https://www.fldepnet.org/content/dear/bureau-laboratories-safety-documents).

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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

Refer to DEP SOP NU-060 section 5.

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.

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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.
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.

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