

SUMMARY SHEET 13A
Total Fluoride

		Run #1	Run #2	Run #3	Avg
Client/Plant Name		FDS 5			
Job No.		FDS 5			
Sampling Location		FDS 5			
Run ID #		FDS 5			
Test Date		FDS 5			
Run Start Time		FDS 5			
Run Finish Time		FDS 5			
Net Traverse Points		FDS 1			
Traverse Matrix (Rectangular)		FDS 1			
Net Run Time, min	θ	FDS 5			
Nozzle Diameter, in.	D_n	FDS 5			
Dry Gas Meter Calibration Factor	Y	CDS 5			
Average ΔH (orifice meter), in. H ₂ O	ΔH	FDS 5			
Barometric Pressure, in. Hg	P_b	FDS 5			
Stack Static Pressure, in. H ₂ O	P_g	FDS 5			
Abs Stack Pressure ($P_b + P_g/13.6$), in. Hg	P_s	SS 5			
Average Stack Temperature, °F	t_s	FDS 5			
Avg Abs Stack Temperature ($t_s + 460$), R	T_s	SS 5			
Carbon Dioxide, % dry	%CO ₂	FDS 3			
Oxygen, % dry	%O ₂	FDS 3			
Carbon Monoxide + Nitrogen, % dry	%(CO + N ₂)	FDS 3			
Dry Molecular Weight, lb/lb-mole	M_d	FDS 3			
Average DGM Temperature, °F	t_m	FDS 5			
Volume of Metered Gas Sample, dcf	V_m	FDS 5			
Volume of Metered Gas Sample, dscf	$V_{m(std)}$	SS 5			
Volume Water Condensed, mL	V_{lc}	FDS 5			
Volume of Water Vapor, scf	$V_{w(std)}$	SS 5			
Moisture Content, fraction	B_{ws}	SS 5			
Pitot Tube Coefficient	C_p	CDS 2a			
Average Velocity Pressure, in. H ₂ O	Δp	FDS 5			
Average $[(t_{si} + 460) \Delta p]^{1/2}$	$[T_{si} \Delta p]^{1/2}$	FDS 5			
Velocity, ft/sec	v_s	SS 5			
Stack Area, ft ²	A	FDS 1			
Isokinetic Sampling Rate, %	%I	SS 5			
Total Fluoride in Sample, mg	F_t	LDS 13A			
In-stack Concentration of F, mg/ft ³	C_s	SS 13A			
Post-test Calibration Checks					
Temperature and Barometric Pressure		CDS 2d			
Differential Pressure Gauges		CDS 2d			
Metering System		CDS 5			

$$C_s = \frac{F_t}{V_{m(std)}}$$

FIELD PROCEDURE 13A
Total Fluoride
(SPADNS Zirconium Lake Method)

This field procedure applies also to Method 13B, except references to chloride and sulfate interferences are not applicable. The sampling procedure is the same as that in FP 5, except for the following:

A. Sampling

1. The filter position is interchangeable (see Figure F13A-1).
 - a. If placed between the probe and first impinger, use a Whatman No. 1 filter and borosilicate glass or stainless steel with a 20-mesh stainless steel screen filter support and a silicone rubber gasket; do not use a glass frit or a sintered metal filter support in this position.
 - b. If placed between the probe and first impinger, use any suitable medium (e.g., paper, organic membrane) with the following specifications: (1) Able to withstand prolonged exposure to temperatures up to 275°F. (2) Has efficiency $\geq 95\%$ for 0.3 μm dioctyl phthalate smoke particles. (3) Has a blank value of $< 0.015 \text{ mg F/cm}^2$ of filter area. (In general, glass fiber filters have high and/or variable F blank values, and will not be acceptable for use.)
2. When moisture condensation is a problem, a filter heating system set at $\leq 248 \pm 25^\circ\text{F}$ may be used.
3. Use impingers rather than an alternative condenser system.
4. For the sample storage containers for impinger water, use high-density polyethylene bottles.
5. The filter need not be weighed. Before the test series, determine the average F blank value of at least three filters from the lot to be used for sampling (see LP 13A).
6. Select the nozzle size to maintain isokinetic sampling rates below 1.0 cfm.
7. Grease on sample-exposed surfaces may cause low F results due to adsorption.

