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July 6, 2007

Florida Department of Environmental Protection  
Bureau of Air Regulation  
Twin Towers Office Building  
2600 Blair Stone Road  
Tallahassee, Florida 32399-2400

063-7647  
**RECEIVED**

JUL 09 2007

BUREAU OF AIR REGULATION

Attention: Trina Vielhauer, Chief

**RE: CF INDUSTRIES, INC., PLANT CITY PHOSPHATE COMPLEX  
DRAFT AIR PERMIT NO. 0570005-021-AC; PSD-FL-355  
'B' SULFURIC ACID PLANT & 'A' AND 'B' PHOSPHORIC ACID PLANTS**

Dear Ms. Vielhauer:

CF Industries, Inc. (CF) has received the DRAFT Air Construction Permit issued on May 25, 2007, by the Florida Department of Environmental Protection (FDEP) for the 'B' Sulfuric Acid Plant (B-SAP) & 'A' and 'B' Phosphoric Acid Plants (A-PAP and B-PAP, respectively) production increase project at the Plant City Phosphate Complex. CF published the Public Notice for the draft permit on June 8, 2007. CF and Golder Associates Inc. (Golder) have reviewed the draft permit and have the following comments.

**Draft Permit**

Page 6 of 12, Condition 1 – The wording is confusing in that it states that the permittee shall continue to comply with the conditions of the original construction/modification permits. The conditions of the original construction/modification permits, however, would be in direct conflict with revised production rates, emission rates, etc. of this new PSD permit. Suggested revised wording to clarify the condition is provided below:

Previous Permits: This permit supplements all previously issued air construction and operation permits for this emissions unit. Except for changes specified in the below conditions, the unit remains subject to the conditions of all other valid air construction and operations permits. [Rule 62-4.070, Florida Administrative Code (F.A.C.)]

Page 7 of 12, Condition 4 – Both hourly and daily production rate limits seem unnecessary. There is also no reason from an air quality standpoint that production rates or emissions need to be limited on an hourly basis, i.e., there are no ambient air quality standards for fluorides. It is requested that the hourly rates specified for A- and B-PAPs be deleted or clarified to be "on a 24-hour basis". If an hourly rate is deemed necessary by FDEP, it is requested that the hourly rate be a nominal amount higher (i.e., 10 percent) than the daily rate to allow for process fluctuations.

Page 11 of 12, condition 1- same comment as for condition 1 on page 6 of 12.

Page 12 of 12, condition 9 – This condition requires that the A and B Shipping Baghouses (SB) be tested initially to demonstrate compliance with the revised particulate matter (PM) emission limit of 1.71 pounds per hour (lb/hr) for each SB. However, it would be difficult and costly to perform such testing on the existing units, as further described below:

A-SB - Setting up a particulate test for A-SB would be very complex. There are no work platforms on the building that are adjacent to the SB exit area. A large crane (duct is 120 feet above ground level) would need to support a work platform where the stack test equipment could be set up. Modifications would have to be made to the outside wall structure to get the sample probe to the sampling area inside the building. Alternatively, the exit stack could be extended to create a sample point acceptable under CFR 40, Part 60. Ideally it would be converted to a round stack (it is a rectangular stack) extending several feet outside the building. Currently, it only extends about 1 foot outside of the building. A catwalk to support the stack test equipment would have to be built instead of using a crane (safety issues). A boom support will have to be constructed. Appropriate sample port holes will have to be installed in the stack.

B-SB would require the following. Scaffolding, a manlift or crane with a work basket would have to set up near the stack exit (~30 feet above ground level) for the stack test equipment. A boom support will have to be constructed. Sample ports would have to be installed.

CF understands FDEP's concern over lowering the PM standard. However, if this were a new emissions unit, manufacturers' data would likely be adequate to provide reasonable assurance to FDEP that the PM standard will be met based on SB design. The manufacturers' data for A- and B-SBs were submitted to FDEP with the January 27, 2007, response letter. Rule 62-297.620(4) allows FDEP to waive the PM test for baghouses with potential emissions of less than 100 tons per year (TPY), provided the 5 percent visible emissions (VE) limit is accepted. Condition 2 on page 11 of 12 contains the 5 percent VE limit, and CF has no objection to this limit.

Based on this information, it is requested that the initial PM testing be waived for A and B SBs.

Also, in regard to condition 23 on page 10 of 12, a protocol for the ambient monitoring is attached. The protocol presents CF's plan to conduct the ambient monitoring for fluorides to satisfy this condition.

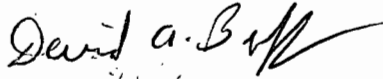
#### Technical Evaluation and Preliminary Determination

Page 11 of 30- Statement above last paragraph indicating fluorides are "primarily HF". CF does not believe this statement is correct: fluorides from the monoammonium/diammonium phosphates (MAP/DAP) plants are believed to be primarily ammonium compounds, while fluorides from the PAPs are believed to be primarily SiF<sub>4</sub>. These observations are based on test data submitted to FDEP on February 4, 2002.

