

Section 3.10

METHOD 13A - DETERMINATION OF TOTAL FLUORIDE  
EMISSIONS FROM STATIONARY SOURCES  
(SPADNS Zirconium Lake Method)

OUTLINE

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## SUMMARY

In Method 13A, total fluorides (gaseous and particulate) are extracted isokinetically from the source by using a sampling train similar to the one specified in Method 5 (Section 3.4 of this Handbook). The filter is not required to be heated and may be located immediately after the probe or between the third and fourth impinger.

The SPADNS zirconium lake colorimetric method for quantitatively measuring the fluorides collected in the train is applicable to fluoride (F) emissions from stationary sources, but not to fluorocarbons such as Freon. The concentration range of the method is from 0.05 to 1.4  $\mu\text{g F/ml}$ ; the method is applicable to much higher concentration by using sample dilutions. Sensitivity of the method has not been determined.

An interferent in the collection of fluorides is grease on sample-exposed surfaces; due to adsorption the grease causes low results. If it can be shown to the satisfaction of the administrator that samples contain only water soluble fluorides, fusion and distillation may be omitted from the analysis.

Interferences, such as  $>300 \text{ mg aluminium/l}$  and  $>0.3 \text{ mg silicon dioxide/l}$ , prevent complete recovery of fluoride during laboratory analysis, however, sample distillation will eliminate this problem. Chloride will distill over and interfere with the SPADNS zirconium lake color reaction. This interference can be prevented by adding silver sulfate (5 mg of silver sulfate/mg of chloride) into the distillation flask. However, if chloride ion is present, use of specific-ion electrode (Method 13B) is recommended. Sulfuric acid carried over during distillation will cause a positive interference; to avoid the carryover, stop the distillation at  $175^\circ\text{C}$  ( $347^\circ\text{F}$ ). Residual chlorine will also interfere with this colorimetric method, but should not be present in the type of sample analyzed.

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The color obtained when colorimetric reagent is mixed with the sample is stable for approximately 2 h. After formation of the color, the absorbances of the sample and standard solutions should be measured at the same temperature. A 3°C (5.4°F) difference between sample and standard solution temperatures will produce an error of approximately 0.005 mg F/l.

The method description which follows is based on the Reference Method<sup>1</sup> that was promulgated on June 20, 1980.

Section 3.10.10 contains a copy of the Reference Method and blank data forms are provided in Section 3.10.12 for the convenience of the Handbook user.

Note: Due to similarities between Method 13A and Method 13B sampling and analytical equipment and procedures, only the differences pertaining to Method 13A will be presented. However, the activity matrices are all included whether or not differences occur in the written descriptions. All other Method 13A descriptions will be referenced to the corresponding description in Section 3.9, Method 13B. This is done for both time savings to the reader and cost savings to the Government.

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#### METHOD HIGHLIGHTS

Section 3.10 (Method 13A) describes specifications for the sampling and analysis of total fluoride emissions from stationary sources. A gas sample is isokinetically extracted from the source stream, and the fluorides in the stream are collected in the sampling train.

The sampling train is similar to that in EPA Method 5, with a few exceptions--the filter does not have to be heated and it may be located either immediately after the probe or between the third and fourth impingers. If it is between the probe and the first impinger, a borosilicate glass or stainless steel filter holder with a 20-mesh stainless steel screen filter support and a silicone rubber gasket must be used. If it is between the third and fourth impingers, a glass frit filter support may be used.

Sampling is generally the same as in Method 5, but a nozzle size that will maintain an isokinetic sampling rate of  $<28 \text{ l/min}$  ( $<1.0 \text{ ft}^3/\text{min}$ ) must be used. Samples and standards must be the same temperature during analysis by the colorimetric method. A change of  $3^\circ\text{C}$  ( $5.4^\circ\text{F}$ ) will cause an error of  $0.005 \text{ mg F/l}$  in the sample measurements. Distillation during sample analysis has been found to be the main cause of error in this method.

The collected sample is recovered by transferring the measured condensate and impinger water to a sample container, adding the filter and the rinsings of all sample-exposed surfaces to this container, and fusing and distilling the sample for colorimetric analysis. Fusion and distillation may be omitted if it can be shown to the satisfaction of the administrator that the samples contain only water soluble fluorides.

Results of collaborative tests<sup>2</sup> show that fluoride concentrations from  $0.1$  to  $1.4 \text{ mg F/m}^3$  could be determined with an intralaboratory precision of  $0.044 \text{ mg F/m}^3$  and an interlaboratory

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precision of 0.064 mg F/m<sup>3</sup>. Six contractors each simultaneously took duplicate samples from the stack. The collaborative test did not find any bias in the analytical method.<sup>2</sup>

The Method Description (Sections 3.10.1 to 3.10.9) is based on the detailed specifications in the Reference Method (Section 3.10.10) promulgated by EPA on June 20, 1980.<sup>1</sup>

The appropriate blank data forms at the end of the Method Highlights Section of Method 13B (Section 3.9) may be removed from the Handbook and used in the pretest, test, and posttest operations. Each form has a subtitle to assist the user in finding a similar filled-in form in the method description. On the blank and filled-in forms, the items/parameters that can cause the most significant errors are designated with an asterisk.

#### 1. Procurement of Apparatus and Supplies

Section 3.10.1 (Procurement of Apparatus and Supplies) gives specifications, criteria, and design features for the required equipment and materials. The sampling apparatus for Method 13A has the same design features as that of Method 5, except for the positioning of the filter in the sampling train. This section can be used as a guide for procurement and initial checks of equipment and supplies. The activity matrix (Table 1.1) at the end of the section is a summary of the details given in the text and can be used as a quick reference.

#### 2. Pretest Preparations

Section 3.10.2 (Calibration of Apparatus) describes the required calibration procedures for the Method 13A sampling equipment (same as Method 13B) for the colorimetric method. A pretest checklist (Figure 3.1 in Section 3.9.3 or a similar form) should be used to summarize the calibration and other pertinent pretest data.

Section 3.10.3 (Presampling Operations) is the same as for Method 13B.

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Activity matrices for the calibration of equipment and the presampling operations (Tables 2.1 and 3.1) summarize the activities.

### 3. On-site Measurements

Section 3.10.4 (On-Site Measurements) describes procedures for sampling and sample recovery and is the same as for Method 13B.

### 4. Posttest Operations

Section 3.10.5 (Postsampling Operation) describes the postsampling activities for checking the equipment and the analytical procedures. A form is given for recording data from the posttest equipment calibration checks; a copy of the form should be included in the emission test final report. A control sample of known (F) concentration should be analyzed before analyzing the sample for a quality control check on the analytical procedures. The detailed analytical procedures can be removed for use as easy references in the laboratory. An activity matrix (Table 5.1) summarizes the postsampling operations.

Section 3.10.6 (Calculations) describes calculations, nomenclature, and significant digits for the data reduction. A programmed calculator is recommended to reduce calculation errors.

Section 3.10.7 (Maintenance) recommends routine and preventive maintenance programs. The programs are not required, but their use should reduce equipment downtime.

### 5. Auditing Procedures

Section 3.10.8 describes performance and system audits. Performance audits for both the analytical phase and the data processing are described. A checklist (Figure 8.2) outlines a recommended system audit.

Section 3.10.9 lists the primary standards to which the working standards or calibration standards should be traceable.

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6. References

Section 3.10.10 contains the promulgated Reference Method; Section 3.10.11 contains the references cited throughout the text; and Section 3.10.12 either contains copies of data forms recommended for Method 13A or references the user to forms in Method 13B.

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## METHOD DESCRIPTION

### 1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

A schematic of the sampling train used in Method 13 is shown in Figure 1.1. The train and the sampling procedures are similar to EPA Method 5; the procedures and equipment for Methods 13A and 13B are identical. Commercial models of the train are available. For those who want to build their own, construction details are in APTD-0581;<sup>3</sup> allowable modifications are described therein. The operating, maintenance, and calibration procedures for the sampling train are in APTD-0576.<sup>4</sup> Since correct usage is important in obtaining valid results, all users are advised to read that document and to adopt its procedures unless alternatives are outlined therein.

Specifications, criteria, and/or design features are given in this section to aid in the selection of equipment or any components that are different from those in Section 3.9.1. Procedures and limits (where applicable) for acceptance checks are also given.

Table 1.1 at the end of this section summarizes the quality assurance activities for the procurement and acceptance of apparatus and supplies.

#### 1.1 Miscellaneous Glassware

1.1.1 Pipettes - Several volumetric pipettes (Class A)--including 2, 4, 5, 6, 8, 10, 12, 14, 20, 25, 50 ml's--should be available. Record the stock numbers, and visually check for cracks, breaks, or manufacturer's flaws. If irregularities are found, either replace or return to the supplier.

1.1.2 Volumetric Flask - Several glass volumetric flasks, Class A, (50-ml, 100-ml, 250-ml, 1000-ml) are needed to dilute the sample and to prepare standards and agents.

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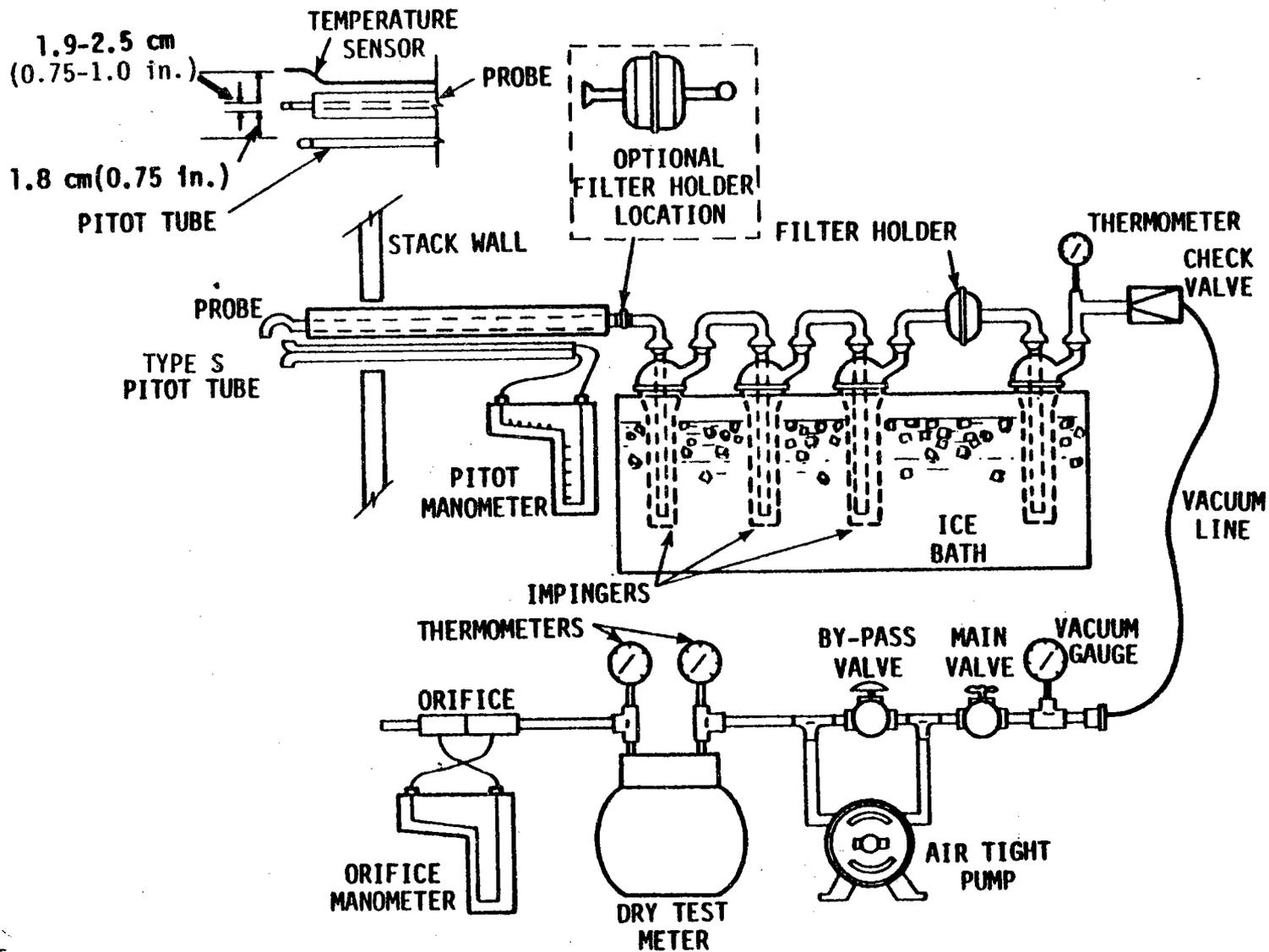


Figure 1.1. Fluoride sampling train.

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1.1.3 Erlenmeyer Flask or Plastic Bottle - A 500-ml Erlenmeyer flask or plastic bottle is needed to store the SPADNS solution.

1.2 Reagents and Supplies (Sample Recovery and Analysis)

Unless otherwise indicated, all reagents should meet the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS); otherwise, use the best available grade.

1.2.1 Calcium Oxide (CaO) - A reagent grade or a certified ACS grade of CaO containing  $\leq 0.005\%$  F is needed.

1.2.2 Filters - Whatman No. 541 (or equivalent) filters are required for filtration of the impinger contents and recovery of the sample.

1.2.3 Hydrochloric Acid (HCl) - An ACS reagent grade or the equivalent concentrated HCl is needed.

1.2.4 Phenolphthalein Indicator - A reagent grade or a certified ACS 0.1% phenolphthalein should be a 1:1 ethanol-water mixture.

1.2.5 Silver Sulfate ( $Ag_2SO_4$ ) - An ACS reagent grade or the equivalent  $Ag_2SO_4$  should be used.

1.2.6 Sodium Hydroxide (NaOH) Pellets - An ACS reagent grade or the equivalent is needed.

1.2.7 Sodium Fluoride (NaF) Standard - Dissolve 0.2210 g  $\pm 0.0005$  g of reagent grade NaF in deionized distilled water and dilute to 1000 ml. Dilute 100 ml of this solution to 1000 ml with distilled water; 0.01 mg F/ml water. NaF should be oven dried at 110°C for at least 2 h prior to weighing.

1.2.8 Sulfuric Acid ( $H_2SO_4$ ) - An ACS reagent grade or the equivalent concentrated  $H_2SO_4$  is needed.

1.2.9 Sulfuric Acid, 25 Percent (v/v) - Cautiously add 1 part of concentrated  $H_2SO_4$  to 3 parts deionized distilled water.

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1.2.10 Water - Deionized distilled water needed as specified in Table 1.1 at the end of this section and in Section 3.9.1.

1.2.11 SPADNS Solution - Dissolve  $0.960 \pm 0.010$  g of SPADNS reagent 4,5 dihydroxy-3-(parasulfophenylazo)-2,7-naphthalenedisulfonic acid trisodium salt (also called sodium-2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonate) in distilled water and dilute to 500 ml. This diluted solution is stable for about 1 mo if stored in a sealed bottle and protected from direct sunlight.

1.6.12 Reference Solution - Add 10 ml of the SPADNS solution to 100 ml distilled water. Dilute 7 ml of concentrated HCl to 10 ml; then add the diluted HCl to the diluted SPADNS. This reference solution, which is needed to set the spectrophotometer zero point, is stable for at least 2 mo.

