

Figure 12-1. Inorganic Lead Sampling Train.

METHOD 13A—DETERMINATION OF TOTAL FLUORIDE EMISSIONS FROM STATIONARY SOURCES (SPADNS ZIRCONIUM LAKE METHOD)

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from

other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total fluorides as Fluorine .....	7782-41-4	Not determined.

1.2 **Applicability.** This method is applicable for the determination of fluoride ( $F^-$ ) emissions from sources as specified in the regulations. It does not measure fluorocarbons, such as Freons.

1.3 **Data Quality Objectives.** Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

#### 2.0 Summary

Gaseous and particulate  $F^-$  are withdrawn isokinetically from the source and collected in water and on a filter.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.

#### 3.0 Definitions [Reserved]

#### 4.0 Interferences

4.1 **Chloride.** 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 11.3). If chloride ion is present, it may be easier to use the specific ion electrode method of analysis (Method 13B).

4.2 **Grease.** Grease on sample-exposed surfaces may cause low  $F^-$  results due to adsorption.

#### 5.0 Safety

5.1 **Disclaimer.** This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 **Corrosive Reagents.** The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 **Hydrochloric Acid (HCl).** Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 **Sodium Hydroxide (NaOH).** Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat,

and lungs. Reacts exothermically with limited amounts of water.

5.2.3 **Sulfuric Acid ( $H_2SO_4$ ).** Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/ $m^3$  for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

#### 6.0 Equipment and Supplies

6.1 **Sample Collection.** A schematic of the sampling train used in performing this method is shown in Figure 13A-1; it is similar to the Method 5 sampling train except that the filter position is interchangeable. The sampling train consists of the following components:

6.1.1 **Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Filter Heating System, Temperature Sensor, Metering System, Barometer, and Gas Density Determination Equipment.** Same as Method 5, Sections 6.1.1.1, 6.1.1.3 through 6.1.1.7, 6.1.1.9, 6.1.2, and 6.1.3, respectively. The filter heating system and temperature sensor are needed only when moisture condensation is a problem.

6.1.2 **Probe Liner.** Borosilicate glass or 316 stainless steel. When the filter is located immediately after the probe, a probe heating system may be used to prevent filter plugging resulting from moisture condensation, but the temperature in the probe shall not be allowed to exceed  $120 \pm 14$  °C ( $248 \pm 25$  °F).

6.1.3 **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, borosilicate glass with a glass frit filter support and a silicone rubber gasket may be used. Other materials of construction may be used, subject to the approval of the Administrator.

6.1.4 **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 ( $\frac{1}{2}$  in.) ID 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. Modifications (*e.g.*, flexible connections between the impingers or materials other than glass) may be used, subject to the approval of the Administrator. Place a temperature sensor, capable of measuring temperature to within 1 °C (2 °F), at the outlet of the fourth impinger for monitoring purposes.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Probe-liner and Probe-Nozzle Brushes, Wash Bottles, Graduated Cylinder and/or Balance, Plastic Storage Containers, Funnel and Rubber Policeman, and Funnel. Same as Method 5, Sections 6.2.1, 6.2.2 and 6.2.5 to 6.2.8, respectively.

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

6.3 Sample Preparation and Analysis. The following items are needed for sample preparation and analysis:

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

6.3.2 Bunsen Burner.

6.3.3 Electric Muffle Furnace. Capable of heating to 600 °C (1100 °F).

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

6.3.5 Beakers. 500-ml and 1500-ml.

6.3.6 Volumetric Flasks, 50-ml.

6.3.7 Erlenmeyer Flasks or Plastic Bottles. 500-ml.

6.3.8 Constant Temperature Bath. Capable of maintaining a constant temperature of  $\pm 1.0$  °C at room temperature conditions.

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

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

6.3.11 Spectrophotometer Cells. 1-cm path length.

#### 7.0 Reagents and Standards

Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are needed for sample collection:

7.1.1 Filters.

7.1.1.1 If the filter is located between the third and fourth impingers, use a Whatman No. 1 filter, or equivalent, sized to fit the filter holder.

7.1.1.2 If the filter is located between the probe and first impinger, use any suitable medium (*e.g.*, paper, organic membrane) that can withstand prolonged exposure to temperatures up to 135 °C (275 °F), and has at least 95 percent collection efficiency (<5 percent penetration) for 0.3  $\mu$ m dioctyl phthalate smoke particles. Conduct the filter effi-

ciency test before the test series, using ASTM D 2986-71, 78, or 95a (incorporated by reference—see §60.17), or use test data from the supplier's quality control program. The filter must also have a low F<sup>-</sup> blank value (<0.015 mg F<sup>-</sup>/cm<sup>2</sup> of filter area). Before the test series, determine the average F<sup>-</sup> blank value of at least three filters (from the lot to be used for sampling) using the applicable procedures described in Sections 8.3 and 8.4 of this method. In general, glass fiber filters have high and/or variable F<sup>-</sup> blank values, and will not be acceptable for use.