Thank you for consideration of this information. If you have any questions, please do not hesitate to call me at (352) 336-5600.

Sincerely,

GOLDER ASSOCIATES INC.



David A. Buff, P.E., Q.E.P.  
Principal Engineer  
Florida P.E. #19011  
SEAL

DB/all

Enclosures

cc: Ron Brunk, CF Industries  
Bob May, CF Industries

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## **AMBIENT MONITORING PROTOCOL FOR FLUORIDE**

### **CF INDUSTRIES, INC. PLANT CITY, FLORIDA**

#### **INTRODUCTION**

Draft Air Construction Permit No. 0570005-021-AC/PSD-FL-355 issued to CF Industries, Inc. (CF), Plant City, Florida, requires that the permittee conduct pre- and post-construction ambient monitoring for fluorides. A minimum of 6 months of pre-construction monitoring is required, while a minimum of 1 year post-construction monitoring is required. The data must comply with the requirements of Title 40 of the Code of Federal Regulations (40 CFR), Section 52.21(m). The fluorides monitor must be placed within the plant boundary and located downwind of the emissions units. A report must be submitted to the Florida Department of Environmental Protection (FDEP) after each monitoring phase is completed. This air monitoring protocol addresses these requirements.

Federal requirements for pre-application air quality (ambient monitoring) analysis are contained in 40 CFR, Section 52.21(m). For pollutants for which no ambient standards exist, the regulation states that "the analysis shall contain such air quality monitoring data as the Administrator determines is necessary to assess ambient air quality for that pollutant in any area that the emissions of that pollutant would affect." Therefore, FDEP has discretion in determining acceptable monitoring requirements.

"Continuous" air monitoring data are not specifically required for pollutants that do not have National Ambient Air Quality Standards (NAAQS). There is neither state of Florida or federal NAAQS for fluorides.

#### **OBJECTIVE**

CF is receiving an air construction permit from FDEP to increase production rates at the A- and B- Phosphoric Acid Plants (PAPs), and at the B Sulfuric Acid Plant (B-SAP). The B-SAP does not emit fluorides; however, the A and B PAPs emit fluorides. In addition, the A, X, Y and Z Monoammonium/Diammonium Phosphates (MAP/DAP) Plants at the CF facility will be affected by

the project, since their production rates may also increase due to the increase in the A and B PAPs 'production rates. These emissions units also emit fluorides.

The "pre-construction" phase of the air monitoring will be conducted over a 6-month period. To satisfy the spirit of the permit condition, during the "pre-construction" phase of the monitoring, CF will operate at current operating rates, or no more than 15 percent above current operating rates, on days when the ambient fluoride monitor is operating. Since CF cannot sustain operating rates above this level, much of the fluorides data obtained are expected to be reflective of current operating rates.

During the post-construction monitoring phase, operating rates should at times approach the higher permitted operating rate allowed under the construction permit. The objective of the air monitoring will be to measure fluoride concentrations during periods of high production rates.

### **AIR MONITORING TECHNIQUE**

CF will utilize the following method for measuring ambient fluoride concentrations: Standard Test Method for Automated Separation and Collection of Particulate and Acidic Gaseous Fluoride in the Atmosphere (Double Paper Tape Sampler Method). This method is ASTM D 3266-91 (copy attached). U.S. Agri-Chemicals (USAC) has been using this method to monitor for gaseous fluorides to satisfy the requirements of a Development of Regional Impact order. That program is ending and CF is purchasing the monitor.

The monitor CF will utilize is a Research Appliance Co. Dual Filter Tape System, Model G2DT. A vacuum pump draws an air sample through the upper tape (collects dust) and then through the lower tape (absorbs gaseous fluorides). The monitor will be operated once every 6 days for 24 hours (eight 3-hour samples). Operating duration is controlled by a Tenor Model 652 timer. The lower tapes (gaseous) will be sent to a qualified laboratory for fluoride analysis, while the upper tapes (dust) will be discarded.

### **AIR MONITOR LOCATION**

The air construction permit requires that the ambient fluorides monitor be placed within the plant boundary and located downwind of the emissions units. The emissions units emitting fluorides at the Plant City complex consist of A and B PAPs, and the A, X, Y and Z MAP/DAP Plants. The locations of these emissions units in relation to the CFI plant boundary are shown in Figure 1. The process cooling pond and gypsum stack are also sources of fugitive fluorides emissions.

The intent of the permit condition is to monitor at a location likely to experience a high frequency of impacts from the emissions units. The initial ambient air sampling effort will be conducted over a period of 6 months (approximately July through December 2007). To determine the direction of the prevailing winds during this period, a 5-year wind rose for July through December from Tampa Airport was examined. The wind rose is shown in Figure 2. As shown, the prevailing winds during this period are towards the southwest.