1.2.13 SPADNS Mixed Reagent ( $ZrOCl_2 \cdot 8H_2O + HCl$  Mixed with SPADNS Solution) - First prepare the zirconyl-acid reagent by dissolving  $0.135 \pm 0.005$  g of zirconyl chloride octahydrate ( $ZrOCl_2 \cdot 8H_2O$ ) in 25 ml of distilled water. Then add 350 ml of concentrated HCl, and dilute to 500 ml with distilled water. Next, prepare the SPADNS mixed reagent (acid zirconyl-SPADNS solution) by combining equal volumes of the SPADNS solution and the zirconyl-acid reagent. The mixed reagent will be stable for at least 2 mo.

Check all reagents for grades and ACS certifications. Replace or return to the manufacturer any reagent which does not meet the standards.

### 1.3 Analytical Equipment

1.3.1 Bunsen Burner - A Bunsen burner capable of distilling 200 ml in <15 min is required to heat the boiling flasks.

1.3.2 Crucible - A nickel crucible with a capacity of 75 to 100 ml is needed to evaporate the water from the sample on a hot plate.

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Upon receipt, check for cracks or manufacturing flaws as well as for capacity. If it does not meet specifications replace or return it to the manufacturer.

1.3.3 Hot Plate - A hot plate capable of 500°C (932°F) is required for heating the sample in a nickel crucible.

Check upon receipt and before each use for damage. Check the heating capacity against a mercury-in-glass thermometer. If inadequate, repair or return the hot plate to the supplier.

1.3.4 Electric Muffle Furnace - An electric muffle furnace capable of heating to 600°C (1112°F) is needed to fuse the sample.

Check the heating capacity against a mercury-in-glass thermometer. Replace or return to the manufacturer any unit which does not meet specifications.

1.3.5 Balance - A balance with a capacity of 300 g  $\pm$ 0.5 g is needed to determine moisture.

Check for damage against a series of standard weights upon receipt and before each use. Replace or return to the manufacturer if damaged or if it does not meet specifications.

1.3.6 Analytical Balance - An analytical balance capable of weighing to within 0.1 mg is needed for preparation of the standard fluoride solution and the analytical reagents. Check the balance frequently with Class S weights.

1.3.7 Constant Temperature Bath - For optimum measurement of the sample concentration, a water bath is needed to maintain a constant room temperature. This bath must maintain a constant temperature of  $\pm$ 1°C (1.8°F) in the room temperature range.

Check upon receipt and before each use for damage and temperature constancy.

1.3.8 Spectrophotometer - A spectrophotometer is required for determining the absorbance of the sample and the calibration standards at a wavelength of 570 nanometers using a 1-cm path-length.

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Check the spectrophotometer upon receipt and before each use for proper operation according to the manufacturer's manual.

1.3.9 Spectrophotometer Cells - Glass cuvettes with 1-cm path-length are required to contain sample and standards during the absorbance measurements. Check upon receipt and before each use for cracks or scratches on optical surfaces. Replace the cuvettes necessary.

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TABLE 1.1. ACTIVITY MATRIX FOR PROCUREMENT OF APPARATUS AND SUPPLIES

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
<u>Sampling</u> Probe liner	Specified material of construction; equipped with heating system capable of maintaining $120^{\circ}\pm 14^{\circ}\text{C}$ ( $248^{\circ}\pm 25^{\circ}\text{F}$ ) at the exit	Visually check the probe and run the heating system	Repair, return to supplier, or reject
Probe nozzle	Stainless steel (316) with sharp, tapered angle $<30^{\circ}$ ; difference in measured diameters $<0.1$ mm (0.004 in.); no nicks, dents, or corrosion	Visually check upon receipt and before each test; use a micrometer to measure ID before field use after each repair	Reshape and sharpen, return to the supplier, or reject
Pitot tube	Type S (Meth 2, Sec 3.1.2); attached to probe with impact (high pressure) opening plane even with or above nozzle entry plane	Visually check for vertical and horizontal tip alignments; check the configuration and the clearances; calibrate (Sec 3.9.2)	Repair or return to supplier
Differential pressure gauge (inclined manometer)	Meets criteria (Sec 3.1.2); agrees within 5% of gauge-oil manometer	Check against a gauge-oil manometer at a minimum of three points: 0.64(0.025); 12.7 (0.5); 25.4(1.0) mm (in.) $\text{H}_2\text{O}$	As above
Filters	Capable of withstanding temperatures to $135^{\circ}\text{C}$ ( $275^{\circ}\text{F}$ ), 95% collection efficiency for $0.3\ \mu\text{m}$ particles, low F blank ( $\leq 0.015$ mg F/cm <sup>2</sup> )	Check each batch for F blank values, visibly inspect for pin holes or flaws	Reject batch

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TABLE 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Filter holder	Leak free; borosilicate glass	Visually check before use	Return to supplier
Condenser	Four impingers, standard stock glass; pressure drop not excessive	Visually check upon receipt; check pressure drop	As above
Vacuum gauge	0-760 mm (0-30 in.) Hg, $\pm 25$ mm (1 in.) at 380 mm (15 in.) Hg	Check against mercury U-tube manometer upon receipt	Adjust or return to supplier
Vacuum pump	Leak free; capable of maintaining flow rate of 0.02-0.03 m <sup>3</sup> /min (0.7 to 1.1 ft <sup>3</sup> /min) for pump inlet vacuum of 380 mm (15 in.) Hg	Check upon receipt for leaks and capacity	Repair or return to supplier
Barometer	Capable of measuring atmospheric pressure $\pm 2.5$ mm (0.1 in.) Hg	Check against a mercury-in-glass barometer or equivalent; calibrate (Sec 3.1.2)	Determine correction factor, or reject if difference more than $\pm 2.5$ mm (0.1 in.) Hg
Orifice meter	$\Delta H_0$ of $46.74 \pm 6.35$ mm ( $1.84 \pm 0.25$ in.) H <sub>2</sub> O at 20°C (68°F); optional	Upon receipt, visually check for damage; calibrate against wet test meter	Repair or return to supplier
Dry gas meter	Capable of measuring volume within $\pm 2\%$ at a flow rate of 0.02 m <sup>3</sup> /min (0.7 ft <sup>3</sup> /min)	Check for damage upon receipt and calibrate (Sec 3.9.2) against wet test meter	Reject if damaged, behaves erratically, or cannot be properly adjusted

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TABLE 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Thermometers	$\pm 1^{\circ}\text{C}$ ( $2^{\circ}\text{F}$ ) of true value in the range of $0^{\circ}$ to $25^{\circ}\text{C}$ ( $32^{\circ}$ to $77^{\circ}\text{F}$ ) for impinger thermometer and $\pm 3^{\circ}\text{C}$ ( $5.4^{\circ}\text{F}$ ) of true value in the range of $0^{\circ}\text{C}$ to $90^{\circ}\text{C}$ ( $32^{\circ}$ to $194^{\circ}\text{F}$ ) for dry gas meter thermometers	Check upon receipt for dents or bent stem, and calibrate (Sec 3.9.2) against mercury-in-glass thermometer	Reject if unable to calibrate
<u>Sample Recovery</u>			
Probe liner and probe nozzle brushes	Nylon bristles with stainless steel handles; properly sized and shaped	Visually check for damage upon receipt	Replace or return to supplier
Wash bottles	Polyethylene or glass, 500 ml	Visually check for damage upon receipt	As above
Storage container	High-density polyethylene, 1000 ml	Visually check for damage upon receipt; be sure caps make proper seals	As above
Graduated cylinder	Glass, Class A, 250 ml	Upon receipt, check for stock number, cracks, breaks, and manufacturer flaws	As above
Funnel	Glass, diameter 100 mm; stem length 100 mm	Visually check for damage upon receipt	As above
Rubber policeman	Properly sized	Visually check for damage upon receipt	As above

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TABLE 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Pipettes, volumetric flask, beaker, flask adapter, condenser, connection tube, Erlenmeyer flask	Glass, Class A	Upon receipt, check for stock number, cracks, breaks and manufacturer flaws	Replace or return to supplier
<u>Distillation Apparatus</u> Bunsen burner	Capable of distilling 220 ml in <15 min	Visually check upon receipt; check heating capacity, check for damage	Replace or return to manufacturer
Crucible	Nickel material; 75-100 ml	Check upon receipt for cracks or flaws	Replace or return to manufacturer
<u>Analytical Equipment</u> Hot plate	Heating capacity of 500°C (932°F)	Check upon receipt and before each use for damage; check heating capacity against mercury-in-glass thermometer	Replace or return to manufacturer
Electric muffle furnace	Heating capacity of 600°C (1112°F)	Check upon receipt and before each use for damage; check heating capacity upon receipt against mercury-in-glass thermometer	Replace or return to manufacturer

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TABLE 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Balance	Capacity of 300 g $\pm$ 0.5g	Check for damage and against series of standard weights upon receipt and before each use	Replace or return to manufacturer
Water bath	Capable of maintaining constant room temperature	Check with mercury-in-glass thermometer	Repair
Spectrophotometer	Capable of measuring absorbance at 570 nm and providing $\geq$ 1 cm light path	Check upon receipt and before each use for damage; see manufacturers' operating manual	Replace or return to manufacturer
<u>Reagents</u>			
Filters	Whatman No. 541 or equivalent	Visually check for damage upon receipt	Replace or return to supplier
Silica gel	Indicating Type 6-16 mesh	Upon receipt check label for grade or certification	Replace or return to manufacturer
Distilled water	Must conform to ASTM-D1193-74, Type 3	Check each lot	Replace or return to manufacturer
Crushed ice		Check frozen condition	
Stopcock grease	Acetone insoluble, and heat stable silicon grease	Upon receipt, check label for grade or certification	As above

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TABLE 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
<u>Reagents</u>			
Calcium oxide powder	Reagent grade or certified ACS	As above	As above
Phenolphthalein	0.1% in 1:1 ethanol-water mixture; reagent grade or certified ACS	As above	As above
Sodium hydroxide	NaOH pellet, 5M NaOH reagent grade or certified ACS	As above	As above
Sulfuric acid	Concentrated, reagent grade or certified ACS; 25% (v/v) reagent grade or ACS	As above	As above
Silver sulfate powder	Reagent grade or certified ACS	Upon receipt, check label for grade or certification	Replace or return to manufacturer
Hydrochloric acid	Concentrated, reagent grade or certified ACS	As above	As above
Sodium fluoride solution	0.01 mg F/ml, reagent grade or certified ACS	As above	As above
SPADNS solution	Dissolve 0.960 + 0.010 g of SPADNS reagent, 4,5-dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalenedisulfonic acid trisodium salt, reagent grade or certified ACS	As above	As above

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TABLE 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Reference solution	Add 10 ml SPADNS solution to 100 ml distilled water; dilute 7 ml conc HCl to 10 ml with distilled water; add to diluted SPADNS solution; reagent grade or certified ACS	As above	As above
SPADNS mixed reagent	Dissolve 0.135 + 0.005 g $[ZrOCl_2 \cdot 8H_2O]$ in 25 ml distilled water; add 350 ml conc HCl; dilute to 500 ml with distilled water; mix equal volumes of SPADNS solution and the above zirconyl acid reagent; reagent grade or certified ACS	As above	As above

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## 2.0 CALIBRATION OF APPARATUS

Calibration of apparatus is one of the most important functions in maintaining data quality. The detailed calibration procedures included in this section are designed for the equipment specified in Method 13A and described in the previous section (Section 3.9.2). A laboratory log book of all calibrations must be maintained. Table 2.1 at the end of this section summarizes the quality assurance activities for calibration. This section is the same as Method 13B (Section 3.9.2) with the exception of the calibration of the spectrophotometer as detailed below.

### 2.1 Spectrophotometer

An initial calibration curve should be made to check the operation of the spectrophotometer. Conduct the check as follows:

1. Prepare the blank standard by adding 10 ml of SPADNS mixed reagent to 50 ml of distilled water.
2. Pipette 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, and 14.0 ml of the standard fluoride working solution into separate 100-ml volumetric flasks. Dilute to the mark with distilled water.
3. Pipette 50 ml of each dilution into 100-ml beakers; then pipette 10.0 ml of SPADNS mixed reagent into each and mix. These standards will contain 0, 10, 20, 30, 40, 50, 60, and 70  $\mu\text{g F}$ , respectively.
4. Place the reference standards and the reference solution in a constant temperature bath for 30 min before reading the absorbances with the spectrophotometer. The bath must be within  $\pm 3^\circ\text{C}$  ( $5.4^\circ\text{F}$ ) of ambient temperature.
5. Set the spectrophotometer at 570 nm and use the reference solution to set at zero absorbance.
6. Determine the absorbance of the standards. Record data on the standard data form as shown in Figure 2.1.

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Spectrophotometer number 5-100 Analyst B. E. B.

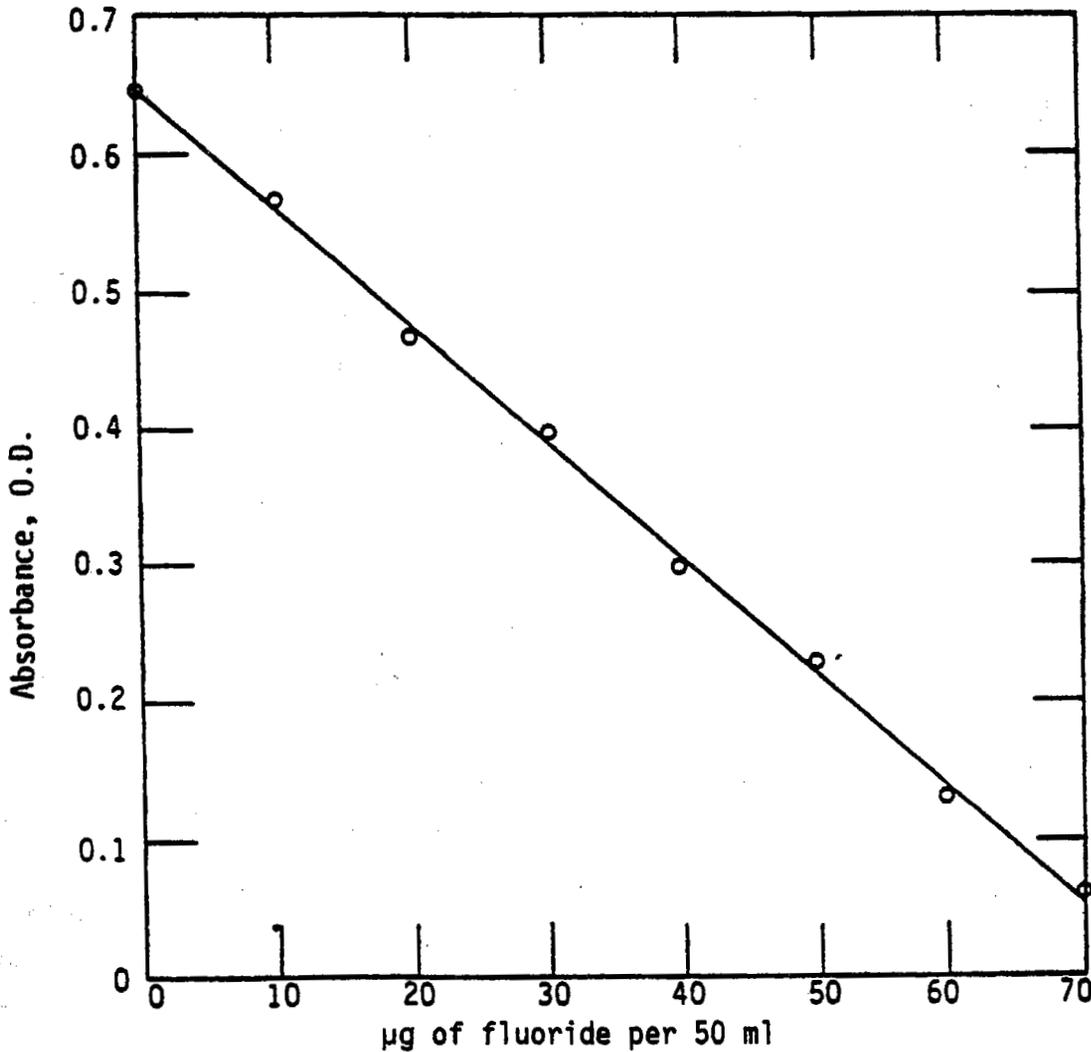
Calibration date 5/15/80 SPADNS mix date 4/15/80

Ambient temperature 22 °C Bath temperature 21 °C

Spectrophotometer set at 570 nm  yes  no

Reference solution used to set zero absorbance  yes  no

Absorbance readings: 0.567 10 µg 0.470 20 µg 0.395 30 µg  
0.300 40 µg 0.230 50 µg 0.135 60 µg 0.060 70 µg 0.640 blank



Signature of Analyst Barbara E. Blagun

Signature of Reviewer William J. Mitchell

Figure 2.1. Fluoride calibration curve.