7.1.2 Water. Deionized distilled, to conform to ASTM D 1193-77 or 91, Type 3 (incorporated by reference—see §60.17). If high concentrations of organic matter are not expected to be present, the potassium permanganate test for oxidizable organic matter may be deleted.

7.1.3 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, Sections 7.1.2, 7.1.4, and 7.1.5, respectively.

7.2 Sample Recovery. Water, as described in Section 7.1.2, is needed for sample recovery.

7.3 Sample Preparation and Analysis. The following reagents and standards are needed for sample preparation and analysis:

7.3.1 Calcium Oxide (CaO). Certified grade containing 0.005 percent F<sup>-</sup> or less.

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

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

7.3.4 Sodium Hydroxide (NaOH), Pellets.

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

7.3.6 Sulfuric Acid, 25 Percent (v/v). Mix 1 part of concentrated H<sub>2</sub>SO<sub>4</sub> with 3 parts of water.

7.3.7 Filters. Whatman No. 541, or equivalent.

7.3.8 Hydrochloric Acid (HCl), Concentrated.

7.3.9 Water. Same as in Section 7.1.2.

7.3.10 Fluoride Standard Solution, 0.01 mg F<sup>-</sup>/ml. Dry approximately 0.5 g of sodium fluoride (NaF) in an oven at 110 °C (230 °F) for at least 2 hours. Dissolve 0.2210 g of NaF in 1 liter of water. Dilute 100 ml of this solution to 1 liter with water.

7.3.11 SPADNS Solution [4,5 Dihydroxyl-3-(p-Sulfophenylazo)-2,7-Naphthalene-Disulfonic Acid Trisodium Salt]. Dissolve 0.960  $\pm$  0.010 g of SPADNS reagent in 500 ml water. If stored in a well-sealed bottle protected from the sunlight, this solution is stable for at least 1 month.

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

7.3.13 SPADNS Mixed Reagent. Dissolve 0.135  $\pm$  0.005 g of zirconyl chloride octahydrate (ZrOCl<sub>2</sub> 8H<sub>2</sub>O) in 25 ml of 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.

#### 8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Follow the general procedure given in Method 5, Section 8.1, except that the filter need not be weighed.

8.2 Preliminary Determinations. Follow the general procedure given in Method 5, Section 8.2, except that the nozzle size must be selected such that isokinetic sampling rates below 28 liters/min (1.0 cfm) can be maintained.

8.3 Preparation of Sampling Train. Follow the general procedure given in Method 5, Section 8.3, except for the following variation: 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 filter may be placed between the probe and first impinger. A filter heating system to prevent moisture condensation may be used, but shall not allow the temperature to exceed  $120 \pm 14$  °C ( $248 \pm 25$  °F). Record the filter location on the data sheet (see Section 8.5).

8.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Section 8.4.

8.5 Sampling Train Operation. Follow the general procedure given in Method 5, Section 8.5, keeping the filter and probe temperatures (if applicable) at  $120 \pm 14$  °C ( $248 \pm 25$  °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 5-3.

8.6 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

8.6.1 When the probe 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 as this would create a vacuum in the filter holder, thus drawing water from the impingers into the filter holder.

8.6.2 Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off any silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Remove the filter assembly, wipe off any 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 any silicone grease, cap off the filter holder outlet and any open impinger inlets and outlets.

Ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

8.6.3 Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

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

8.6.4.1 Container No. 1 (Probe, Filter, and Impinger Catches).

8.6.4.1.1 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 a 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 water. Use less than 500 ml for the entire wash. Add the washings to the sample container. Perform the water rinses as follows:

8.6.4.1.2 Carefully remove the probe nozzle and rinse the inside surface with 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 water in a similar way.

8.6.4.1.3 Rinse the probe liner with 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. A funnel (glass or polyethylene) may be used 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 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 water, and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as described above.

8.6.4.1.4 It is recommended that two people clean the probe to minimize sample

losses. Between sampling runs, keep brushes clean and protected from contamination.

8.6.4.1.5 Rinse the inside surface of each of the first three impingers (and connecting glassware) three separate times. Use a small portion of 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.

8.6.4.1.6 After ensuring that all joints have been wiped clean of the silicone grease, brush and rinse with 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.