A site reconnaissance will be conducted to identify a suitable air monitoring site location based on accessibility, power availability, presence of obstructions, security, etc. The monitor will be located generally southwest of the location of the emissions units emitting fluorides.

### **MONITORING FREQUENCY**

Monitoring will be conducted on a once-every-sixth-day schedule, coincident with the national air sampling schedule. Samples will be obtained for 24-hour periods, from midnight to midnight on the sampling days. The "pre-construction" monitoring period will last 6 months. Upon completion of construction of the A and B PAPs emissions units, a second monitoring period lasting 1 year will commence.

### **DATA COLLECTION PROCEDURES**

CF personnel will service the monitor. After each monitoring day, the paper tape will be extracted from the monitor, placed in a clean container, and shipped to the laboratory for analysis.

Flow rate calibrations will be performed on the monitor prior to the first sample, and at quarterly intervals thereafter. The calibrations will insure the flow rate through the monitor is within acceptable ranges of accuracy.

### **LABORATORY ANALYTICAL PROCEDURES**

The samples will be prepared by the laboratory according to the ASTM method (D 3266-91). Only the gaseous paper tape will be analyzed. The analysis will be by NIOSH Method P&CAM 212. Data will be converted to parts per billion (ppb).

## **DATA REPORTING**

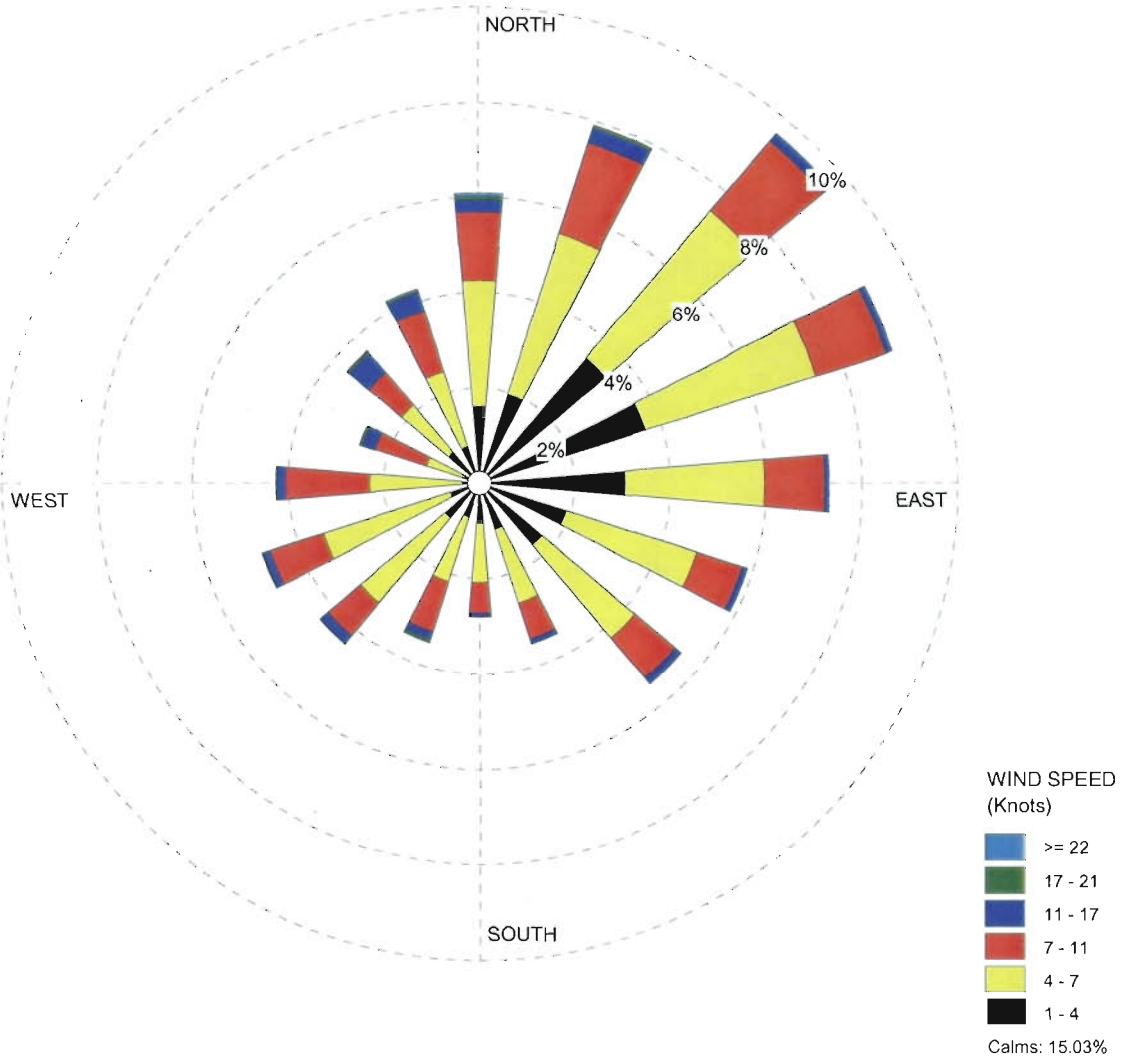
A report summarizing the results of the ambient fluorides data collected will be prepared and submitted to the FDEP by February 15, 2008. The report will also include the production rates of the A and B PAPs. The results will be segregated into data representative of pre-construction operation (i.e., production rates up to 15 percent higher than current permitted production rate), and post-construction operation (production rates greater than 15 percent higher than current permitted production rate). This will allow pre-construction and post-construction data to be evaluated for data trends.