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7. The wavelength calibration should be checked initially and yearly thereafter. This can be done using a didymium filter. See suppliers instructions for its use. The wavelength should agree within  $\pm 10$  nm. If not, contact the manufacturer's representative for adjustment.

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TABLE 2.1. ACTIVITY MATRIX FOR CALIBRATION OF EQUIPMENT

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Wet test meter	Capacity of $\geq 3.4 \text{ m}^3/\text{h}$ ( $120 \text{ ft}^3/\text{h}$ ); accuracy within $\pm 1.0\%$	Calibrate initially and yearly by liquid displacement	Adjust to meet specifications, or return to manufacturer
Dry gas meter	$Y_i = Y \pm 0.02 Y$ at flow rate of $0.02 - 0.03 \text{ m}^3/\text{min}$ ( $0.7 - 1.1 \text{ ft}^3/\text{min}$ )	Calibrate with wet test meter initially to agree within $Y \pm 0.02 Y$ and when post-test check is not within $Y \pm 0.05 Y$	Repair or replace, and then recalibrate
Thermometers	Impinger thermometer $+1^\circ\text{C}$ ( $2^\circ\text{F}$ ); dry gas meter thermometer $+3^\circ\text{C}$ ( $5.4^\circ\text{F}$ ) over applicable range	Calibrate each initially against a mercury-in-glass thermometer; before field trip compare each with mercury-in-glass thermometer	Adjust, determine a constant correction factor, or reject
Barometer	$\pm 2.5 \text{ mm}$ ( $0.1 \text{ in.}$ ) Hg of mercury-in-glass barometer	Calibrate initially vs mercury-in-glass barometer; check before and after each field test	Adjust to agree with certified barometer
Probe nozzle	Average three ID measurements of nozzle; difference between high and low $< 0.1 \text{ mm}$ ( $0.004 \text{ in.}$ )	Use a micrometer to measure to nearest $0.025 \text{ mm}$ ( $0.001 \text{ in.}$ )	Recalibrate, reshape, and sharpen when nozzle becomes nicked, dented, or corroded

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TABLE 2.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Stack temperature sensor	$\pm 1.5\%$ of average absolute stack temperature, °R	Calibrate initially; check after each field test	Adjust or reject
Trip balance	Standard Class-S weights within $\pm 0.5$ g of stated value	Verify calibration when first purchased, any time moved or subject to rough handling, and during routine operations when not within $\pm 0.5$ g	Have the manufacturer recalibrate or adjust
Pitot tube	Type S; initially calibrated according to Section 3.1, Meth 2; tube tips undamaged	Visually check before each field test	Repair or replace
Spectrophotometer	Standard solutions agree within $\pm 2\%$ of calibration curve	Check standard solutions for each test; new calibration curve made when standards do not agree within $\pm 2\%$ of existing curve or when SPADNS mixed reagent is newly made	Make new reagents and calibration curve
Wavelength	$\pm 10$ nm	Yearly	Contact manufacturer's representative for adjustment

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### 3.0 PRESAMPLING OPERATIONS

The quality assurance activities for presampling operations are summarized in Table 3.1. See Section 3.0, of this Handbook for details on preliminary site visits. This section is the same as Method 13B (Section 3.9.3).

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TABLE 3.1. ACTIVITY MATRIX FOR PRESAMPLING OPERATIONS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Sampling train probe and nozzle	1. Probe, nozzle, and liner free of contaminants; constructed of borosilicate glass, quartz, or equivalent; metal liner must be approved by administrator  2. Probe leak free at 380 mm (15 in.) Hg  3. Probe heating system prevents moisture condensation	1. Clean internally by brushing with tap water, deionized distilled water, and acetone; air dry before test  2. Visually check before test  3. Check heating system initially and when moisture cannot be prevented during testing (Sec 3.4.1)	1. Repeat cleaning and assembly procedures  2. Replace  3. Repair or replace
Impingers, filter holders, and glass connectors	Clean; free of breaks cracks, leaks, etc.	Clean with detergent, tap water, and deionized distilled water	Repair or discard
Pump	Sampling rate of 0.02-0.03 m <sup>3</sup> /min (0.7 to 1.1 ft <sup>3</sup> /min) up to 380 mm (15 in.) Hg at pump inlet	Service every 3 mo or upon erratic behavior; check oiler jars every 10 tests	Repair or return to manufacturer
Dry gas meter	Clean; readings $\pm 2\%$ of of average calibration factor	Calibrate according to Sec 3.4.2; check for excess oil	As above

(continued)

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TABLE 3.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
<u>Reagents and Equipment</u>			
Filters	No irregularities, flaws, pinhole leaks; $\leq 0.015$ mgF/cm <sup>2</sup>	Visually check before testing; check each lot of filters for F content	Replace
Water	Deionized distilled conforming to ASTM-D1193-74, Type 3	Run blank evaporations before field use to eliminate high solids (only required if impinger contents to be analyzed)	Redistill or replace
Stopcock grease	Acetone insoluble; heat stable	Check label upon receipt	Replace
<u>Packing Equipment for Shipment</u>			
Probe	Rigid container lined with polyethylene foam	Prior to each shipment	Repack
Impingers, connectors, and assorted glassware	Rigid container lined with polyethylene foam	As above	As above
Pump	Sturdy case lined with polyethylene foam material if not part of meter box	As above	As above
Meter box	Meter box case and/or additional material to protect train components; pack spare meter box	As above	As above
Wash bottles and storage containers	Rigid foam-lined container	As above	As above

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#### 4.0 ON-SITE MEASUREMENTS

The on-site activities include transporting equipment to the test site, unpacking and assembling the equipment, making duct measurements, performing the velocity traverse, determining molecular weights and stack gas moisture contents, sampling for particulates, and recording the data. Table 4.1 summarizes the quality assurance activities for on-site activities. Blank data forms are in Sections 3.9.12 and 3.10.12 for the convenience of the Handbook user. This section is the same as Method 13B (Section 3.9.4).

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TABLE 4.1. ACTIVITY MATRIX FOR ON-SITE MEASUREMENT CHECKS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
<u>Sampling</u> Filter	Centered in holder; no breaks, damage, or contamination during loading	Use tweezers or surgical gloves to load	Discard filter, and reload
Condenser (addition of reagents)	100 ml of distilled water in first two impingers; 200-300 g of silica gel in fourth impinger	Use graduated cylinder to add water, or weigh each impinger and its contents to the nearest 0.5 g	Reassemble system
Assembling sampling train	1. Specifications in Fig 1.1  2. Leak rate <4% of sampling volume or 0.00057 m <sup>3</sup> /min (0.02 ft <sup>3</sup> /min), whichever is less	1. Check specifications before each sampling run  2. Leak check before sampling by plugging nozzle or inlet to first impinger and pulling a vacuum of 380 mm (15 in.) Hg	1. Reassemble  2. Correct the leak
Sampling (isokinetically)	1. Within ±10% of isokinetic condition and at a rate of less than 1.0 ft <sup>3</sup> /min  2. Standard checked for minimum sampling time and volume; sampling time ≥2 min point	1. Calculate for each sample run  2. Make a quick calculation before test, and exact calculation after	1. Repeat the test run  2. As above

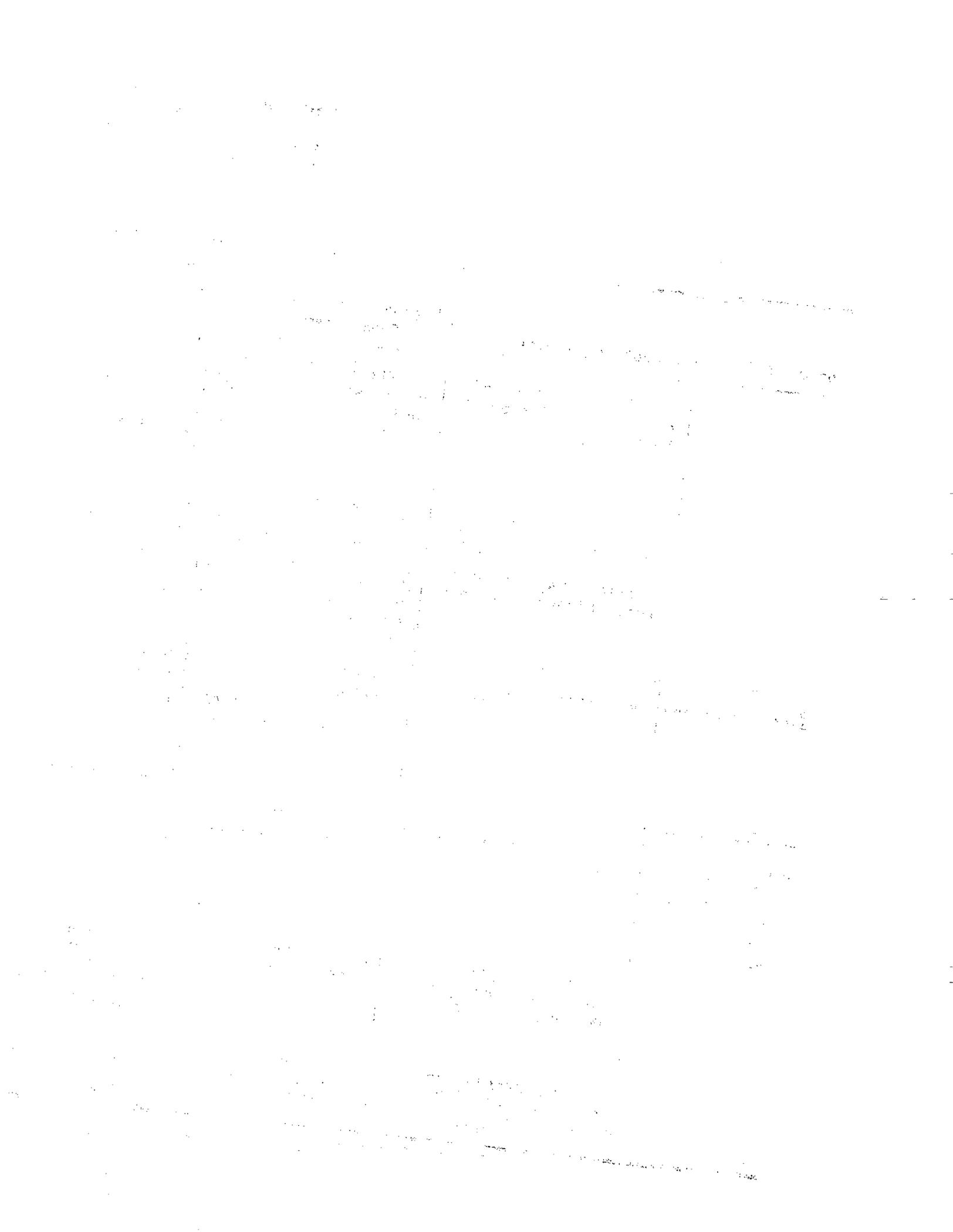
(continued)

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TABLE 4.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
	<p>3. Minimum number of points specified by Method 1</p> <p>4. Leakage rate &lt;math&gt;&lt;0.00057\text{ m}^3/\text{min}&lt;/math&gt; (0.02 <math>\text{ft}^3/\text{min}</math>) or 4% of the average sampling volume, whichever is less</p>	<p>3. Check before the first test run by measuring duct and using Method 1</p> <p>4. Leak check after each test run or before equipment replacement during test at the maximum vacuum during the test (mandatory)</p>	<p>3. Repeat the procedure to comply with specifications of Method 1</p> <p>4. Correct the sample volume or repeat the sampling</p>
Sample recovery	Noncontaminated sample	Transfer sample to labeled polyethylene container after each test run; mark level of solution in the container	Repeat the sampling
Sample logistics, data collection, and packing of equipment	<p>1. All data recorded correctly</p> <p>2. All equipment examined for damage and labeled for shipment</p> <p>3. All sample containers and blanks properly labeled and packaged</p>	<p>1. After each test and before packing</p> <p>2. As above</p> <p>3. Visually check after each sampling</p>	<p>1. Complete the data</p> <p>2. Repeat the sampling if damage occurred during the test</p> <p>3. Correct when possible</p>

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## 5.0 POSTSAMPLING OPERATIONS

The postsampling operations include checks on the apparatus used in the field during sampling to measure volumes, temperatures, and pressures, and analyses of the samples collected in the field and forwarded to the base laboratory. Table 5.1 at the end of this section summarizes the quality assurance activities for the postsampling operations.

The postsampling checks on the sample collection train are the same as for Method 13B (Section 3.9.5). The analytical method is different with exception of some of the sample preparation. The entire analytical procedure is detailed below.

### 5.1 Base Laboratory Analysis

All fluoride samples should be checked by the analyst upon receipt in the base laboratory for identification and sample integrity. Any losses should be noted on the analytical data form (Figure 5.1). Either void the sample or correct the data using a technique approved by the administrator. If a noticeable amount of sample has been lost by leakage, the following procedure may be used to correct the volume.