8.6.4.1.7 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 transport. Label the container clearly to identify its contents.

8.6.4.2 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.

8.6.4.3 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. A funnel may be used 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, follow the analytical procedure for Container No. 3 in Section 11.4.2.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.1 .....	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate and sample volume.
10.2 .....	Spectrophotometer calibration .....	Evaluate analytical technique, preparation of standards.
11.3.3 .....	Interference/recovery efficiency check during distillation.	Minimize negative effects of used acid.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Sampling Equipment. Calibrate the probe nozzle, pitot tube, metering system, probe heater, temperature sensors, and barometer according to the procedures outlined in Method 5, Sections 10.1 through 10.6. Conduct the leak-check of the metering system according to the procedures outlined in Method 5, Section 8.4.1.

10.2 Spectrophotometer.

10.2.1 Prepare the blank standard by adding 10 ml of SPADNS mixed reagent to 50 ml of water.

10.2.2 Accurately prepare a series of standards from the 0.01 mg F<sup>-</sup>/ml standard fluoride solution (Section 7.3.10) 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 (Section 7.3.13) to each. These standards will contain 0, 10, 20, 30, 40, 50, 60, and 70 µg F<sup>-</sup> (0 to 1.4 µg/ml), respectively.

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

10.2.4 With the spectrophotometer at 570 nm, use the blank standard to set the absorbance to zero. Determine the absorbance of the standards.

10.2.5 Prepare a calibration curve by plotting µg F<sup>-</sup>/50 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 more than ±2 percent, prepare a new standard curve.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the liquid levels in Containers No. 1 and No. 2, determine whether leakage occurred during transport, and note this finding on the analytical data sheet. If noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Treat the contents of each sample container as described below:

11.2.1 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.

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

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

11.2.1.2.1 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.

11.2.1.2.2 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 char the filters completely.

11.2.1.2.3 Place the crucible in a cold muffle furnace. Gradually (to prevent smoking) increase the temperature to 600 °C (1100 °F), and maintain this temperature until the contents are reduced to an ash. Remove the crucible from the furnace, and allow to cool.

11.2.1.2.4 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 600 °C.

11.2.1.2.5 Remove the sample from the furnace, and cool to ambient temperature. Using several rinsings of warm water, transfer the contents of the crucible to the beaker containing the filtrate. To ensure complete sample removal, rinse finally with two 20-ml portions of 25 percent  $H_2SO_4$ , and carefully add to the beaker. Mix well, and transfer to a 1-liter volumetric flask. Dilute to volume with water, and mix thoroughly. Allow any undissolved solids to settle.

11.2.2 Container No. 2 (Sample Blank). Treat in the same manner as described in Section 11.2.1 above.

11.2.3 Adjustment of Acid/Water Ratio in Distillation Flask. Place 400 ml of water in the distillation flask, and add 200 ml of concentrated  $H_2SO_4$ . 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 (347 °F) to adjust the acid/water ratio for subsequent distillations. Discard the distillate.

CAUTION: Use a protective shield when carrying out this procedure. Observe standard precautions when mixing  $H_2SO_4$  with water. Slowly add the acid to the flask with constant swirling.

11.3 Distillation.

11.3.1 Cool the contents of the distillation flask to below 80 °C (180 °F). Pipet an aliquot of sample containing less than 10.0 mg  $F^-$  directly into the distillation flask, and add water to make a total volume of 220 ml added to the distillation flask. (To estimate the appropriate aliquot size, select an aliquot of the solution, and treat as described in Section 11.4.1. This will be an approximation of the  $F^-$  content because of possible interfering ions.)

NOTE: If the sample contains chloride, add 5 mg of  $Ag_2SO_4$  to the flask for every mg of chloride.

11.3.2 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 (347 °F). 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. Be careful not to exceed 175 °C (347 °F) to avoid causing  $H_2SO_4$  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 water and distill it over as in the acid adjustment step to remove residual  $F^-$  from the distillation system.

11.3.3 The acid in the distillation flask may be used until there is carry-over of interferences or poor  $F^-$  recovery. Check for interference and for recovery efficiency every tenth distillation using a 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.

11.4 Sample Analysis.

11.4.1 Containers No. 1 and No. 2.

11.4.1.1 After distilling suitable aliquots from Containers No. 1 and No. 2 according to Section 11.3, dilute the distillate in the volumetric flasks to exactly 250 ml with water, and mix thoroughly. Pipet a suitable aliquot of each sample distillate (containing 10 to 40 µg  $F^-$ /ml) into a beaker, and dilute to 50 ml with water. Use the same aliquot size for the blank. Add 10 ml of SPADNS mixed reagent (Section 7.3.13), and mix thoroughly.