WIND ROSE PLOT:

**5-Year Windrose, Tampa International Airport, Florida  
July through December, 2001 - 2005**

DISPLAY:

**Wind Speed  
Direction (blowing from)**



COMMENTS:	DATA PERIOD: <b>2001 2002 2003 2004 2005 Jul 1 - Dec 31 00:00 - 23:00</b>	COMPANY NAME: <b>Golder Associates</b>	
	CALM WINDS: <b>15.03%</b>	MODELER:	
	AVG. WIND SPEED: <b>5.44 Knots</b>	TOTAL COUNT: <b>21721 hrs.</b>	DATE: <b>6/11/2007</b>





Designation: D 3266 – 91 (Reapproved 2005)

## Standard Test Method for Automated Separation and Collection of Particulate and Acidic Gaseous Fluoride in the Atmosphere (Double Paper Tape Sampler Method)<sup>1</sup>

This standard is issued under the fixed designation D 3266; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

### 1. Scope

1.1 This test method describes the automatic separation and collection on chemically treated paper tapes of particulate and gaseous forms of acidic fluorides in the atmosphere by means of a double paper tape sampler. The sampler may be programmed to collect and store individual air samples obtained over time periods from several minutes to 3 h. A 30.5-m [100-ft] tape will allow unattended operation for the automatic collection of up to 600 samples.

1.2 The values stated in SI units are to be regarded as standard. The values given in brackets are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:<sup>2</sup>

- D 1071 Test Methods for Volumetric Measurement of Gaseous Fuel Samples
- D 1193 Specification for Reagent Water
- D 1356 Terminology Relating to Sampling and Analysis of Atmospheres
- D 1357 Practice for Planning the Sampling of the Ambient Atmosphere
- D 3195 Practice for Rotameter Calibration

D 3268 Test Method for Separation and Collection of Particulate and Gaseous Fluorides in the Atmosphere (Sodium Bicarbonate-Coated Glass Tube and Particulate Filter Method)

D 3269 Test Methods for Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Manual Procedures)

D 3270 Test Methods for Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Semiautomated Method)

D 3609 Practice for Calibration Techniques Using Permeation Tubes

D 3614 Guide for Laboratories Engaged in Sampling and Analysis of Atmospheres and Emissions

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1356.

### 4. Summary of Test Method

4.1 Air is drawn through an air inlet tube (see Practice D 1357) and is first passed through an acid-treated prefilter paper tape to remove particulate matter which may contain fluoride and then through an alkali-treated paper tape to remove acidic fluoride gases.

4.2 The exhaust air is filtered through soda lime-glass wool, and the cleaned air is used to pressurize the front compartment to prevent fluoride contamination of the paper tapes from the ambient air.

4.3 Automatically, at the end of the preset sampling period, the vacuum pump is turned off, the tapes are indexed, and after indexing the vacuum pump is turned on. Indexing results in a “dead time” of several seconds.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

Current edition approved Oct. 1, 2005. Published January 2006. Originally approved in 1973. Last previous edition approved in 2000 as D 3266 - 91(2000)<sup>1</sup>.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

4.4 The paper tapes are removed from the sampler after a selected period of operation and taken to an analytical work area where the individual sample spots are cut out, treated to dissolve the fluoride, and analyzed by potentiometric or photometric methods.<sup>3,4,5</sup>

### 5. Significance and Use

5.1 This test method provides a means of automatically separating and collecting atmospheric particulate and acidic gaseous fluoride samples.

5.2 Since the samples are collected on dry tapes, the samples are in a form which allows elution of the fluoride content with a small volume of eluent. Consequently, the method allows analyses of air samples taken for a time period as short as several minutes.

### 6. Interferences

6.1 Particulate metallic salts, such as those of aluminum, iron, calcium, magnesium or rare-earth elements, may react with and remove some or all of the acidic gaseous fluoride on the prefilter. If interfering quantities of such particulate metallic salts are present, the use of Test Methods D 3268 is recommended because the acidic fluoride gases are collected prior to the filter.