1. Mark the new level of the sample container.
2. Treat the sample as described in Subsection 5.2.3 and note the final dilution volume ( $V_{\text{soln}}$ ).
3. Add water up to the initial mark on the container, transfer the water to a graduated cylinder and record the initial sample volume ( $V_{\text{solni}}$ ) in milliliters.
4. Add water to the new mark on the container. Transfer the water to a graduated cylinder, and record the final volume ( $V_{\text{solnf}}$ ) in milliliters.
5. Correct the volume by using the following equation:

$$V_{\text{soln}} = V_{\text{soln}} \frac{V_{\text{solni}}}{V_{\text{solnf}}}$$

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Plant ACME FERTILIZER Location HAZARD  
 Date 3/20/80 Analyst WSM SPADNS mix date 3/15/80  
 Samples identifiable  yes  no All liquid levels at mark  yes  no  
 Ambient temperature 22°C Temperature of samples 21°C Temperature of standards 21°C  
 Sample was concentrated  yes  no Solids fused and added to liquid  yes  no

Sample number	Sample identification	Total volume of sample before distill. (V <sub>t</sub> ), ml	Aliquot of sample for distill. (A <sub>t</sub> ), ml	mg of chloride per liter of sample	mg of silver chloride added	Sample volume from still (V <sub>d</sub> ), ml	Aliquot of sample for analysis (A <sub>d</sub> ), ml	Absorb. of sample at 570 nm OD	µg F in sample <sup>a</sup>	Total weight of F <sup>b</sup> (F <sub>t</sub> ), mg
AFFB	BLANK FILTER	1000	200	0	—	250	50	0.595	5.9	0.148
AFC	distilled CONTROL	1000	200	0	—	250	10	0.480	19.7	2.46
AFDB	distillation BLANK	—	200	0	—	250	50	0.640	—	—
AF-1	AT-485	1000	50	1000	250	250	2	0.285	42.7	107
AFC	undistilled CONTROL	—	—	—	—	250	100	0.475	20.0	—

<sup>b</sup>Total weight of fluoride in sample (F<sub>t</sub>)

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

<sup>a</sup>Control samples results must be between 19.6 µg and 20.4 µg for undistilled sample on 18.0 and 22.0 µg for distilled sample

Remarks: \_\_\_\_\_

Signature of analyst William J. Mitchell

Signature of reviewer Thomas J. Wagner

Figure 5.1. Method 13A analytical data form.

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where

$V_{\text{soln}}$  = sample volume to be used in the calculations, ml;

$V_{\text{soln}}$  = total volume of solution in which fluoride is contained, ml;

$V_{\text{solni}}$  = initial volume added to the container in the field, ml;

$V_{\text{solnf}}$  = final volume removed from the container in the base laboratory, ml.

6. Both the corrected and uncorrected values should be submitted in the test report to the agency.

If the spent silica was not weighed in the field, weigh the silica gel and report the weight to the nearest 0.5 g on the sample integrity and recovery form.

In the SPADNS colorimetric method, the volume measurements of the sample and the reagents are very important to the accuracy of the determination. The temperatures of the samples and standards not only must be within 2°C (4°F), but also must be constant throughout color development. Calibration curves may be prepared for different temperatures. The analytical balance must be checked with Class-S standard weights before each series of weighings, and the data on the weighings must be recorded on a calibration form (Figure 5.2).

The colorimetric method is based on the reaction between fluoride and a zirconium-dye; more specifically, fluoride reacts with the dye lake, and dissociates a portion of the dye into a colorless complex anion ( $\text{ZrF}_6^-$ ) and the dye. As the amount of fluoride increases, the color either becomes progressively lighter or changes in hue. The reaction rate between the fluoride and zirconium ions is accelerated by the acidity of the reagent; by increasing the proportion of acid, the reaction can be practically instantaneous.

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Balance name CHRISTIAN BECKER TORBAL Number EA-1, 43758  
Classification of standard weights "5"

Date	0.5000 g	1.0000 g	10.0000 g	50.0000 g	100.0000 g	Analyst
5/7/80	0.5001	0.9998	10.000	50.0001	100.0002	DLB

Figure 5.2. Analytical balance calibration form.

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Colorimetric methods are subject to errors from interfering ions; thus it will be necessary to distill the sample before making the fluoride determination.

Procedures are detailed herein for preparing reagents, blanks, control samples, distillation aliquots, reference and working standards, and measuring the fluoride in samples.

5.2.1 Reagents - The following reagents are needed for the analyses of fluoride samples.

1. Calcium oxide (CaO) - ACS reagent grade powder or ACS certified grade containing  $\leq 0.005\%$  fluoride.
2. Phenolphthalein indicator - 0.1% in 1:1 ethanol-water mixture (v/v).
3. Sodium hydroxide (NaOH) - Pellets, ACS reagent grade or the equivalent.
4. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) - Concentrated, ACS reagent grade or the equivalent.
5. Filters - Whatman No. 541 or the equivalent.
6. Water - Deionized distilled to conform to ASTM specification D1193-74, Type 3. The analyst may omit the KMnO<sub>4</sub> test for oxidizable organic matter if high concentrations of organic matter are not expected.
7. Silver sulfate (Ag<sub>2</sub>SO<sub>4</sub>) - ACS reagent grade or the equivalent.
8. Hydrochloric acid (HCl) - Concentrated, ACS reagent grade or the equivalent.
9. Sodium fluoride (NaF) standard - Dissolve 0.2210 g  $\pm$  0.0005 g ACS reagent grade NaF, which has been dried for a minimum of 2 h at 110°C (230°F) and stored in a desiccator, in deionized distilled water, and dilute to 1-ℓ with deionized distilled water; this solution contains 0.1 mgF/ml.
10. Sodium fluoride (NaF) working standard - Pipette 100 ml of the NaF standard into a 1-ℓ volumetric flask and dilute to mark with deionized distilled water; this solution contains 0.01 mg F/ml.

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11. SPADNS solution - Dissolve 0.960  $\pm$ 0.010 g of SPADNS reagent 4,5 dihydroxy-3-(parasulfophenylazo)-2,7-naphthalenedisulfonic acid trisodium salt (also called sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonate) in distilled water, and dilute to 500 ml; this solution is stable for about 1 mo if stored in a well-sealed bottle and protected from direct sunlight.

12. Reference solution - Add 10 ml of SPADNS solution to 100 ml of distilled water; dilute 7 ml of concentrated HCl to 10 ml with distilled water and add it to the diluted SPADNS solution. Prepare the reference solution fresh daily and use it to set the spectrophotometer zero point.

13. SPADNS mixed reagent - Dissolve 0.135  $\pm$ 0.005 g of zirconyl chloride octahydrate ( $ZrOCl_2 \cdot 8H_2O$ ) in 25 ml of distilled water; add 350 ml of concentrated HCl; and finally dilute to 500 ml with distilled water to get the zirconyl acid reagent. Then, mix equal volumes of the SPADNS solution and zirconyl acid reagent to produce the SPADNS mixed reagent, which is stable for at least 2 mo.

5.2.2 Blanks - The three blanks needed for the analysis are a filter blank to ensure that the quality of the filter is acceptable, a distillation blank to protect against cross contamination, and a sample blank to analyze with the samples to verify the purity of the reagents used in sampling and analysis.

1. Filter blanks - Determine the fluoride content of the sampling filters upon receipt of each new lot of and at least once for each test series. Initially, select three filters randomly from each lot.

- a. Add each filter to 500 ml of distilled water.
- b. Treat the filters exactly like a sample (Subsection 5.2.3).
- c. Use a 200-ml aliquot for distillation. The fluoride concentration of the filter blank must be  $<0.015$  mg F/cm<sup>2</sup>; if not, reject this batch and obtain a new supply of filters.

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2. Distillation blank - Check the condition of the acid in the distillation flask (Subsection 5.2.5) for cross-contamination after every 10th sample by adding 220 ml of distilled water to the still pot and then proceed with the analysis. If detectable amounts of fluoride ( $>0.1 \mu\text{g F/ml}$ ) are found in the blank, replace the acid in the distillation flask.

3. Sample blank - Prepare the sample blanks in the field at the same time and with the same reagents used for sample recovery.

a. Add an unused filter from the same batch used in sampling to a volume of distilled water equal to the average amount used to recover the samples.

b. Treat the sample blank in the same manner as the samples are treated (Section 5.2.3). Analyze the sample blanks with the samples.

5.2.3 Sample Preparation - Use the following procedure to prepare samples for distillation. Distillation is not required if it can be shown to the satisfaction of the Administrator that fluoride results are unaffected by the alternate analytical procedure (e.g., ash and fusion of particulate matter with subsequent ion selective electrode analysis, or direct electrode analysis of gases trapped in impingers).

1. Filter the contents of the sample container (including the sample filter) through a Whatman No. 541 filter or the equivalent into a 1500-ml beaker; if the filtrate volume is  $\geq 900$  ml, add NaOH to make the filtrate basic to phenolphthalein, and then evaporate to  $< 900$  ml.

2. Place the Whatman No. 541 filter containing the insolubles (including the sample filter) in a nickel crucible, add a few milliliters of water; and macerate the filter with a glass rod.

3. Add 100 mg or sufficient quantity of CaO to the nickel crucible to make the slurry basic; mix thoroughly; and add a couple drops of phenolphthalein indicator, which turns pink in a basic medium. Note: If the slurry does not remain basic (pink)

during the evaporation of the water, fluoride will be lost; if the slurry becomes colorless, it is acidic so add CaO until the pink returns.

4. Place the crucible in a hood area either under infrared lamps or on a hot plate at low heat (approximately 50-60°C) (122-140°F), and evaporate the water completely; then place the crucible on a hot plate under a hood and slowly increase the temperature for several hours or until the filter is charred.

5. Place the crucible in a cold muffle furnace and gradually (to prevent smoking) increase the temperature to 600°C (1112°F); maintain the temperature until the crucible contents are reduced to an ash containing no organic materials; and remove the crucible from the furnace to cool.

6. Add approximately 4 g of crushed NaOH pellets to the crucible, and mix; return the crucible to the furnace, and fuse the sample for 10 min at 600°C (1112°F); and then remove the sample from the furnace, and cool it to ambient temperature.

7. Use several rinsings of warm distilled water to transfer the contents of the crucible to the beaker containing the filtrate (step 1) and finally, rinse the crucible with two 20-ml portions of 25% (v/v) H<sub>2</sub>SO<sub>4</sub>, and carefully add the rinses to the beaker.

8. Mix well, and transfer the beaker contents to a 1-l volumetric flask. Record the volume as V<sub>t</sub> on the data form (Figure 5.1). Dilute to volume with distilled water, and mix thoroughly; and allow any undissolved solids to settle.

5.2.4 Acid-water Ratio - The acid-water ratio in the distillation flask should be adjusted by following this procedure. Use a protective shield when carrying out the procedure.

1. Place 400 ml of distilled water in the 1-l distilling flask, and add 200 ml of concentrated H<sub>2</sub>SO<sub>4</sub>. Slowly add the H<sub>2</sub>SO<sub>4</sub>, while constantly swirling the flask.

2. Add soft glass beads and several small pieces of broken glass tubing, and assemble the apparatus.

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3. Heat the flask until it reaches a temperature of 175°C (347°F), and discard the distillate, and hold the flask for fluoride separation by distillation.

5.2.5 Fluoride Separation (Distillation) - Fluoride can be separated from other constituents in the aqueous sample by distilling fluosilicic (or hydrofluoric) acid from a solution of the sample in an acid with a higher boiling point. Samples with low concentrations of fluoride (e.g., samples from an outlet of a scrubber) should be distilled first to eliminate contamination by carryover of fluoride from the previous sample. If fluoride distillation in the milligram range is to be followed by distillation in the fractional milligram range, add 200 ml of deionized distilled water and redistill similar to the acid adjustment procedure, Subsection 5.2.4, to remove residual fluoride from the distillation system.

1. Cool the contents of the distillation flask (acid-water adjusted) to <80°C (176°F).

2. Pipette an aliquot of sample containing <10.0 mg F into the distillation flask, and add distilled water to make 220 ml. The aliquot size ( $A_t$ ) should be entered on the data form (Figure 5.1). Note: For an estimate of the aliquot size that contains <10 mg F, see Subsection 5.2.7.

3. Add 5 mg silver sulfate ( $Ag_2SO_4$ )/mg chloride to the distillation flask; if the sample contains chloride, use procedures described in Subsection 5.2.8 to determine the chloride concentration.

4. Place a 250-ml volumetric flask at the condenser exit; heat the distillation flask as rapidly as possible with a burner, while moving the flame up and down the sides of the flask to prevent bumping; conduct the distillation as rapidly as possible (<15 min). Slow distillations have been found to give low fluoride recoveries. Collect all distillate up to 175°C (347°F). Caution: Heating >175°C (347°F) will cause  $H_2SO_4$  to distill over. Note: The  $H_2SO_4$  in the distillation flask can be

reused until carryover of interferent or until poor fluoride recovery is shown by the distillation blanks or the control samples.

5. Before distilling the field samples and after every tenth distillation of any sample, distill a control sample to check the analytical procedures and interferences (Subsection 5.2.6).

5.2.6 Control Samples - A control sample should be used to verify the calibration curve and the distillation recovery before and during the analysis of the field samples. Use the following procedures. Data should be recorded on the control sample analytical data form (Figure 5.3).

1. 125 mg F/l NaF control sample stock solution - Add 0.276 g of reagent grade anhydrous NaF to a 1-l volumetric flask; add enough distilled water to dissolve; and dilute to 1-l with distilled water.

2. 2.5 mg F/l NaF distillation solution - Pipette 20 ml of the 125 mg F/l stock solution into a 1-l volumetric flask, and dilute to the mark with distilled water to get the 2.5 mg F/l NaF distillation solution. Distill 200 ml of this solution according to Subsection 5.2.5.

3. Pipette 4.0 ml of the control sample stock solution into a 250-ml volumetric flask and dilute to the mark with distilled water. Analyze this solution colorimetrically in the same manner as the samples are analyzed (Subsection 5.2.10).

5.2.7 Distillation Aliquot - The sample volume for distillation should contain <10 mg F. Use the following procedure to estimate the aliquot size.

1. Pipette a 1.0-ml aliquot of sample into a polyethylene beaker.

2. Add 50 ml of distilled water.

3. Analyze by the procedure described in 5.2.10.

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Plant Acme Fertilizer Date of analysis 5/13/80  
 Analyst W. Mitchell Ambient temperature 22°C  
 Date of calibration curve 5/13/80 Temp. of calibration curve 21°C

	Concentration of control sample	
	Distilled	Undistilled
Control sample temperature	<u>21°C</u>	<u>21°C</u>
Absorbance of control sample	<u>0.480</u>	<u>0.475</u>
Amount of F in control sample from calibration curve	<u>19.7</u>	<u>20.1</u>
Percent error between measured and calculated concentration	<u>-1.5%</u>	<u>+0.5%</u>

Were acceptable results obtained on control samples (less than 2% undistilled and <10% distilled) yes

Signature of analyst W. J. Mitchell  
 Signature of reviewer T. Logan

Figure 5.3. Control sample analytical data form.