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

NOTE: After the sample and colorimetric reagent are mixed, the color formed is stable for approximately 2 hours. Also, a 3 °C (5.4 °F) temperature difference between the sample and standard solutions produces an error

of approximately 0.005 mg F<sup>-</sup>/liter. To avoid this error, the absorbencies of the sample and standard solutions must be measured at the same temperature.

11.4.1.3 Set the spectrophotometer to zero absorbance at 570 nm with the zero reference solution (Section 7.3.12), and check the spectrophotometer calibration with the standard solution (Section 7.3.10). 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.

11.4.2 Container No. 3 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

#### 12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant 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.

##### 12.1 Nomenclature.

A<sub>d</sub>=Aliquot of distillate taken for color development, ml.

A<sub>t</sub>=Aliquot of total sample added to still, ml.

B<sub>ws</sub>=Water vapor in the gas stream, portion by volume.

C<sub>s</sub>=Concentration of F<sup>-</sup> in stack gas, mg/dscm (gr/dscf).

F<sub>c</sub>=F<sup>-</sup> concentration from the calibration curve, µg.

F<sub>t</sub>=Total F<sup>-</sup> in sample, mg.

T<sub>m</sub>=Absolute average dry gas meter (DGM) temperature (see Figure 5-3 of Method 5), °K (°R).

T<sub>s</sub>=Absolute average stack gas temperature (see Figure 5-3 of Method 5), °K (°R).

V<sub>d</sub>=Volume of distillate as diluted, ml.

V<sub>m(std)</sub>=Volume of gas sample as measured by DGM at standard conditions, dscm (dscf).

V<sub>t</sub>=Total volume of F<sup>-</sup> sample, after final dilution, ml.

V<sub>w(std)</sub>=Volume of water vapor in the gas sample at standard conditions, scm (scf)

12.2 Average DGM Temperature and Average Orifice Pressure Drop (see Figure 5-3 of Method 5).

12.3 Dry Gas Volume. Calculate V<sub>m(std)</sub>, and adjust for leakage, if necessary, using Equation 5-1 of Method 5.

12.4 Volume of Water Vapor and Moisture Content. Calculate V<sub>w(std)</sub> and B<sub>ws</sub> from the data obtained in this method. Use Equations 5-2 and 5-3 of Method 5.

12.5 Total Fluoride in Sample. Calculate the amount of F<sup>-</sup> in the sample using the following equation:

$$F_t = \frac{K V_t V_d F_c}{A_t A_d} \quad \text{Eq. 13A-1}$$

Where:

K=10<sup>-3</sup> mg/µg (metric units)

=1.54 × 10<sup>-5</sup> gr/µg (English units)

12.6 Fluoride Concentration in Stack Gas. Determine the F<sup>-</sup> concentration in the stack gas using the following equation:

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

12.7 Isokinetic Variation. Same as Method 5, Section 12.11.

#### 13.0 Method Performance

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 mg F<sup>-</sup>/m<sup>3</sup>.

13.1 Precision. The intra- and inter-laboratory standard deviations, which include sampling and analysis errors, were 0.044 mg F<sup>-</sup>/m<sup>3</sup> with 60 degrees of freedom and 0.064 mg F<sup>-</sup>/m<sup>3</sup> with five degrees of freedom, respectively.

13.2 Bias. The collaborative test did not find any bias in the analytical method.

13.3 Range. The range of this method is 0 to 1.4 µg F<sup>-</sup>/ml.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

#### 16.0 Alternative Procedures

16.1 Compliance with ASTM D 3270-73T, 80, 91, or 95 (incorporated by reference—see §60.17) "Analysis of Fluoride Content of the Atmosphere and Plant Tissues (Semiautomated Method) is an acceptable alternative for the requirements specified in Sections 11.2, 11.3, and 11.4.1 when applied to suitable aliquots of Containers 1 and 2 samples.

#### 17.0 References

1. Bellack, Ervin. Simplified Fluoride Distillation Method. J. 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-300/4-77-050. U.S. Environmental Protection Agency, Research Triangle Park, NC. December 1977.