6.2 Acid aerosols or gases might neutralize or acidify the alkali-treated tape and prevent quantitative uptake of the acidic fluoride gases from the atmosphere. If this potential interference is present the decreased alkalinity of the water extract (13.2.2.1) may provide relevant information.

6.3 Aluminum or certain other metals or phosphates can interfere with subsequent analyses of the tapes by photometric or electrometric methods. These potential interferences are discussed in Test Methods D 3269 and D 3270.

6.4 There are several limitations of the test method that could possibly occur:

6.4.1 Although the acid-treated medium retentive prefilter has been shown to allow passage of hydrofluoric acid, it will restrict passage of particulate matter only as small as about 1  $\mu\text{m}$ . Thus, smaller particulate matter may pass through the filter and impinge on or pass through the alkali-treated second tape.

6.4.2 The maximum sampling time recommended in the method is 3 h. This time is limited to minimize the possible effect of particulate matter sorbing the acidic fluoride gases or reducing the sampling rate.

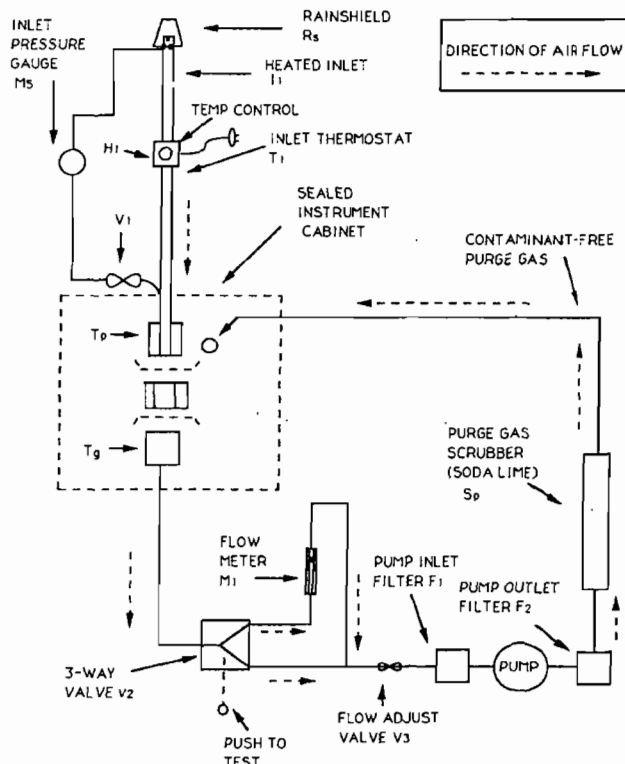


FIG. 1 Dual Tape Sampler Flow Schematic

### 7. Apparatus<sup>6</sup>

7.1 The double paper tape sampler is a modification of and utilizes the basic principles of the sequential paper tape sampler used for dust collection. The commercially available apparatus requires modification, as described in this test method, prior to use.<sup>7</sup> It consists of the following:

7.1.1 Heated Inlet— $I_1$ , TFE-fluorocarbon, 1 m [3.3 ft] in length, 9.5 mm [ $\frac{3}{8}$  in.] (outside diameter), encased in a 9.5 mm [ $\frac{3}{8}$  in.] (inside diameter) aluminum tube. See Fig. 1. The aluminum jacket is wrapped in a constant wattage heating wire of 25 W/m (8 W/ft). The tube is connected to the instrument with a TFE-fluorocarbon fitting.

7.1.1.1 Rainshield,  $R_s$ —Constructed of TFE-fluorocarbon.

7.1.1.2 Proportional Temperature Controller— $H_1$ , with thermocouple reference point located at the bottom of the sample chamber.

<sup>3</sup> Mandl, R. H., Weinstein, L. H., Weiskopf, G. J., and Major, J. L. "The Separation and Collection of Gaseous and Particulate Fluorides." Paper CP-25A, 2D International Clean Air Congress, Washington, DC, 1970.

<sup>4</sup> Weinstein, L. H., and Mandl, R. H. "The Separation and Collection of Gaseous and Particulate Fluorides." VDI Berichte Nr. Vol 164, 1971, pp. 53 to 63.

<sup>5</sup> Lodge, James P. Jr., ed., "Methods of Air Sampling and Analysis," Intersociety Committee, 3rd ed., Lewis Publishers, Inc., 1988, pp. 352-356.

<sup>6</sup> The sole source of supply of this apparatus known to the Committee is Anderson Samplers, Atlanta, GA. If you are aware of alternate suppliers, please provide this information to ASTM Headquarters, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

<sup>7</sup> Zankel, K. L., McGirr, R., Romm, M. Campbell, Miller, R. "Measurement of Ambient Ground-Level Concentrations of Hydrogen Fluoride," *Journal of The Air Pollution Control Association*, Vol 37: 1191-1196 (1987).