B. Sample Recovery

The quantitative sample recovery technique is the same as that in FP 5. Water is used as the wash rather than acetone. Recover the samples in the following containers:

1. **Container No. 1** (Probe, Filter, and Impinger Catches).
 - a. Using a graduated cylinder, measure to the nearest mL the volume of the water in the first three impingers; include any condensate in the probe in this determination.
 - b. Transfer the impinger water from the graduated cylinder into this polyethylene container.
 - c. Add the filter to this container. (The filter may be handled separately using procedures subject to the Administrator's approval.)
 - d. Add the water washings from all sample-exposed surfaces (including the probe nozzle, probe fitting, probe liner, first three impingers, impinger connectors, and filter holder). Use $< 500 \text{ mL}$ for the entire wash.
2. **Container No. 2** (Sample Blank)
 - a. Prepare a blank by placing an unused filter in a polyethylene container and adding a volume of water equal to the total volume in Container No. 1.
 - b. Process the blank in the same manner as that for Container No. 1.
3. **Container No. 3** (Silica Gel). Use FP 5, step E5.

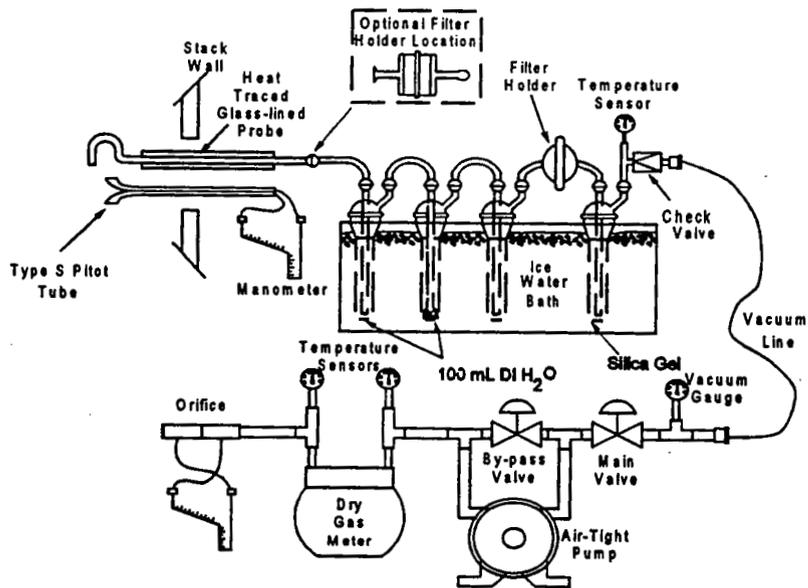


Figure F13A-1. Fluoride Sampling Train.

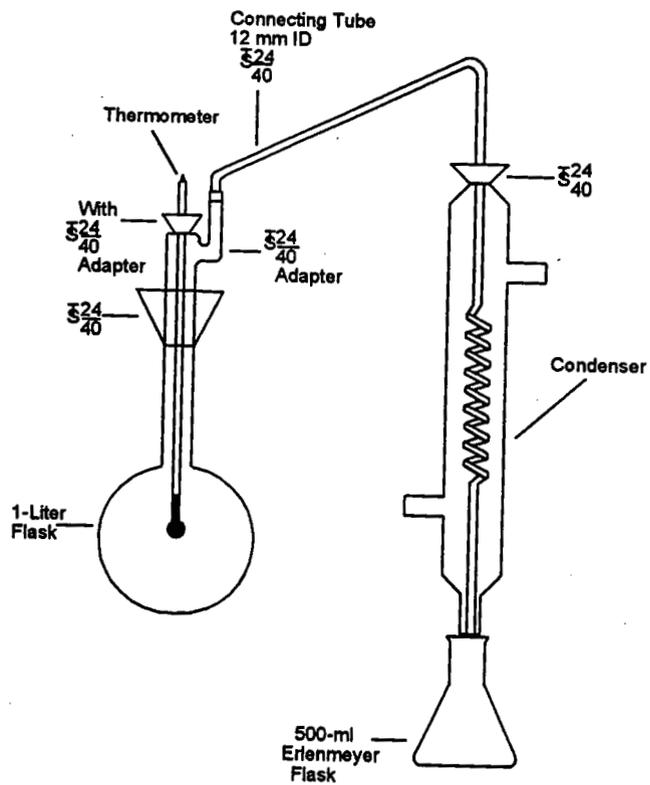


Figure L13A-1. Fluoride Distillation Apparatus.