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4. Determine the  $\mu\text{g}$  of F in the nondistilled sample from the calibration curve, and determine the maximum size of the aliquot for distillation by substituting the amount of F ( $\mu\text{g}$ ) in the nondistilled sample in the following equation:

$$\text{aliquot for distillation (ml)} = \frac{(\text{size aliquot used})(10 \text{ mg})(1000 \mu\text{g})}{\mu\text{g F determined} (1 \text{ mg})}$$
$$= \frac{10,000}{\mu\text{g F determined}} \quad \text{when a 1.0 ml nondistilled aliquot is used.}$$

If the amount of F in the nondistilled sample is  $>70 \mu\text{g}$ , decrease the aliquot taken for this estimation and change the aliquot value input into the above equation. The aliquot size is only an approximation since the interfering ions have not been removed by distillation. If the estimate is  $>220 \text{ ml}$ , use  $220 \text{ ml}$ ; if it is  $<220 \text{ ml}$ , add distilled water to make the total volume added to the distillation flask  $220 \text{ ml}$ ; if required, dilute the sample so that a minimum  $1\text{-ml}$  sample aliquot is added to the distillation flask.

**5.2.8 Determination of Chloride** - A chloride determination is necessary because of major interferences with Method 13A when a relatively high concentration of chloride ions ( $\text{Cl}^-$ ) are present in the collected sample. Chloride concentration depends on the plant's material balance.

The mercuric nitrate procedure is introduced here for estimating how much  $\text{Ag}_2\text{SO}_4$  is required for removal of chloride interference. This procedure is easy to perform and has good precision and accuracy. Reagents needed for this procedure follow:

1. Standard sodium chloride solution ( $\text{NaCl}$ ), 0.141 N

Dissolve  $8.241 \text{ g}$   $\text{NaCl}$  (dried at  $140^\circ\text{C}$  ( $285^\circ\text{F}$ ) for 1-h) in chloride-free water, and dilute to 1-l; contains  $5 \text{ mg Cl/ml}$ .

2. Nitric acid ( $\text{HNO}_3$ ), 0.1 N - Dilute  $5 \text{ ml}$  of concentrated  $\text{HNO}_3$  to  $800 \text{ ml}$  with distilled water.

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3. Mixed indicator reagent - Dissolve 5 g of diphenylcarbazone powder and 0.5 g of bromphenol blue powder in 750 ml of 95% ethyl or isopropyl alcohol, and dilute to 1 l with the same alcohol.

4. Standard mercuric nitrate (Hg(NO<sub>3</sub>)<sub>2</sub>) titrant, 0.141 N - Dissolve 25 g of Hg(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O in 900 ml of distilled water containing 5 ml of concentrated HNO<sub>3</sub> (nitric acid). Dilute to 1 l. The chloride equivalent of the titrant is 5.00 mg/ml.

The sample analysis for chloride determination is as follows:

1. Pipette 25 ml of a sample into a 150-ml beaker.
2. Add approximately 0.5 ml of indicator, and mix well; the color should be purple.
3. Add 0.1N HNO<sub>3</sub> drop-by-drop until the color just turns yellow.
4. Titrate with 0.141N Hg(NO<sub>3</sub>)<sub>2</sub> to the first appearance of dark purple and record the number of milliliters used.
5. Check the blank by titrating 100 ml of distilled water containing 10 mg NaHCO<sub>3</sub>.
6. Calculate the concentration of chloride with the following equation.

$$\text{mg/l of Cl} = \frac{(A - B) \times N \times 35,450}{\text{ml sample}}$$

where

A = titrant used for sample, ml,

B = titrant used for blank, ml, and

N = normality of Hg (NO<sub>3</sub>)<sub>2</sub>, meg/ml.

Standardization of Hg (NO<sub>3</sub>)<sub>2</sub> for Chloride -

1. Titrate 15 ml of the standard NaCl with Hg (NO<sub>3</sub>)<sub>2</sub> reagent, using the method as previously described. Make at least three replicates and obtain the average normality of Hg (NO<sub>3</sub>)<sub>2</sub>.

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2. Calculate the normality of Hg (NO<sub>3</sub>)<sub>2</sub>.

$$\text{ml NaCl} \times N \text{ NaCl} = \text{ml Hg(NO}_3)_2 \times N \text{ Hg (NO}_3)_2;$$

therefore,

$$N \text{ Hg(NO}_3)_2 = \frac{\text{ml NaCl} \times N \text{ NaCl}}{\text{ml Hg(NO}_3)_2}$$

3. Calculate and add the required amount of silver sulfate for each sample:

$$\text{mg Ag}_2\text{SO}_4 = \frac{\text{mg/l Cl}^- \times \text{ml aliquot (distilled)} \times 5}{1000 \text{ ml}}$$

5.2.9 Calibration Standards - Use the sodium fluoride working standard in Subsection 5.2.1 (0.01 mg/ml) in the following procedure. These standards cover the range of 0.2 - 1.4 µg F/ml.

1. Pipette 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, and 14.0 ml volumes of 0.01 mg F/ml NaF solution into seven separate 100-ml volumetric flasks, and dilute to the mark with distilled water.

2. Pipette 50 ml of each of the each solutions into separate 100-ml polyethylene beakers, add 10 ml of SPADNS mixed reagent to each, and mix well.

3. Prepare the blank standard by pipetting 10 ml of SPADNS mixed reagent to 50 ml of distilled water. These standards will contain 0, 10, 20, 30, 40, 50, 60, and 70 µg of fluoride.

4. After mixing, place the calibration standards and reference solution Subsection 5.2.1 in a constant temperature bath for 30 minutes before reading the absorbance within ±3°C (5.4°F) of the spectrophotometer. Note: Adjust all samples to this same temperature before analysis. Since a 3°C difference between samples and standards will produce an error of approximately 0.005 mg F/l, take care to see that samples and standards are at nearly identical temperatures when absorbances are measured.

5.2.10 Determination of Fluoride Concentration - In Method 13A, use the following steps to determine the amount of fluoride.

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1. Dilute the distillate to the mark in the 250-ml volumetric flask with distilled water, and mix thoroughly. Enter this volume ( $V_d$ ) on the analytical data form (Figure 5.1).

2. Pipette a suitable aliquot (maximum of 50 ml) from the distillate (containing 10 to 40  $\mu\text{g}$  F) (for the control samples, a 10 ml aliquot is required); dilute to 50 ml with distilled water; add 10 ml of SPADNS mixed reagent; and mix thoroughly. Record the aliquot  $A_d$  on the data form.

3. Place the sample in a bath that is constant at  $\pm 3^\circ\text{C}$  ( $5.4^\circ\text{F}$ ) of ambient temperature and which contains the standard solutions for 30 min before reading absorbance with the spectrophotometer.

4. Warm up the spectrophotometer for a suitable time (5 to 10 min) depending on the instrument; set the photometer to zero absorbance with the reference solution at 570 nm; and immediately obtain the absorbance readings of the standards, control sample, and field samples.

5. Prepare a calibration curve by plotting the micrograms ( $\mu\text{g}$ ) F/50 ml versus absorbance on linear graph paper, as described in Section 3.10.2. Note: Prepare a new standard curve whenever a fresh batch of any reagent is made up or when a different standard temperature is desired. Also, run an undistilled control sample with each set of samples; if it differs from the calibration curve by  $>\pm 2\%$ , prepare a new standard curve.

6. Determine the  $\mu\text{g}$  fluoride from the calibration curve and record on the data form (Figure 5.1). The values of the control samples should be 20  $\mu\text{g}$ . For the undistilled sample, a value between 19.6 and 20.4  $\mu\text{g}$  is acceptable; for the distilled sample, a value between 18.0 and 22.0  $\mu\text{g}$  is the acceptable range. If both values for the control samples fall within their limits, the field sample results should also be acceptable. However, if the undistilled sample is acceptable and the distilled is not, replace the contents of the distillation flask and redistill all samples. If the distilled is acceptable and

the undistilled sample is not, prepare fresh calibration standards and carefully check the temperature equilibrium. When both samples are unacceptable, prepare a new calibration curve. If this does not correct the problem, start over with all new solutions and check with an analyst familiar with the procedure.

7. Repeat the procedure using a smaller size aliquot of distillate if the fluoride concentration of the sample is not within the range of the calibration curve.

8. Calculate the total weight as milligrams and the concentration of fluoride using the equations in Section 3.10.6 and record on the data form (Figure 5.1).

The value of  $F_t$  obtained using Equation 6.4 of Section 3.10.6 for the distilled control sample should be 2.50 mg F; acceptable values are between 2.25 and 2.75 mg F. The final emission concentration in mg/dscm (lb/dscf) should be reported in the test report to the agency both corrected and uncorrected for the sample blank.

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TABLE 5.1. ACTIVITY MATRIX FOR POSTSAMPLING OPERATIONS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
<u>Sampling Apparatus</u>  Dry gas meter	±5% of calibration factor	Make three runs at a single intermediate orifice setting at highest volume of test (Sec 3.10.2)	Recalibrate; use factor that gives lower gas volume
Meter thermometers	±6°C (10.8°F) ambient temperature	Compare with ASTM mercury-in-glass thermometer after each test	Recalibrate; use higher temperature for calculations
Barometer	±5 mm (0.2 in.) at ambient pressure	Compare with mercury-in-glass barometer after each test	Recalibrate; use lower barometric value for calculations
Stack temperature sensors	±1.5% of the reference thermometer or thermocouple	Compare with reference temperature after each run	Recalibrate; calculate with and without temperature corrections
<u>Base Laboratory Analysis</u>  Reagents	Prepare according to Subsec 5.2	Prepare a calibration curve for each new SPADNS reagent mix	Prepare new solutions and calibration curves

(continued)

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TABLE 5.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Control sample	±2% when run with fluoride standards and ±10% when distilled and run with field samples	Prepare new controls before and during analysis of field samples	Prepare new solution and calibration curve, and/or change distillate solution

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## 6.0 CALCULATIONS

Calculation errors due to procedural or mathematical mistakes can be a large part of total system error. Thus, each set of calculations should be repeated or spotchecked, preferably by a team member other than the one that performed the original calculations. If a difference greater than a typical roundoff error is detected, the calculations should be checked step-by-step until the source of error is found and corrected.

A computer program is advantageous in reducing calculation errors. If a standardized computer program is used, the original data entry should be checked and if differences are observed, a new computer run should be made.

Table 6.1 at the end of this section summarizes the quality assurance activities for calculations. Retain at least one significant digit beyond that of the acquired data. Roundoff after the final calculations for each run or sample to two significant digits, in accordance with ASTM 380-76. All calculations should be recorded on a calculation form such as the ones in Figures 6.1A and 6.1B.

### 6.1 Nomenclature

Terms used in Equations 6-1 through 6-7 are defined here for use in the sections that follow.

- $A_d$  = Aliquot of distillate taken for color development, ml
- $A_n$  = Area of nozzle, cross-sectional,  $m^2$  ( $ft^2$ )
- $A_t$  = Aliquot of total sample added to still, ml
- $B_{ws}$  = Water vapor in the gas stream, proportion by volume
- $C_s$  = Concentration of fluoride in stack gas corrected to standard conditions of  $20^\circ C$ , 760 mm Hg ( $68^\circ F$ , 29.92 in. Hg) on dry basis,  $mg/m^3$  ( $lb/ft^3$ )
- $F_t$  = Total weight of fluoride in sample, mg (lb)
- (1354)

SAMPLE VOLUME (ENGLISH UNITS)

$$V_m = 42.658 \text{ ft}^3, T_m = 558.0 \text{ }^\circ\text{R}, P_{\text{bar}} = 29.21 \text{ in. Hg}$$

$$Y = 0.996, \Delta H = 1.42 \text{ in. H}_2\text{O}$$

$$V_{m(\text{std})} = 17.64 V_m Y \frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} = 44.912 \text{ ft}^3$$

Equation 6-1

FLUORIDE CONTENT IN SAMPLE

$$V_t = 1000.0 \text{ ml}, A_t = 200.0 \text{ ml}, V_d = 250.0 \text{ ml}$$

$$A_d = 10.0 \text{ ml} \quad \mu\text{g F} = 19.7 \mu\text{g}$$

$$F_t = 2.205 \times 10^{-9} \frac{V_t V_d}{A_t A_d} (\mu\text{g F}) = 5.430 \times 10^{-6} \text{ lb}$$

Equation 6-4

CONCENTRATION OF FLUORIDE (ENGLISH UNITS)

$$V_{m(\text{std})} = 44.91 \text{ ft}^3, F_t = 5.430 \times 10^{-6} \text{ lb}$$

$$F_{\text{tb}} = 0.000 \times 10^{-6} \text{ lb}$$

$$C_s = \frac{F_t - F_{\text{tb}}}{V_{m(\text{std})}} = 1.21 \times 10^{-7} \text{ lb/dscf}$$

Equation 6-5

All other equations same as Methods 2 and 5.

Figure 6.1A. Fluoride calculation form (English units).

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SAMPLE VOLUME (METRIC UNITS)

$$V_m = 1.378 \text{ m}^3, T_m = 310. \text{ }^\circ\text{K}, P_{\text{bar}} = 742. \text{ mm Hg}$$

$$Y = 0.996, \Delta H = 36. \text{ mm H}_2\text{O}$$

$$V_{m(\text{std})} = 0.3858 V_m Y \frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} = 1.272 \text{ m}^3 \text{ Equation 6-1}$$

FLUORIDE CONTENT IN SAMPLE

$$V_t = 1000.0 \text{ ml}, A_t = 200.0 \text{ ml}, V_d = 250.0 \text{ ml}$$

$$A_d = 10.0 \text{ ml} \quad \mu\text{g F} = 19.7 \mu\text{g}$$

$$F_t = 10^{-3} \frac{V_t V_d}{A_t A_d} (\mu\text{g F}) = 2.463 \text{ mg} \quad \text{Equation 6-4}$$

CONCENTRATION OF FLUORIDE (METRIC UNITS)

$$V_{m(\text{std})} = 1.272 \text{ dscm} \quad F_t = 2.463 \text{ mg} \quad F_{\text{tb}} = 0.000 \text{ mg}$$

$$C_s = \frac{F_t - F_{\text{tb}}}{V_{m(\text{std})}} = 1.936 \text{ mg/dscm} \quad \text{Equation 6-5}$$

All other equations same as Methods 2 and 5.

Figure 6.1B. Fluoride calculation form (metric units).