7.1.1.3 *Inlet Thermostat*— $T_1$ .

7.1.1.4 *Inlet Pressure Gauge*— $M_5$  with shutoff valve,  $V_1$ . One side of the gauge is connected to a TFE-fluorocarbon run tee placed between the intake tube and the sample block, and the other side is connected to a TFE-fluorocarbon run tee placed at the entrance to the intake tubing.

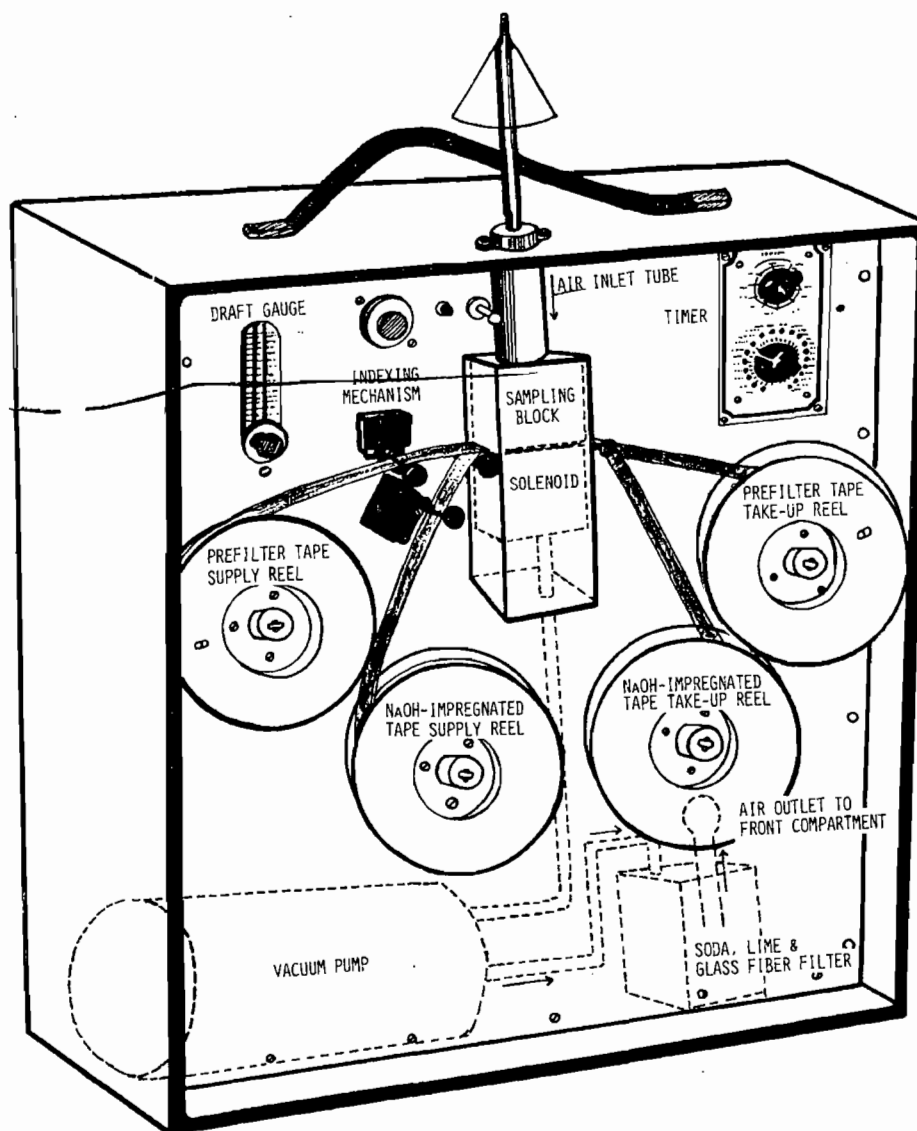
7.1.2 *Sampler*—See Figs. 1 and 2.

7.1.2.1 The upper part of the sampling block and sample inlet tube (Note 1) are constructed of polytetrafluoroethylene to minimize reactivity with acidic fluoride gases. The upper part of the sampling block ( $T_p$ ) has a cylindrical cavity 25.4 mm [1 in.] in diameter with the inlet tube to the cavity perpendicular to the paper tapes. The lower part of the sampling block ( $T_g$ ) shall be constructed of stainless steel with a 25.4 mm [1-in.] cylindrical cavity. The outlet tube from the cylindrical cavity

passes at a right angle into the pump compartment. The lower block shall be spring-loaded with a total force of 1.36 kg [3 lb] against the lower surface of the upper block. The surfaces of the two blocks shall be machined flat to ensure a tight seal. The lower block shall be lowered by means of an electric solenoid which counteracts the spring pressure.