LABORATORY PROCEDURE 13A
Total Fluoride
(SPADNS Zirconium Lake Method)

A. Reagent Preparation

1. Phenolphthalein Indicator. Dissolve 0.1 g phenolphthalein in a mixture of 50 mL 90% ethanol and 50 mL water.
2. Sulfuric Acid, 25%. Mix 1 part of conc. H_2SO_4 with 3 parts of water.
3. Fluoride Standard Solution, 0.01 mg F/mL. Oven dry at 110°C for ≥ 2 hr. Dissolve 0.2210 g of NaF in 1 L water. Dilute 100 mL of this solution to 1 L with water.
4. SPADNS Solution [4,5 Dihydroxy-3-(p-Sulfophenylazo)-2,7-Naphthalene-Disulfonic Acid Trisodium Salt]. Dissolve 0.960 ± 0.010 g SPADNS reagent in 500 mL water. Solution stored in a well-sealed bottle protected from the sunlight is stable for at least 1 month.
5. Spectrophotometer Zero Reference Solution. Prepare daily. Add 10 mL SPADNS solution to 100 mL water, and acidify with a solution prepared by diluting 7 mL conc. HCl to 10 mL with water.
6. SPADNS Mixed Reagent. Dissolve 0.135 ± 0.005 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 25 mL water. Add 350 mL conc. HCl, and dilute to 500 mL with water. Mix equal volumes of this solution and SPADNS solution to form a single reagent. This reagent is stable for at least 2 months.

B. Sample Preparation and Distillation

1. Check the liquid levels in Containers No. 1 and No. 2, and determine and record loss (if any) on LDS 13A.
2. **Container No. 1** (Probe, Filter, and Impinger Catches)
 - a. Filter contents, including the sampling filter, through Whatman No. 541 filter paper into a 1500-mL beaker.
 - b. If the filtrate volume > 900 mL, make the filtrate basic (red to phenolphthalein) with NaOH, and evaporate to < 900 mL.
 - c. Place the filtered material (including sampling filter) in a nickel crucible, add a few mL of water, and macerate the filters with a glass rod.
 - d. Add 100 mg CaO (certified grade $\leq 0.005\%$ F) to the crucible, and mix the contents thoroughly to form a slurry. Add two drops of phenolphthalein indicator. Place the crucible in a hood under infrared lamps or on a hot plate at

low heat. Evaporate the water completely. During the evaporation of the water, keep the slurry basic (red to phenolphthalein) to avoid loss of F. If the indicator turns colorless (acidic) during the evaporation, add CaO until the color turns red again.

- e. After evaporating the water, place the crucible on a hot plate under a hood, and slowly increase the temperature until the Whatman No. 541 and sampling filters char completely (may take several hours).
 - f. Place the crucible in a cold muffle furnace. Gradually (to prevent smoking) increase the temperature to 600°C , and maintain until the contents are reduced to an ash. Remove the crucible from the furnace, and allow to cool.
 - g. Add about 4 g crushed NaOH to the crucible, and mix. Return the crucible to the muffle furnace, and fuse the sample for 10 min at 600°C .
 - h. Remove the sample from the furnace, and cool to ambient temperature. Using several rinsings of warm water, transfer the contents of the crucible to the beaker containing the filtrate. To assure complete sample removal, rinse finally with two 20-mL portions of 25% H_2SO_4 , and carefully add to the beaker. Mix well, and transfer to a 1-L volumetric flask. Dilute to volume with water, and mix thoroughly. Allow any undissolved solids to settle.
3. **Container No. 2** (Sample Blank). Treat in the same manner as described in step B2.

C. Distillation

1. Adjust the acid/water ratio of the distillation flask as follows:
 - a. Using a protective shield, place 400 mL water in the distillation flask, and add 200 mL conc. H_2SO_4 . (Caution: Observe standard precautions when mixing H_2SO_4 with water. Slowly add the acid to the flask with constant swirling.)
 - b. Add some soft glass beads and several small pieces of broken glass tubing, and assemble the apparatus as shown in Figure L13A-1. Heat the flask until it reaches 175°C . Discard the distillate.