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- $F_{tb}$  = Total weight of fluoride in sample blank, mg (lb)
- $I$  = Percent of isokinetic sampling, %
- $M_w$  = Molecular weight of water, 18.0 g/g-mole  
(18.0 lb/lb-mole)
- $P_{bar}$  = Barometric pressure at sampling site, mm (in.) Hg
- $P_s$  = Absolute stack gas pressure at sampling site, mm  
(in.) Hg
- $P_{std}$  = Standard absolute pressure, 760 mm (29.92 in.) Hg
- $R$  = Ideal gas constant, 0.066236 mm Hg-m<sup>3</sup>/K-g-mole  
(21.83 in. Hg-ft<sup>3</sup>/°R-lb-mole)
- $T_m$  = Absolute average dry gas meter temperature,  
K (°R)
- $T_s$  = Absolute average stack gas temperature, K (°R)
- $T_{std}$  = Standard absolute temperature, 293K (528°R)
- $V_d$  = Total volume of distillate, ml
- $V_{ic}$  = Total volume of liquid collected in impingers and  
silica gel, ml. (Volume of water in silica gel =  
grams of silica gel weight increase × 1 ml/g;  
volume of liquid collected in impinger = final  
volume - initial volume)
- $V_m$  = Volume of gas sample measured by dry gas  
meter, dcm (dcf)
- $V_{m(std)}$  = Volume of gas sample measured by dry gas meter  
corrected to standard conditions, dscm (dscf)
- $V_s$  = Stack gas velocity calculated by Method 2 (Equa-  
tion 2-7) using data from Method 13, m/s (ft/s)
- $V_t$  = Total volume of sample, ml
- $V_{w(std)}$  = Volume of water vapor in gas sample corrected to  
standard conditions, scm (scf)
- $Y$  = Dry gas meter calibration factor
- $\Delta H$  = Average pressure differential across the orifice  
meter, mm (in.) H<sub>2</sub>O

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- $\rho_w$  = Density of water, 1 g/ml (0.00220 lb/ml)  
 $\theta$  = Total sampling time, min  
 $\mu g F$  = Weight of fluoride/50 ml taken from the calibration curve,  $\mu g$   
 13.6 = Specific gravity of mercury  
 60 = s/min  
 100 = Factor for converting to percent, %

### 6.2 Dry Gas Volume, Corrected to Standard Conditions

Correct the sample volume measured by the dry gas meter ( $V_m$ ) to standard conditions (20°C and 760 mm Hg or 68°F and 29.92 in. Hg) by using Equation 6-1. The absolute dry gas meter temperature ( $T_m$ ) and orifice pressure drop ( $\Delta H$ ) are obtained by averaging the field data.

$$V_{m(std)} = V_m Y \frac{T_{std}}{T_m} \frac{P_{bar} + (\Delta H/13.6)}{P_{std}}$$

$$= K_1 V_m Y \frac{P_{bar} + (\Delta H/13.6)}{T_m} \quad \text{Equation 6-1.}$$

where

$$K_1 = 0.3858 \text{ K/mm Hg for metric units, and}$$

$$= 17.64 \text{ }^\circ\text{R/in. Hg for English units.}$$

Note: If the leak rate observed during any mandatory leak check exceeds the acceptable rate, the tester shall either correct the value of  $V_m$  in Equation 6-1 (Section 6.3, Method 3), or invalidate the test runs.

### 6.3 Volume of Water Vapor

$$V_{w(std)} = V_{ic} \frac{\rho_w}{M_w} \frac{R T_{std}}{P_{std}} = K V_{ic} \quad \text{Equation 6-2}$$

where

$$K = 0.00133 \text{ m}^3/\text{ml for metric units, and}$$

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$K = 0.0472 \text{ ft}^3/\text{ml}$  for English units.

#### 6.4 Moisture Content of Stack Gas

$$B_{ws} = \frac{V_{w(\text{std})}}{V_{m(\text{std})} + V_{w(\text{std})}} \quad \text{Equation 6-3}$$

Note: If liquid droplets are in the gas stream, assume the stream to be saturated; use a psychrometric chart to obtain estimate of the moisture percentage.

#### 6.5 Fluoride Content in Sample (Concentration)

$$F_t = K \frac{V_t V_d \mu\text{g F}}{A_t A_d} \quad \text{Equation 6-4}$$

where

$K = 10^{-3} \text{ mg}/\mu\text{g}$  for metric units, and

$K = 2.205 \times 10^{-6} \text{ lb}/\mu\text{g}$  for English units.

#### 6.6 Concentration of Fluoride in Stack Gas

$$C_s = K \frac{F_t - F_{tb}}{V_{m(\text{std})}} \quad \text{Equation 6-5}$$

$K = 1.00 \text{ m}^3/\text{m}^3$  for metric units, and

$K = 35.31 \text{ ft}^3/\text{m}^3$  for English units.

#### 6.7 Isokinetic Variation (I)

The isokinetic variation (I) can be calculated from either raw data or intermediate values using the following equations.

##### 6.7.1 Calculation of I from Raw Data

$$I = \frac{100 \times T_s [K V_{ic} + (Y V_m/T_m) (P_{\text{bar}} + \Delta H/13.6)]}{60 v_s P_s A_n} \quad \text{Equation 6-6}$$

where

$K = 0.003454 \text{ mm Hg-m}^3\text{ml-K}$  for metric units, and

$= 0.002669 \text{ in. Hg-ft}^3/\text{ml-}^\circ\text{R}$  for English units.

##### 6.7.2 Calculations of I from Intermediate Values

$$I = \frac{100 \times T_s V_{m(\text{std})} P_{\text{std}}}{T_{\text{std}} v_s \theta P_s A_n 60 (1-B_{ws})} \quad \text{Equation 6-7}$$

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$$= K \frac{T_s V_{m(std)}}{v_s P_s A_n \theta (1-B_{ws})}$$

where

K = 4.320 for metric units, and  
= 0.09450 for English units.

6.7 Acceptable Results

If  $90\% \leq I \leq 110\%$ , the results are acceptable. If the results are low in comparison to the standards and if I is beyond the acceptable range, the administrator may opt to accept the results; if not, reject the results and repeat the test.

TABLE 6.1. ACTIVITY MATRIX FOR CALCULATIONS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Analysis data form	All data and calculations given	Visual check	Complete the missing data values
Calculations	Difference between check and original calculations within roundoff error; one decimal figure retained beyond that of acquired data	Repeat all calculations starting with raw data for hand calculations; check all raw data input for computer calculations and hand calculate one sample per test	Indicate errors on analysis data form
Isokinetic variation	$90\% \leq I \leq 110\%$ ; see Eqs 6.6 and 6.7 for calculation of I	Calculate I for each traverse point	Repeat test; adjust flow rates to maintain I within $\pm 10\%$ variation

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## 7.0 MAINTENANCE

Normal use of emission testing equipment subjects it to corrosive gases, temperature extremes, vibrations, and shocks. Keeping the equipment in good operating order over an extended time requires routine maintenance and knowledge of the equipment. Maintenance of the entire sampling train should be performed either quarterly or after 1000 ft<sup>3</sup> of operation, whichever occurs sooner. Maintenance activities are summarized in Table 7.1. The following routine checks are recommended, but not required, to increase reliability. This section is the same as for Method 13B (Section 3.9.7).

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TABLE 7.1. ACTIVITY MATRIX FOR EQUIPMENT MAINTENANCE CHECKS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Fiber vane pump	Leak free; required flow; no erratic behavior	Periodic check of oil and oiler jar; remove head yearly and change fiber vanes	Replace as needed
Diaphragm pump	Leak-free valves functioning properly; required flow	Clean valves during yearly disassembly	Replace when leaking or when running erratically
Dry gas meter	No excess oil, corrosion, or erratic dial rotation	Check every 3 mo for excess oil or corrosion; check valves and diaphragm if dial runs erratically or if meter will not calibrate	Replace parts as needed, or replace meter
Inclined manometer	No discoloration of or visible matter in the fluid	Check periodically; change fluid during yearly disassembly	Replace parts as needed
Other sampling train components	No damage or leaks; no erratic behavior	Visually check every 3 mo; disassemble and clean or replace yearly	If failure noted, replace meter box, sample box, or umbilical cord
Nozzle	No dents, corrosion, or other damage	Visually check before and after each test run	Replace nozzle or clean, sharpen, and recalibrate

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8.0 AUDITING PROCEDURES

An audit is an independent assessment of data quality. Independence is achieved by using apparatus and standards that are different from those used by the regular field crew. Routine quality assurance checks by a field team are necessary for obtaining good quality data, but they are not part of the auditing procedure. Table 8.1 summarizes the quality assurance activities for the auditing. This section is the same as Method 13B (Section 3.9.8).

TABLE 8.1. ACTIVITY MATRIX FOR AUDITING PROCEDURES

Audit	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Performance Audit</u>  Analytical phase of Method 13 A using aqueous sodium fluoride	Measured concentrations of audit sample within acceptable limits of true value, Section 3.9.8	Once during every enforcement source test; measure audit samples and compare their values with known concentrations	Review operating technique
Data processing errors	Difference between original and audit calculations within roundoff error	Once during every enforcement source test, perform independent calculations starting with data recorded on field and laboratory forms	Check and correct all data; recalculate if necessary
Systems audit	Operation technique as described in Section 3.10.8	Once during every enforcement test, until experience gained and then every fourth test, observe techniques; use audit checklist (Fig 8.2, Section 3.9.8)	Explain to team deviations from recommended techniques; note on Fig 8.2

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## 9.0 RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY

To acquire data of good quality, two considerations are essential:

1. The measurement process must be in a state of statistical control at the time of the measurement, and
2. The systematic errors, when combined with the random variations (errors of measurement), must result in acceptable uncertainty.

Other quality assurance activities include quality control checks and independent audits of the total measurement system (Section 3.10.8); documentation of data by using quality control charts (as appropriate); use of materials, instruments, and procedures that can be traced to appropriate standards of reference; and use of control standards and working standards for routine data collection and equipment calibration. Working standards should be traceable to primary standards:

1. Dry gas meter calibrated against a wet test meter that has been verified by liquid displacement (Section 3.9.2) or by a spirometer.
2. Field samples analyzed by comparisons with standard solutions (aqueous NaF) that have been validated with independent control samples.

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1  REFERENCE METHOD<sup>a</sup>

40 CFR Part 60 is amended by revising Methods 13A and 13B of Appendix A to read as follows:

Appendix A—Reference Test Methods

Method 13A. Determination of Total Fluoride Emissions From Stationary Sources; SPADNS Zirconium Lake Method

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of fluoride (F) emissions from sources as specified in the regulations. It does not measure fluorocarbons, such as freons.

1.2 Principle. Gaseous and particulate F are withdrawn isokinetically from the source and collected in water and on a filter. The total F is then determined by the SPADNS Zirconium Lake colorimetric method.

2. Range and Sensitivity

The range of this method is 0 to 1.4  $\mu\text{g F/ml}$ . Sensitivity has not been determined.

3. Interferences

Large quantities of chloride will interfere with the analysis, but this interference can be prevented by adding silver sulfate into the distillation flask (see Section 7.3.4). If chloride ion is present, it may be easier to use the Specific Ion Electrode Method (Method 13B). Grease on sample-exposed surfaces may cause low F results due to adsorption.

4. Precision, Accuracy, and Stability

4.1 Precision. The following estimates are based on a collaborative test done at a primary aluminum smelter. In the test, six laboratories each sampled the stack simultaneously using two sampling trains for a total of 12 samples per sampling run. Fluoride concentrations encountered during the test ranged from 0.1 to 1.4  $\text{mg F/m}^3$ . The within-laboratory and between-laboratory standard deviations, which include sampling and analysis errors, were 0.044  $\text{mg F/m}^3$  with 60 degrees of freedom and 0.064  $\text{mg F/m}^3$  with five degrees of freedom, respectively.

4.2 Accuracy. The collaborative test did not find any bias in the analytical method.

4.3 Stability. After the sample and colorimetric reagent are mixed, the color formed is stable for approximately 2 hours. A 3°C temperature difference between the sample and standard solutions produces an error of approximately 0.005  $\text{mg F/liter}$ . To avoid this error, the absorbances of the sample and standard solutions must be measured at the same temperature.

5. Apparatus

5.1 Sampling Train. A schematic of the sampling train is shown in Figure 13A-1; it is similar to the Method 5 train except the filter position is interchangeable. The sampling train consists of the following components:

5.1.1 Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Filter Heating System, Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.1, 2.1.3, 2.1.4, 2.1.6, 2.1.8, 2.1.9, and 2.1.10. When moisture condensation is a problem, the filter heating system is used.

5.1.2 Probe Liner. Borosilicate glass or 316 stainless steel. When the filter is located immediately after the probe, the tester may use a probe heating system to prevent filter plugging resulting from moisture condensation, but the tester shall not allow the temperature in the probe to exceed  $120 \pm 14^\circ\text{C}$  ( $248 \pm 25^\circ\text{F}$ ).

5.1.3 Filter Holder. With positive seal against leakage from the outside or around the filter. If the filter is located between the probe and first impinger, use 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. If the filter is located between the third and fourth impingers, the tester may use borosilicate glass with a glass frit filter support and a silicone rubber gasket. The tester may also use other materials of construction with approval from the Administrator.

5.1.4 Impingers. Four impingers connected as shown in Figure 13A-1 with ground-glass (or equivalent), vacuum-tight fittings. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3-cm-inside-diameter ( $\frac{1}{2}$  in.) glass tube extending to 1.3 cm ( $\frac{1}{2}$  in.) from the bottom of the flask. For the second impinger, use a Greenburg-Smith impinger with the standard tip. The tester may use modifications (e.g., flexible connections between the impingers or materials other than glass), subject to the approval of the Administrator. Place a thermometer, capable of measuring temperature to within  $1^\circ\text{C}$  ( $2^\circ\text{F}$ ), at the outlet of the fourth impinger for monitoring purposes.

5.2 Sample Recovery. The following items are needed:

5.2.1 Probe-Liner and Probe-Nozzle Brushes, Wash Bottles, Graduated Cylinder and/or Balance, Plastic Storage Containers, Rubber Policeman, Funnel. Same as Method 5, Sections 2.2.1 to 2.2.2 and 2.2.5 to 2.2.8, respectively.

5.2.2 Sample Storage Container. Wide-mouth, high-density-polyethylene bottles for impinger water samples, 1-liter.

5.3 Analysis. The following equipment is needed:

5.3.1 Distillation Apparatus. Glass distillation apparatus assembled as shown in Figure 13A-2.

5.3.2 Bunsen Burner.

5.3.3 Electric Muffle Furnace. Capable of heating to  $600^\circ\text{C}$ .

5.3.4 Crucibles. Nickel, 75- to 100-ml.

5.3.5 Beakers. 500-ml and 1500-ml.

5.3.6 Volumetric Flasks. 50-ml.

5.3.7 Erlenmeyer Flasks or Plastic Bottles. 500-ml.

5.3.8 Constant Temperature Bath. Capable of maintaining a constant temperature of  $\pm 1.0^\circ\text{C}$  at room temperature conditions.

5.3.9 Balance. 300-g capacity to measure to  $\pm 0.5$  g.

5.3.10 Spectrophotometer. Instrument that measures absorbance at 570 nm and provides at least a 1-cm light path.

5.3.11 Spectrophotometer Cells. 1-cm pathlength.

6. Reagents

6.1 Sampling. Use ACS reagent-grade chemicals or equivalent, unless otherwise specified. The reagents used in sampling are as follows:

6.1.1 Filters.

6.1.1.1 If the filter is located between the third and fourth impingers, use a Whatman<sup>1</sup> No. 1 filter, or equivalent, sized to fit the filter holder.

BILLING CODE 6860-01-M

<sup>1</sup> Mention of company or product names does not constitute endorsement by the U.S. Environmental Protection Agency.

<sup>a</sup> Taken from Federal Register, Vol. 45, No. 121, pp. 41852-41857, Friday, June 20, 1980.