7.1.2.2 *Capstans*, positioned to guide the paper tapes through the sampling block and to the take-up reel.

7.1.2.3 The paper tapes shall be drawn through the sample block and wound on the take-up reels by  $\frac{1}{30}$  Hz (2 rpm) synchronous motors. Indexing is accomplished either by mechanical or photoelectric means to provide even spacing between samples. Provision is made by the use of tape perforated at regular intervals, or by some other means, to locate the collected sample spots for subsequent analysis. A



Double Paper Tape Sampler  
 FIG. 2 Schematic Drawing of Double Paper Tape Sampler

relay is wired in series with the indexing mechanism to turn off the vacuum pump during tape transport.

7.1.2.4 *Interval Timer*, used to provide desired sampling times.

7.1.2.5 *Carbon-Vane Vacuum Pump*, to sample air, of nominal 30 L/min (1 ft<sup>3</sup>/min) free-air capacity. This provides a sampling rate through two tapes of about 15 L/min (0.5 ft<sup>3</sup>/min). Exhaust air from the pump is passed through a soda lime-glass wool filter ( $S_p$ ) and the filtered air is used to pressurize the front compartment and prevent contamination by fluorides from the ambient air.

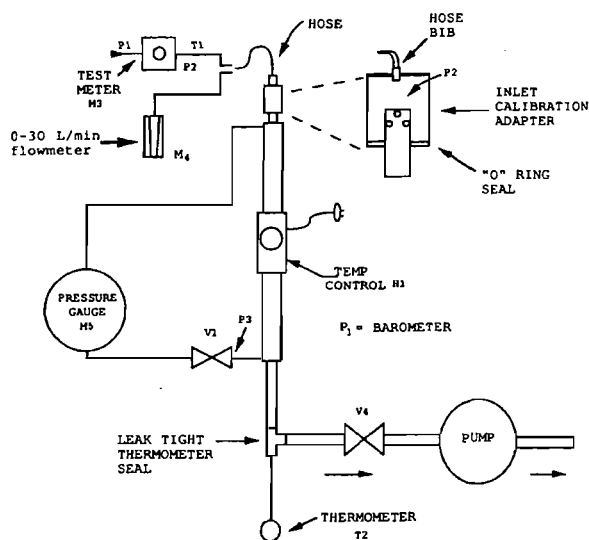


FIG. 3 Inlet Flow Calibration Schematic

7.1.2.6 *Sample Flow Adjustment Valve*—An inline needle valve,  $V_3$ .

7.1.2.7 *Flow Indicator*—0–30 L/min (0–1 ft<sup>3</sup>/min)  $M_1$ .

7.1.2.8 *Paper Tape*—38-mm [1.5-in.] wide, appropriately treated chemically (10.1).

7.1.2.9 Provision shall be made for manual override of the tape transport mechanism.

7.1.2.10 All fittings shall be constructed of TFE-fluorocarbon.

7.2 *Calibration Equipment*—See Fig. 3.

7.2.1 *Inlet Calibration Adapter*—To connect hose from flow calibration equipment to sampler inlet.

7.2.2 *Flow Meter*— $M_4$ , 0–30 L/min (0–1 ft<sup>3</sup>/min), calibrated in accordance with Practice D 3195.

7.2.3 *Wet Testmeter*— $M_3$ , calibrated in accordance with Test Methods D 1071.

7.3 *HF Permeation Tube Calibrator*—A permeation tube device, modified as described in Footnote 10. See also Practice D 3609. All components of the calibrator that come into contact with HF shall be constructed of TFE-fluorocarbon.

## 8. Reagents and Materials

8.1 *Purity of Reagents*—All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>8</sup>

8.2 *Purity of Water*—Water shall be Grade II Reagent conforming to Specification D 1193. Additionally, the water used in the sampling and analytical procedures shall be demonstrated by testing with a specific ion electrode or by concentration and photometric analysis to contain less than 0.005 µg/mm of fluoride.

8.3 Chemically treated medium retentive filter paper tape 38-mm [1.5-in.] wide shall be used as the prefilter.

8.4 Chemically treated soft open filter paper 38-mm [1.5-in.] wide shall be used to remove acidic gaseous fluorides.

8.5 *Citric Acid, Alcoholic, Solution (0.1 M)*—Dissolve 4.203 g of citric acid monohydrate in 200 mL of 95 % ethyl alcohol.

8.6 *Sodium Hydroxide, Alcoholic Glycerin Solution (0.5 N)*—Dissolve 4.000 g of NaOH pellets in 200 mL of 95 % ethyl alcohol containing 5 % glycerol.

8.7 *Total Ionic Strength Adjustment Buffer (TISAB)*—Add 57 mL of glacial acetic acid, 58 g of NaCl and 4.0 g of CDTA ((1,2-cyclohexylenedinitrilo)tetraacetic acid) to 500 mL of distilled water. Stir and add 5 N NaOH solution (8.11) slowly until pH is between 5.0 and 5.5. Cool and dilute to 1 L.