2. Cool the contents of the distillation flask to $<80^{\circ}\text{C}$. Pipet an aliquot of sample containing less than 10.0 mg F directly into the distillation flask, and add water to make a total volume of 220 mL added to the distillation flask. (To estimate the appropriate aliquot size, select an aliquot of the solution, and treat as described in step D2.)
 3. If the sample contains chloride, add 5 mg Ag_2SO_4 to the flask for every mg of chloride. **Note:** It may be easier to use the Specific Ion Electrode Method (Method 13B).
 4. Place a 250-mL volumetric flask at the condenser exit. Heat the flask as rapidly as possible with a Bunsen burner, and collect all the distillate up to 175°C . During heatup, play the burner flame up and down the side of the flask to prevent bumping. Conduct the distillation as rapidly as possible (15 min or less). Slow distillations produce low F recoveries. Caution: Be careful not to exceed 175°C to avoid causing H_2SO_4 to distill over.
 5. If F distillation in the fractional mg range is to follow distillation in the mg range, add 220 mL of water, and distill it over as in the acid adjustment step to remove residual F from the distillation system.
 6. After every tenth distillation, check the distillation flask for carry-over of interferences or poor F recovery by using a water blank and a standard solution. Change the acid whenever the F recovery is less than 90% or the blank value exceeds $0.1 \mu\text{g/mL}$.
- e. With the spectrophotometer at 570 nm, use the reference solution (step D1a) to set the absorbance to zero.
 - f. Determine the absorbance of the standards. Prepare a calibration curve by plotting $\mu\text{g F}/50 \text{ mL}$ versus absorbance on linear graph paper. Prepare the standard curve initially and thereafter whenever the SPADNS mixed reagent is newly made. Also, run a calibration standard with each set of samples and, if it differs from the calibration curve by $\pm 2\%$, prepare a new standard curve.

2. Containers No. 1 and No. 2

- a. Dilute the distillate in the volumetric flasks to exactly 250 mL with water, and mix thoroughly. Pipet a suitable aliquot of each sample distillate (containing 10 to $40 \mu\text{g F/mL}$) into a beaker, and dilute to 50 mL with water. Use the same aliquot size for the blank. Add 10 mL SPADNS mixed reagent and mix thoroughly.
 - b. Place the sample in the same constant-temperature bath as that containing the standard solutions for 30 min. A 3°C difference between the sample and standard solutions produces an error of about 0.005 mg F/L.
 - c. Set the spectrophotometer to zero absorbance at 570 nm with the reference solution, and check the spectrophotometer calibration with the standard solution.
 - d. Determine the absorbance of the samples, and determine the concentration from the calibration curve.
 - e. If the concentration does not fall within the range of the calibration curve, repeat the procedure using a different size aliquot.
- ## 3. Container No. 3 (Silica Gel). If not done in the field, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

D. *Analysis*

1. Spectrophotometer Calibration

- a. Add 10 mL SPADNS mixed reagent to 50 mL water for the blank standard.
- b. Dilute 0, 2, 4, 6, 8, 10, 12, and 14 mL of the 0.01 mg F/mL standard fluoride solution to 100 mL with water.
- c. Pipet 50 mL from each solution, and transfer each to a separate 100-mL beaker. Then add 10 mL SPADNS mixed reagent to each to make 0, 10, 20, 30, 40, 50, 60, and $70 \mu\text{g F}$ (0 to $1.4 \mu\text{g/mL}$), respectively.
- d. After mixing, place the reference standards and reference solution in a constant temperature ($\pm 1^{\circ}\text{C}$) bath for 30 min. Then read the absorbance with the spectrophotometer within 2 hr.

LABORATORY DATA SHEET 13A
Total Fluoride - SPADNS Zirconium Lake

Client/Plant Name _____ Job # _____ Date/Time _____

Spectrophotometer ID# _____ Analyst _____

Wavelength 750 nm (✓) _____ Ambient Temp. _____ °F Bath Temp. _____ °F Calibration Date _____

Working Standards (µg F/mL)	0.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0
Absorbance 1								
Absorbance 2								

_____ SPADNS reagent prepared within the last two months? _____ Zero reference solution prepared daily?

_____ Plot of calibration curve attached?

Note: Run a calibration standard with every set of samples and if it differs from the curve by $\geq \pm 2\%$, run a new calibration curve.