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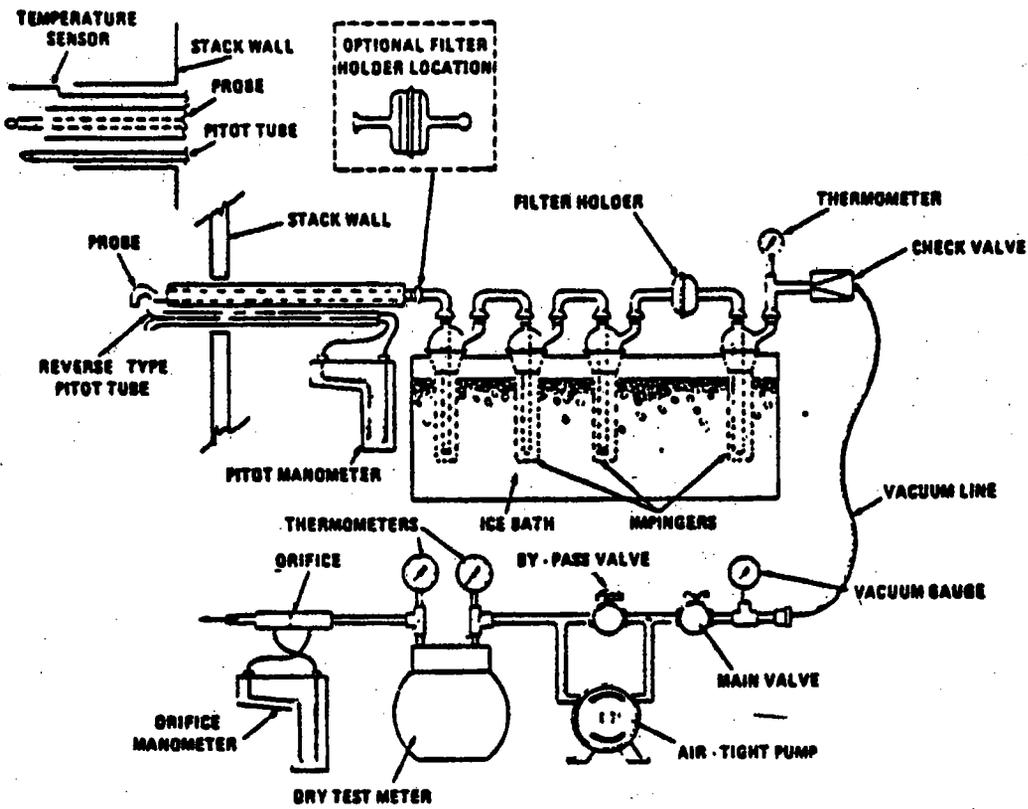


Figure 13A-1. Fluoride sampling train.

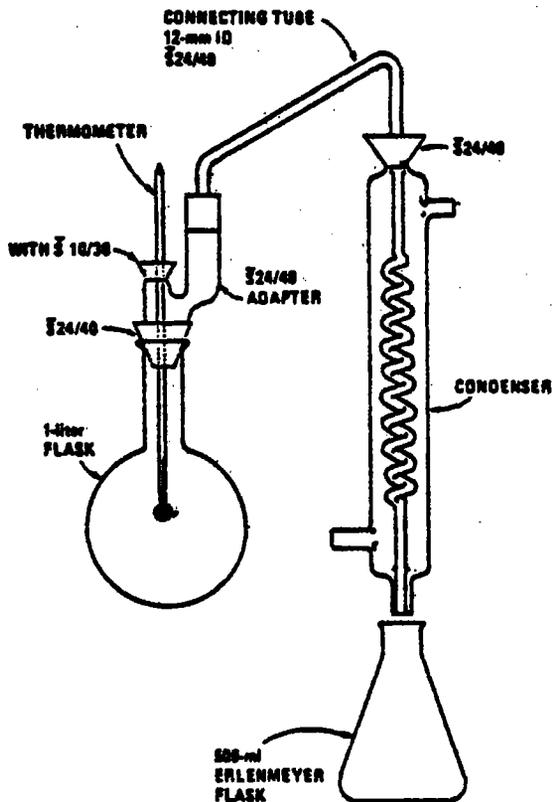


Figure 13A-2. Fluoride distillation apparatus.

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6.1.1.2 If the filter is located between the probe and first impinger, use any suitable medium (e.g., paper organic membrane) that conforms to the following specifications: (1) The filter can withstand prolonged exposure to temperatures up to 135°C (275°F). (2) The filter has at least 95 percent collection efficiency (<5 percent penetration) for 0.3 µm dioctyl phthalate smoke particles. Conduct the filter efficiency test before the test series, using ASTM Standard Method D 2986-71, or use test data from the supplier's quality control program. (3) The filter has a low F blank value (<0.015 mg F/cm<sup>2</sup> of filter area). Before the test series, determine the average F blank value of at least three filters (from the lot to be used for sampling) using the applicable procedures described in Sections 7.3 and 7.4 of this method. In general, glass fiber filters have high and/or variable F blank values, and will not be acceptable for use.

6.1.2 Water. Deionized distilled, to conform to ASTM Specification D 1193-74, Type 3. If high concentrations of organic matter are not expected to be present, the analyst may delete the potassium permanganate test for oxidizable organic matter.

6.1.3 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, Section 3.1.2, 3.1.4, and 3.1.5, respectively.

6.2 Sample Recovery. Water, from same container as described in Section 6.1.2, is needed for sample recovery.

6.3 Sample Preparation and Analysis. The reagents needed for sample preparation and analysis are as follows:

6.3.1 Calcium Oxide (CaO). Certified grade containing 0.005 percent F or less.

6.3.2 Phenolphthalein Indicator. Dissolve 0.1 g of phenolphthalein in a mixture of 50 ml of 90 percent ethanol and 50 ml of deionized distilled water.

6.3.3 Silver Sulfate (Ag<sub>2</sub>SO<sub>4</sub>).

6.3.4 Sodium Hydroxide (NaOH), Pellets.

6.3.5 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>), Concentrated.

6.3.6 Sulfuric Acid, 25 percent (V/V). Mix 1 part of concentrated H<sub>2</sub>SO<sub>4</sub> with 3 parts of deionized distilled water.

6.3.7 Filters. Whatman No. 541, or equivalent.

6.3.8 Hydrochloric Acid (HCl), Concentrated.

6.3.9 Water. From same container as described in Section 6.1.2.

6.3.10 Fluoride Standard Solution, 0.01 mg F/ml. Dry in an oven at 110°C for at least 2 hours. Dissolve 0.2210 g of NaF in 1 liter of deionized distilled water. Dilute 100 ml of this solution to 1 liter with deionized distilled water.

6.3.11 SPADNS Solution [4, 5-dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalene-disulfonic acid trisodium salt]. Dissolve 0.960 ± 0.010 g of SPADNS reagent in 500 ml deionized distilled water. If stored in a well-sealed bottle protected from the sunlight, this solution is stable for at least 1 month.

6.3.12 Spectrophotometer Zero Reference Solution. Prepare daily. Add 10 ml of SPADNS solution (6.3.11) to 100 ml deionized distilled water, and acidify with a solution prepared by diluting 7 ml of concentrated HCl to 10 ml with deionized distilled water.

6.3.13 SPADNS Mixed Reagent. Dissolve 0.135 ± 0.005 g of zirconyl chloride octahydrate (ZrOCl<sub>2</sub> · 8H<sub>2</sub>O) in 25 ml of deionized distilled water. Add 350 ml of concentrated HCl, and dilute to 500 ml with deionized distilled water. Mix equal volumes of this solution and SPADNS solution to form a single reagent. This reagent is stable for at least 2 months.

## 7. Procedure

7.1 Sampling. Because of the complexity of this method, testers should be trained and experienced with the test procedures to assure reliable results.

7.1.1 Pretest Preparation. Follow the general procedure given in Method 5, Section 4.1.1, except the filter need not be weighed.

7.1.2 Preliminary Determinations. Follow the general procedure given in Method 5, Section 4.1.2, except the nozzle size selected must maintain isokinetic sampling rates below 28 liters/min (1.0 cfm).

7.1.3 Preparation of Collection Train. Follow the general procedure given in Method 5, Section 4.1.3, except for the following variations:

Place 100 ml of deionized distilled water in each of the first two impingers, and leave the third impinger empty. Transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger.

Assemble the train as shown in Figure 13A-1 with the filter between the third and fourth impingers. Alternatively, if a 20-mesh stainless steel screen is used for the filter support, the tester may place the filter between the probe and first impinger. The tester may also use a filter heating system to prevent moisture condensation, but shall not allow the temperature around the filter holder to exceed 120 ± 14°C (248 ± 25°F). Record the filter location on the data sheet.

7.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Sections 4.1.4.1 (Pretest Leak-Check), 4.1.4.2 (Leak-Checks During the Sample Run), and 4.1.4.3 (Post-Test Leak-Check).

7.1.5 Fluoride Train Operation. Follow the general procedure given in Method 5, Section 4.1.5, keeping the filter and probe temperatures (if applicable) at 120 ± 14°C (248 ± 25°F) and isokinetic sampling rates below 28 liters/min (1.0 cfm). For each run, record the data required on a data sheet such as the one shown in Method 5, Figure 5-2.

7.2 Sample Recovery. Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period.

Allow the probe to cool. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to keep from losing part of the sample. Do not cap off the probe tip tightly while the sampling train is cooling down, because a vacuum would form in the filter holder, thus drawing impinger water backward.

Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate, if present. Remove the filter assembly, wipe off the silicone grease from the filter holder inlet,

and cap this inlet. Remove the umbilical cord from the last impinger, and cap the impinger. After wiping off the silicone grease, cap off the filter holder outlet and any open impinger inlets and outlets. The tester may use ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe and filter-impinger assembly to an area that is clean and protected from the wind so that the chances of contaminating or losing the sample is minimized.

Inspect the train before and during disassembly, and note any abnormal conditions. Treat the samples as follows:

7.2.1 Container No. 1 (Probe, Filter, and Impinger Catches). Using a graduated cylinder, measure to the nearest ml, and record the volume of the water in the first three impingers; include any condensate in the probe in this determination. Transfer the impinger water from the graduated cylinder into this polyethylene container. Add the filter to this container. (The filter may be handled separately using procedures subject to the Administrator's approval.) Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, clean all sample-exposed surfaces (including the probe nozzle, probe fitting, probe liner, first three impingers, impinger connectors, and filter holder) with deionized distilled water. Use less than 500 ml for the entire wash. Add the washings to the sampler container. Perform the deionized distilled water rinses as follows:

Carefully remove the probe nozzle and rinse the inside surface with deionized distilled water from a wash bottle. Brush with a Nylon bristle brush, and rinse until the rinse shows no visible particles, after which make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok fitting with deionized distilled water in a similar way.

Rinse the probe liner with deionized distilled water. While squirting the water into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with water. Let the water drain from the lower end into the sample container. The tester may use a funnel (glass or polyethylene) to aid in transferring the liquid washes to the container. Follow the rinse with a probe brush. Hold the probe in an inclined position, and squirt deionized distilled water into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe, and catch any water and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with deionized distilled water, and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as described above.

It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

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Rinse the inside surface of each of the first three impingers (and connecting glassware) three separate times. Use a small portion of deionized distilled water for each rinse, and brush each sample-exposed surface with a Nylon bristle brush, to ensure recovery of fine particulate matter. Make a final rinse of each surface and of the brush.

After ensuring that all joints have been wiped clean of the silicone grease, brush and rinse with deionized distilled water the inside of the filter holder (front-half only, if filter is positioned between the third and fourth impingers). Brush and rinse each surface three times or more if needed. Make a final rinse of the brush and filter holder.

After all water washings and particulate matter have been collected in the sample container, tighten the lid so that water will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container clearly to identify its contents.

**7.2.2 Container No. 2 (Sample Blank).** 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. Process the blank in the same manner as for Container No. 1.

**7.2.3 Container No. 3 (Silica Gel).** Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, the tester may follow the analytical procedure for Container No. 3 in Section 7.4.2.

**7.3 Sample Preparation and Distillation.** (Note the liquid levels in Containers No. 1 and No. 2 and confirm on the analysis sheet whether or not leakage occurred during transport. If noticeable leakage had occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.) Treat the contents of each sample container as described below:

**7.3.1 Container No. 1 (Probe, Filter, and Impinger Catches).** Filter this container's contents, including the sampling filter, through Whatman No. 541 filter paper, or equivalent, into a 1500-ml beaker.

**7.3.1.1** If the filtrate volume exceeds 900 ml, make the filtrate basic (red to phenolphthalein) with NaOH, and evaporate to less than 900 ml.

**7.3.1.2** Place the filtered material (including sampling filter) in a nickel crucible, add a few ml of deionized distilled water, and macerate the filters with a glass rod.

Add 100 mg CaO 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.

After evaporation of 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. It may take several hours to completely char the filters.

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.

Add approximately 4 g of crushed NaOH to the crucible and mix. Return the crucible to the muffle furnace, and fuse the sample for 10 minutes at 800°C.

Remove the sample from the furnace, and cool to ambient temperature. Using several rinsings of warm deionized distilled 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 percent H<sub>2</sub>SO<sub>4</sub>, and carefully add to the beaker. Mix well, and transfer to a 1-liter volumetric flask. Dilute to volume with deionized distilled water, and mix thoroughly. Allow any undissolved solids to settle.

**7.3.2 Container No. 2 (Sample Blank).** Treat in the same manner as described in Section 7.3.1 above.

**7.3.3 Adjustment of Acid/Water Ratio in Distillation Flask.** (Use a protective shield when carrying out this procedure.) Place 400 ml of deionized distilled water in the distillation flask, and add 200 ml of concentrated H<sub>2</sub>SO<sub>4</sub>. (Caution: Observe standard precautions when mixing H<sub>2</sub>SO<sub>4</sub> with water. Slowly add the acid to the flask with constant swirling.) Add some soft glass beads and several small pieces of broken glass tubing, and assemble the apparatus as shown in Figure 13A-2. Heat the flask until it reaches a temperature of 175°C to adjust the acid/water ratio for subsequent distillations. Discard the distillate.

**7.3.4 Distillation.** Cool the contents of the distillation flask to below 80°C. Pipet an aliquot of sample containing less than 10.0 mg F directly into the distillation flask, and add deionized distilled 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 Section 7.4.1. This will be an approximation of the F content because of possible interfering ions.) Note: If the sample contains chloride, add 5 mg of Ag<sub>2</sub>SO<sub>4</sub> to the flask for every mg of chloride.

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 minutes or less). Slow distillations have been found to produce low F recoveries. Caution: Be careful not to exceed 175°C to avoid causing H<sub>2</sub>SO<sub>4</sub> to distill over.

If F distillation in the mg range is to be followed by a distillation in the fractional mg

range, add 220 ml of deionized distilled water and distill it over as in the acid adjustment step to remove residual F from the distillation system.

The tester may use the acid in the distillation flask until there is carry-over of interferences or poor F recovery. Check for these every tenth distillation using a deionized distilled water blank and a standard solution. Change the acid whenever the F recovery is less than 90 percent or the blank value exceeds 0.1 µg/ml.

#### 7.4 Analysis.

**7.4.1 Containers No. 1 and No. 2.** After distilling suitable aliquots from Containers No. 1 and No. 2 according to Section 7.3.4, dilute the distillate in the volumetric flask to exactly 250 ml with deionized distilled water, and mix thoroughly. Pipet a suitable aliquot of each sample distillate (containing 10 to 40 µg F/ml) into a beaker, and dilute to 50 ml with deionized distilled water. Use the same aliquot size for the blank. Add 10 ml of SPADNS mixed reagent (6.3.13), and mix thoroughly.