3. Mitchell, W.J., and M.R. Midgett. Adequacy of Sampling Trains and Analytical

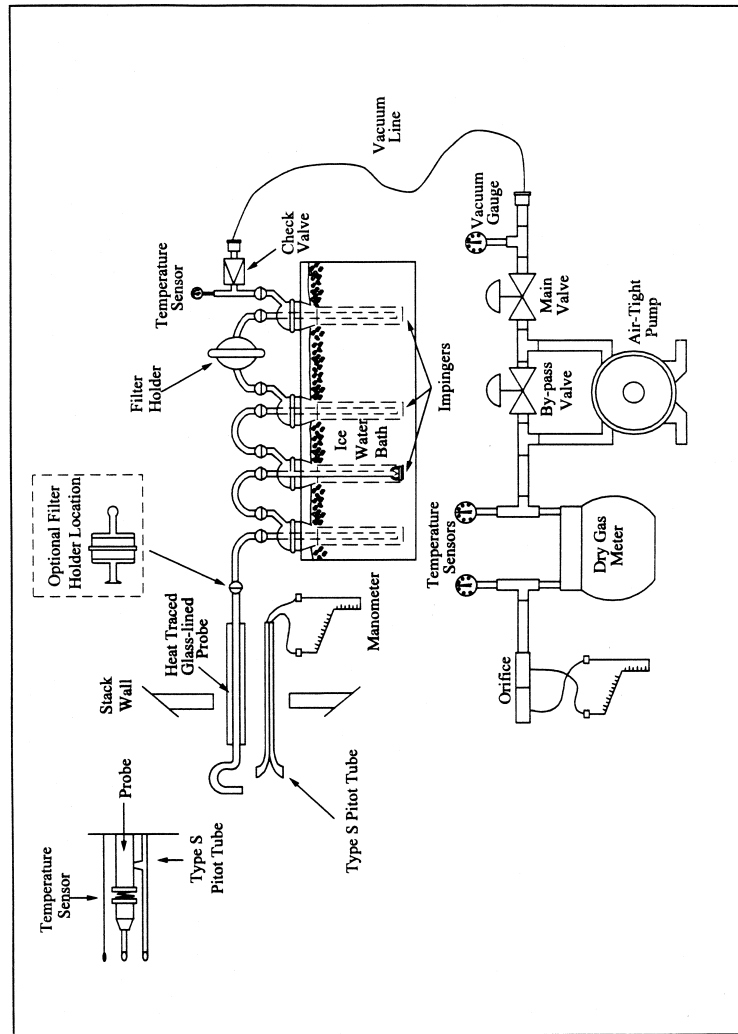


Figure 13A-1. Fluoride Sampling Train.

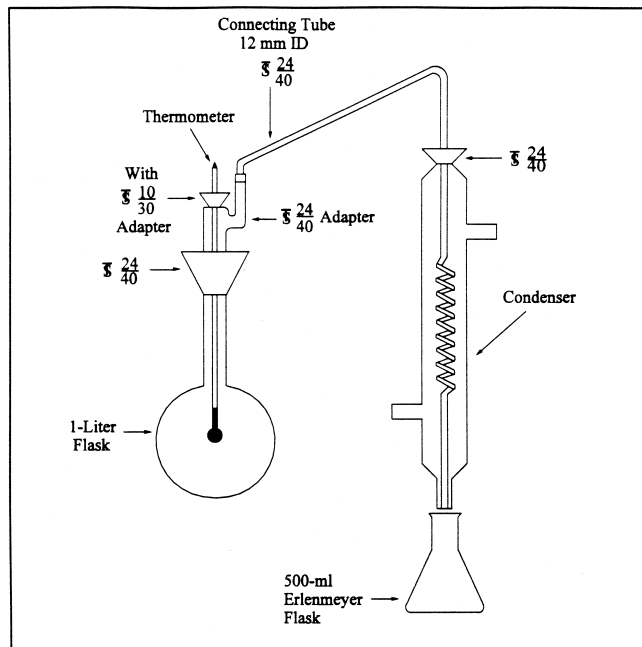


Figure 13A-2. Fluoride Distillation Apparatus.

METHOD 13B—DETERMINATION OF TOTAL FLUORIDE EMISSIONS FROM STATIONARY SOURCES (SPECIFIC ION ELECTRODE METHOD)

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from

other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 13A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total fluorides as Fluorine .....	7782-41-4	Not determined.

1.2 Applicability. This method is applicable for the determination of fluoride (F<sup>-</sup>) emissions from sources as specified in the regulations. It does not measure fluorocarbons, such as Freons.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary

Gaseous and particulate F<sup>-</sup> are withdrawn isokinetically from the source and collected in water and on a filter. The total F<sup>-</sup> is then

determined by the specific ion electrode method.

3.0 Definitions. [Reserved]

4.0 Interferences

Grease on sample-exposed surfaces may cause low F<sup>-</sup> results because of adsorption.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the