Sample ID #	Sample Vol., V_t (mL)	Aliquot Vol., A_t (mL)	Chloride in Sample, (mg)	Ag_2SO_4 Added, (mg)	Vol. of Distillate, V_d (mL)	Aliquot of Distillate, A_d (mL)	Absorption at 570 nm, (O.D.)	µg F in sample	Total weight of F, F_t (mg)
Cal Std									

_____ Standards and samples placed in same constant temperature bath?

Total Fluoride in Sample, mg:

$$F_t = 10^{-3} \frac{V_t V_d}{A_t A_d} (\mu\text{g F})$$

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by: _____
 Personnel (Signature/Date)

_____ Team Leader (Signature/Date)

SUMMARY SHEET 13B
Total Fluoride

		Run #1	Run #2	Run #3	Avg
Client/Plant Name		FDS 5			
Job No.		FDS 5			
Sampling Location		FDS 5			
Run ID #		FDS 5			
Test Date		FDS 5			
Run Start Time		FDS 5			
Run Finish Time		FDS 5			
Net Traverse Points		FDS 1			
Traverse Matrix (Rectangular)		FDS 1			
Net Run Time, min	θ	FDS 5			
Nozzle Diameter, in.	D_n	FDS 5			
Dry Gas Meter Calibration Factor	Y	CDS 5			
Average ΔH (orifice meter), in. H ₂ O	ΔH	FDS 5			
Barometric Pressure, in. Hg	P_b	FDS 5			
Stack Static Pressure, in. H ₂ O	P_g	FDS 5			
Abs Stack Pressure ($P_b + P_g/13.6$), in. Hg	P_s	SS 5			
Average Stack Temperature, °F	t_s	FDS 5			
Avg Abs Stack Temperature ($t_s + 460$), R	T_s	SS 5			
Carbon Dioxide, % dry	%CO ₂	FDS 3			
Oxygen, % dry	%O ₂	FDS 3			
Carbon Monoxide + Nitrogen, % dry	%(CO + N ₂)	FDS 3			
Dry Molecular Weight, lb/lb-mole	M_d	FDS 3			
Average DGM Temperature, °F	t_m	FDS 5			
Volume of Metered Gas Sample, dcf	V_m	FDS 5			
Volume of Metered Gas Sample, dscf	$V_{m(std)}$	SS 5			
Volume Water Condensed, mL	V_{lc}	FDS 5			
Volume of Water Vapor, scf	$V_{w(std)}$	SS 5			
Moisture Content, fraction	B_{ws}	SS 5			
Pitot Tube Coefficient	C_p	CDS 2a			
Average Velocity Pressure, in. H ₂ O	Δp	FDS 5			
Average $[(t_{si} + 460) \Delta p]^{1/2}$	$[T_{si} \Delta p]^{1/2}$	FDS 5			
Velocity, ft/sec	v_s	SS 5			
Stack Area, ft ²	A	FDS 1			
Isokinetic Sampling Rate, %	%I	SS 5			
Total Fluoride in Sample, mg	F_t	LDS 13B			
In-stack Concentration of F, mg/ft ³	C_s	SS 13B			
Post-test Calibration Checks					
Temperature and Barometric Pressure		CDS 2d			
Differential Pressure Gauges		CDS 2d			
Metering System		CDS 5			

$$C_s = \frac{F_t}{V_{m(std)}}$$

LABORATORY PROCEDURE 13B
Total Fluoride
(Specific Ion Electrode Method)

A. Reagent Preparation

1. Phenolphthalein Indicator. Dissolve 0.1 g phenolphthalein in a mixture of 50 mL 90% ethanol and 50 mL water.
2. Sodium Hydroxide, 5 M. Dissolve 20 g NaOH in 100 mL water.
3. H₂SO₄, 25% (v/v). Mix 1 part conc. H₂SO₄ with 3 parts of water.
4. Total Ionic Strength Adjustment Buffer (TISAB). Use commercially-prepared TISAB or prepare as follows: Place about 500 mL water in a 1-L beaker. Add 57 mL glacial acetic acid, 58 g NaCl, and 4 g cyclohexylene dinitrilo tetraacetic acid. Stir to dissolve. Place the beaker in a water bath to cool it. Slowly add 5 M NaOH to the solution, measuring the pH continuously with a calibrated pH/reference electrode pair, until the pH is 5.3. Cool to room temperature. Pour into a 1-L volumetric flask, and dilute to volume with water.
5. Fluoride Standard Solution, 0.1 M. Oven dry some NaF for ≥ 2 hr at 110°C, and store in a desiccator. Then add 4.2 g NaF to a 1-L volumetric flask, and add enough water to dissolve. Dilute to volume with water.