After mixing, place the sample in a constant-temperature bath containing the standard solutions (see Section 8.2) for 30 minutes before reading the absorbance on the spectrophotometer.

Set the spectrophotometer to zero absorbance at 570 nm with the reference solution (6.3.12), and check the spectrophotometer calibration with the standard solution. Determine the absorbance of the samples, and determine the concentration from the calibration curve. If the concentration does not fall within the range of the calibration curve, repeat the procedure using a different size aliquot.

**7.4.2 Container No. 3 (Silica Gel).** Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. The tester may conduct this step in the field.

#### a. Calibration

Maintain a laboratory log of all calibrations.

**8.1 Sampling Train.** Calibrate the sampling train components according to the indicated sections in Method 3: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Probe heater (Section 5.4); Temperature Gauges (Section 5.5); Leak Check of Metering System (Section 5.6); and Barometer (Section 5.7).

**8.2 Spectrophotometer.** Prepare the blank standard by adding 10 ml of SPADNS mixed reagent to 50 ml of deionized distilled water. Accurately prepare a series of standards from the 0.01 mg F/ml standard fluoride solution (6.3.10) by diluting 0, 2, 4, 6, 8, 10, 12, and 14 ml to 100 ml with deionized distilled water. Pipet 50 ml from each solution and transfer each to a separate 100-ml beaker. Then add 10 ml of SPADNS mixed reagent to each. These standards will contain 0, 10, 20, 30, 40, 50, 60, and 70 µg F (0 to 1.4 µg/ml), respectively.

After mixing, place the reference standards and reference solution in a constant temperature bath for 30 minutes before reading the absorbance with the spectrophotometer. Adjust all samples to this same temperature before analyzing.

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With the spectrophotometer at 570 nm, use the reference solution (6.3.12) to set the absorbance to zero.

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  $\pm 2$  percent, prepare a new standard curve.

**8. Calculations**

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation. Other forms of the equations may be used, provided that they yield equivalent results.

**9.1 Nomenclature.**

- $A_s$  = Aliquot of distillate taken for color development, ml.
- $A_t$  = Aliquot of total sample added to still, ml.
- $B_w$  = Water vapor in the gas stream, proportion by volume.
- $C_s$  = Concentration of F in stack gas,  $\text{mg}/\text{m}^3$ , dry basis, corrected to standard conditions of 760 mm Hg (29.92 in. Hg) and 293°K (528°R).

- $F_t$  = Total F in sample, mg.
- $\mu\text{g F}$  = Concentration from the calibration curve,  $\mu\text{g}$ .
- $T_m$  = Absolute average dry gas meter temperature (see Figure 5-2 of Method 5), °K (°R).
- $T_s$  = Absolute average stack gas temperature (see Figure 5-2 of Method 5), °K (°R).
- $V_d$  = Volume of distillate collected, ml.
- $V_{m(\text{std})}$  = Volume of gas sample as measured by dry gas meter, corrected to standard conditions, dscm (dscf).
- $V_t$  = Total volume of F sample, after final dilution, ml.
- $V_{w(\text{std})}$  = Volume of water vapor in the gas sample, corrected to standard conditions scm (scf).

**9.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop.** See data sheet (Figure 5-2 of Method 5).

**9.3 Dry Gas Volume.** Calculate  $V_{m(\text{std})}$  and adjust for leakage, if necessary, using the equation in section 6.3 of Method 5.

**9.4 Volume of Water Vapor and Moisture Content.** Calculate the volume of water vapor  $V_{w(\text{std})}$  and moisture content  $B_w$  from the data obtained in this method (Figure 13A-1); use Equations 5-2 and 5-3 of Method 5.

**9.5 Concentration.**

**9.5.1 Total Fluoride in Sample.** Calculate the amount of F in the sample using the following equation:

$$F_t = 10^{-3} \frac{V_t}{A_t} \frac{V_d}{A_d} (\mu\text{g F}) \quad \text{Eq. 13A-1}$$

**9.5.2 Fluoride Concentration in Stack Gas.** Determine the F concentration in the stack gas using the following equation:

$$C_s = K \frac{F_t}{V_{m(\text{std})}} \quad \text{Eq. 13A-2}$$

Where:

- $K = 35.31 \text{ ft}^3/\text{m}^3$  if  $V_{m(\text{std})}$  is expressed in English units.
- $= 1.00 \text{ m}^3/\text{m}^3$  if  $V_{m(\text{std})}$  is expressed in metric units.

**9.6 Isokinetic Variation and Acceptable Results.** Use Method 5, Sections 6.11 and 6.12.

**10. Bibliography**

1. Belleck, Ervin. Simplified Fluoride Distillation Method. Journal of the American Water Works Association. 50:5306. 1958.
2. Mitchell, W. J., J. C. Suggs, and F. J. Bergman. Collaborative Study of EPA method 13A and Method 13B. Publication No. EPA-600/4-77-050. Environmental Protection Agency, Research Triangle Park, North Carolina, December 1977.
3. Mitchell, W. J. and M. R. Midgett. Adequacy of Sampling Trains and Analytical Procedures Used for Fluoride. Atm. Environ. 10:865-872. 1976.

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## 11.0 REFERENCES

1. Determination of Total Fluoride Emissions from Stationary Sources; SPADNS Zirconium Lake Method. Federal Register, Vol. 45. June 20, 1980.
2. Mitchell, W. J., J. C. Suggs, and F. J. Bergman. Collaborative Study of EPA Method 13A and Method 13B. EPA-600/4-77-050.
3. Martin, R. M. Construction Details of Isokinetic Source Sampling Equipment. APTD-0581, USEPA, Air Pollution Control Office, Research Triangle Park, North Carolina. 1971.
4. Rom, J. J. Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. APTD-0576. USEPA Office of Air Programs, Research Triangle Park, North Carolina. 1972.

## ADDITIONAL REFERENCES

Standard Methods for the Examination of Water and Wastewater, Published jointly by the American Public Health Association, American Water Works Association and Water Pollution Control Federation, 14th Edition (1975).

MacLeod, Kathryn E., and Howard L. Crist, "Comparison of the SPADNS Zirconium Lake and Specific Ion Electrode Network of Fluoride Determinations in Stack Emission Samples," Analytical Chemistry 45:1272-1273. 1973.

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## 12.0 DATA FORMS

Blank data forms are provided on the following pages for the convenience of the Handbook user. Each blank form has the customary descriptive title centered at the top of the page. However, the section-page documentation in the top right-hand corner of each page of other sections has been replaced with a number in the lower right-hand corner that will enable the user to identify and refer to a similar filled-in form in the text section. For example, Form M13A-2.1 indicates that the form is Figure 2.1 in Section 3.10.2 of the Method 13A Handbook. Future revisions of this form, if any, can be documented by 2.1A, 2.1B, etc. Four of the blank forms (the first listed below) are included in this section. Eighteen are in Section 3.9.12 as shown by the M13B following the form number.

<u>Form</u>	<u>Title</u>
2.1	Fluoride Calibration Curve Data Form
5.1	Method 13A Analytical Data Form
5.2	Analytical Balance Calibration Form
5.3	Control Sample Analytical Data Form
1.2 (M13B)	Procurement Log
2.3A & B (M13B)	Dry Gas Meter Calibration Data Form (English and Metric units)
2.4A & B (M13B)	Posttest Meter Calibration Data Form (English and Metric units)
2.5 (M13B)	Stack Temperature Sensor Calibration Data Form
2.6 (M13B)	Nozzle Calibration Data Form
3.1 (M13B)	Pretest Sampling Checks
4.1 (M13B)	Nomograph Data Form
4.2 (M13B)	Fluoride Field Data Form
4.3 (M13B)	Sample Recovery and Integrity Data Form

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<u>Form</u>	<u>Title</u>
4.4 (M13B)	Sample Label
4.5 (M13B)	On-Site Measurement Checklist
5.1 (M13B)	Posttest Calibration Checks
5.2 (M13B)	Fluoride Analytical Data Form
6.1A & 6.1B (M13B)	Fluoride Calculation Data Form (English and Metric units)
8.2 (M13B)	Method 13B Checklist To Be Used by Auditors

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Spectrophotometer number \_\_\_\_\_ Analyst \_\_\_\_\_

Calibration date \_\_\_\_\_ SPADNS mix date \_\_\_\_\_

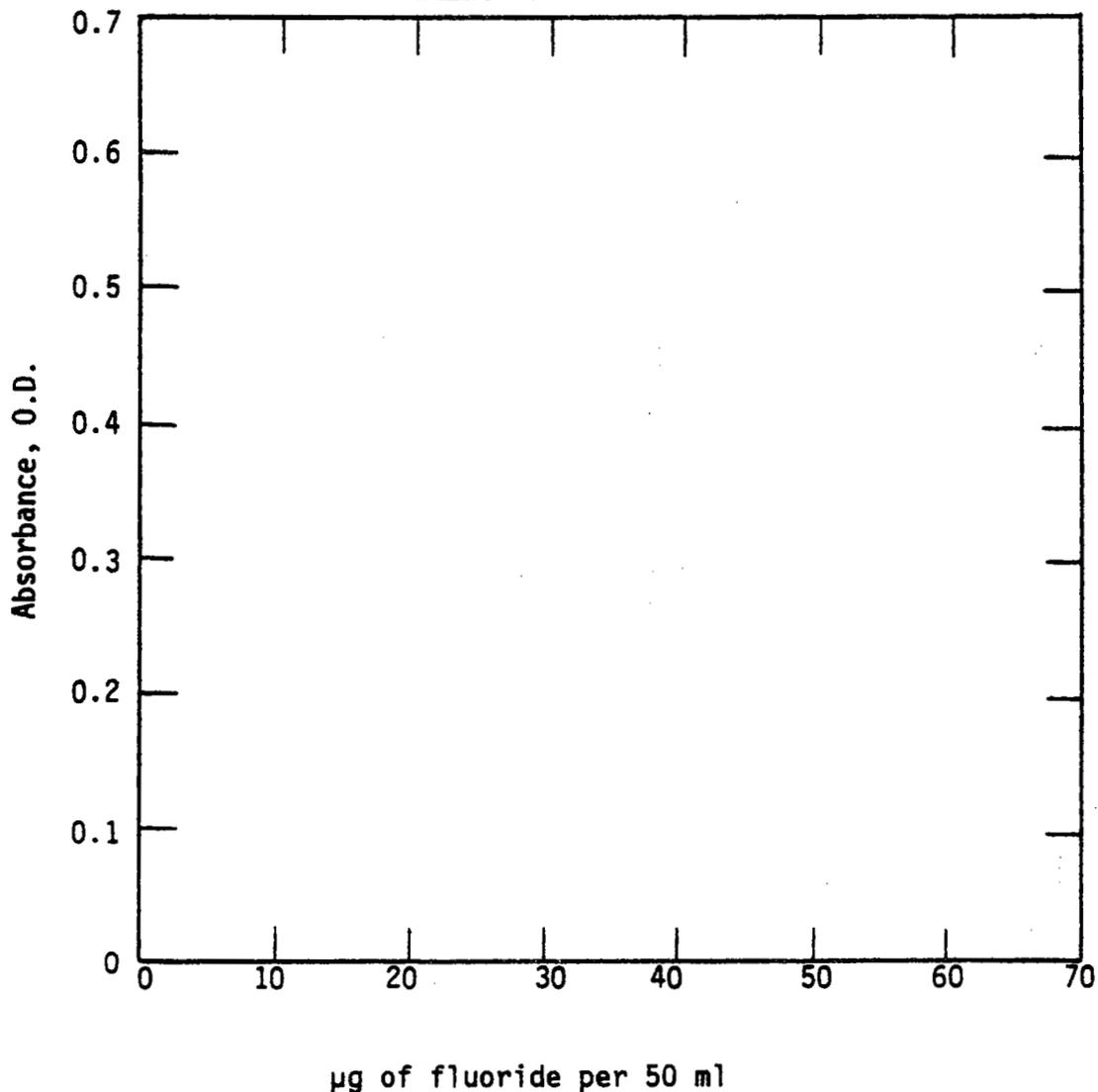
Ambient temperature \_\_\_\_\_ °C Bath temperature \_\_\_\_\_ °C

Spectrophotometer set at 570 nm \_\_\_\_\_ yes \_\_\_\_\_ no

Reference solution used to set zero absorbance \_\_\_\_\_ yes \_\_\_\_\_ no

Absorbance readings: \_\_\_\_\_ 10 µg \_\_\_\_\_ 20 µg \_\_\_\_\_ 30 µg

\_\_\_\_\_ 40 µg \_\_\_\_\_ 50 µg \_\_\_\_\_ 60 µg \_\_\_\_\_ 70 µg \_\_\_\_\_ blank



Signature of Analyst \_\_\_\_\_

Signature of Reviewer \_\_\_\_\_

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METHOD 13A ANALYTICAL DATA FORM

Plant \_\_\_\_\_ Location \_\_\_\_\_

Date \_\_\_\_\_ Analyst \_\_\_\_\_ SPADNS mix date \_\_\_\_\_

Samples identifiable \_\_\_\_\_ yes \_\_\_\_\_ no All liquid levels at mark \_\_\_\_\_ yes \_\_\_\_\_ no

Ambient temperature \_\_\_\_\_ Temperature of samples \_\_\_\_\_ Temperature of standards \_\_\_\_\_

Sample was concentrated \_\_\_\_\_ yes \_\_\_\_\_ no Solids fused and added to liquid \_\_\_\_\_ yes \_\_\_\_\_ no

Sample number	Sample identification	Total volume of sample before distill. (V <sub>t</sub> ), ml	Aliquot of sample for distill. (A <sub>t</sub> ), ml	mg of chloride per liter of sample	mg of silver chloride added	Sample volume from still (V <sub>d</sub> ), ml	Aliquot of sample for analysis (A <sub>d</sub> ), ml	Absorb. of sample at 570 nm OD	µg F in sample <sup>a</sup>	Total weight of F (F <sub>t</sub> ), mg

<sup>b</sup>Total weight of fluoride in sample (F<sub>t</sub>)

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

<sup>a</sup>Control samples results must be between 19.6 µg and 20.4 µg for undistilled sample on 18.0 and 22.0 µg for distilled sample

Remarks: \_\_\_\_\_

Signature of analyst \_\_\_\_\_

Signature of reviewer \_\_\_\_\_

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Balance name \_\_\_\_\_ Number \_\_\_\_\_

Classification of standard weights \_\_\_\_\_

Date	0.5000 g	1.0000 g	10.0000 g	50.0000 g	100.0000 g	Analyst

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Plant \_\_\_\_\_ Date of analysis \_\_\_\_\_

Analyst \_\_\_\_\_ Ambient temperature \_\_\_\_\_

Date of calibration curve \_\_\_\_\_ Temp. of calibration curve \_\_\_\_\_

	Concentration of control sample	
	Distilled	Undistilled
Control sample temperature	_____	_____
Absorbance of control sample	_____	_____
Amount of F in control sample from calibration curve	_____	_____
Percent error between measured and calculated concentration	_____	_____

Were acceptable results obtained on control samples (less than 2% undistilled and <10% distilled) \_\_\_\_\_

Signature of analyst \_\_\_\_\_

Signature of reviewer \_\_\_\_\_

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