B. Specific Ion Electrode Calibration

1. Pipet 10 mL 0.1 M fluoride standard solution into a 100-mL volumetric flask, and make up to the mark with water for a 10⁻² M standard solution. Use 10 mL 10⁻² M solution to make a 10⁻³ M solution in the same manner. Repeat the dilution procedure, and make 10⁻⁴ and 10⁻⁵ solutions.
2. Pipet 50 mL of each standard into a separate beaker. Add 50 mL TISAB to each beaker.
3. Place the electrode in the most dilute standard solution. Stir the solution with a magnetic stirrer during measurement to minimize electrode response time. If the stirrer generates enough heat to change solution temperature, place a piece of temperature insulating material, such as cork, between the stirrer and the beaker. When a steady mv reading is obtained, record that value. This may take several minutes.
4. Between measurements, soak the fluoride sensing electrode in water for 30 sec, and then remove and blot dry.

5. Analyze the standards going from dilute to concentrated standards.
6. Plot the millivolt reading on the linear axis of semilog graph paper versus concentration (nominal value) on the log axis. When 50 mL 10⁻² M standard is diluted with 50 mL TISAB, the nominal concentration is still "10⁻² M." The calibration curve should be a straight line; however, some electrodes may be slightly nonlinear between 10⁻⁵ and 10⁻⁴ M. If this occurs, use additional standards between these two concentrations.
7. Calibrate the fluoride electrode daily, and check it hourly. Prepare fresh fluoride standardizing solutions daily (10⁻² M or less). Store fluoride standardizing solutions in polyethylene or polypropylene containers.
8. **Note:** Certain specific ion meters have been designed specifically for fluoride electrode use and give a direct readout of fluoride ion concentration. These meters may be used in lieu of calibration curves for fluoride measurements over a narrow concentration ranges. Calibrate the meter according to the manufacturer's instructions.

C. Analysis

1. **Containers No. 1 and No. 2**
 - a. Distill suitable aliquots from each container.
 - b. Dilute the distillate in the volumetric flasks to exactly 250 mL with water, and mix thoroughly.
 - c. Pipet a 25-mL aliquot from each of the distillate and separate beakers. Add an equal volume of TISAB, and mix.
 - d. Analyze the samples in the same manner and at the same temperature as that of the calibration standards ($\pm 2^\circ\text{C}$). Hold dilute samples (below 10⁻⁴ M fluoride ion content) in polyethylene beakers during measurement.
 - e. Determine concentration from the calibration curve.
2. **Container No. 3 (Silica Gel).** If not done in the field, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

LABORATORY DATA SHEET 13B
Total Fluoride - Specific Ion Electrode

Client/Plant Name _____ Job # _____

Meter ID# _____ Electrode ID# _____ Date/Time _____

Calibration Date _____ Calibration standard mix date _____

Ambient Temp. _____ °F Bath Temp. _____ °F Analyst _____

Working Standards: Molarity (M)	10 ⁻¹	10 ⁻²	10 ⁻³	10 ⁻⁴	10 ⁻⁵	Control Sample
Electrode Potential (mV) 1						
Electrode Potential (mV) 2						

Note: Concentration of the control sample determined from the curve must be between 0.002M and 0.01M.

_____ Plot of calibration curve attached?

Sample No.	Sample ID#	Sample Vol., V _t (mL)	Aliquot Vol., A _t (mL)	Diluted Distillate Vol., V _d (mL)	Electrode Potential mV			M of F in sample	Total Wgt of F, F _t (mg)
					mV ₁	mV ₂	mV _{avg}		

Total Weight of Fluoride in Sample , mg:

$$F_t = 19 \frac{V_t}{A_t} V_d M$$

_____ Fluoride electrode calibrated daily?

_____ Electrode calibration checked hourly?

_____ Fluoride standardizing solution prepared fresh daily?

_____ Fluoride standardizing solutions stored in polyethylene or polypropylene containers?

_____ Ambient temperatures fluctuate > ± 2°C from the temperature that the standards were measured?

_____ Sample and standards conditioned in a constant temperature bath before measuring?

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by: _____ Personnel (Signature/Date) _____ Team Leader (Signature/Date)