8.8 *TISAB (1 + 1)*—Dilute the full strength TISAB (8.7) 1 + 1 with an equal amount of reagent water.

8.9 *Sulfuric Acid (1.0 N)*—Add 28.0 mL of concentrated H<sub>2</sub>SO<sub>4</sub>(sp gr 1.84) to 250 mL of reagent water in a 1-L volumetric flask. Swirl to mix, cool, and dilute to 1 L with reagent water. Mix thoroughly.

8.10 *Sodium Hydroxide Solution (1.0 N)*—Dissolve 40.0 g of NaOH in 250 mL of reagent water in a 1000-mL volumetric flask. Swirl to mix, cool, and dilute to 1000 mL with reagent water. Mix thoroughly.

8.11 *Sodium Hydroxide Solution (5.0 N)* Dissolve 200.0 g of NaOH in a 1-L volumetric flask. Swirl to mix, cool, and dilute to 1 L with water. Mix thoroughly.

8.12 *Hydrogen Fluoride Permeation Tube*—200 ng/min at 35°C is satisfactory.<sup>7</sup>

## 9. Sampling

9.1 See Practice D 1357 for general sampling guidelines.

9.2 Carefully align the sample block assembly to minimize leakage.

9.3 Adjust temperature controller for a temperature of 54°C [130°F].

9.4 Adjust flow rate to 15 L/min (0.5 ft<sup>3</sup>/min).

<sup>8</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

9.5 Adjust timer to required sample time.

9.6 When temperature of inlet is stable at 54°C, at a flow rate of 15 L/min, advance tape, and commence sampling.

9.7 Record the reading of the inlet pressure gauge,  $M_5$ , for measurement of the air flow through the inlet tube. The air flow should remain reasonably constant over the sampling period selected.

9.8 Prior to removing the tapes, the reading of the static pressure meter should again be recorded to provide an average air flow measurement over the total operational period.

9.9 Remove the paper tapes at convenient intervals and place each in separate clean containers.

9.10 Analyze the individual samples by photometric or electrometric methods as referenced below and described in Test Methods D 3269 and D 3270.

## 10. Preparation of Apparatus

10.1 *Treatment of Paper Tapes*—Treat the paper tapes by passing the tapes through the appropriate impregnating solution and under a dryer and then rewinding. This is preferably done with a continuous motor-driven system.

10.1.1 *Treatment of the Medium Retentive Prefilter*—Treat this tape with the alcoholic citric acid solution, 0.1 *M* (8.5).

10.1.2 *Treatment of the Soft Open Prefilter*—Treat this tape with the alcoholic NaOH glycerol solution, 0.5 *N* (8.6).

10.2 Place the prefilter tape on the upper supply reel and the acidic gaseous fluoride tape on the lower supply reel. Thread the tapes through the sampling block and to their respective take-up reels.

## 11. Flow Calibration

11.1 Remove the inlet from the calibration system, and set up calibration equipment in accordance with Fig. 3.

11.2 Open valve  $V_1$ .

11.3 Adjust temperature controller for a temperature of 54°C [130°F] at  $T_2$ , when 30 L/min (1.0 ft<sup>3</sup>/min) is flowing through the system.

11.4 Connect tubing from inlet calibration adapter to flow meter  $M_4$ , and adjust the flow rate to 30 L/min.

11.5 Without changing the valve setting, connect inlet hose to the test meter ( $M_3$ ). Allow the system to establish equilibrium, and record the pressure at  $P_3$ , with pressure gauge  $M_5$ .

11.6 Measure the flow through the system, using the wet test meter and stopwatch.

11.7 Repeat at 6 other flowrates, such as 1.5, 6, 12, 18, and 24 L/min, adjusting the outlet temperature at  $T_2$  to 54°C each time.

11.8 Draw a calibration curve of corrected flow into the instrument versus indicating gauge scale ( $M_5$ ).

11.9 Reinstall the inlet on the instrument after removing the thermometer  $T_2$  and the inlet calibration adapter. Close valve  $V_1$  when flow is not being monitored. See Note 1.

NOTE 1—If other inlet temperatures are used within the limits of the control, prepare a new calibration curve for each temperature selected. An empirical calibration of this type is more accurate than a calculated correction based on the gas laws.

## 12. Procedure for Obtaining Tape “Blank Values”

12.1 *Blank on Reagents*—About 50 % of the treated tapes should be checked for fluoride levels by preparing and analyzing the unused tape as outlined in Section 13.

12.2 *Field Blanks on Tapes*—Cut the equivalent of four spots from the section of tape following the last sample after removing and discarding the last few inches of the tape which may have been handled during removal of the tape from the tape sampler. Analyze these four spots as one sample. The total fluoride content of these field blanks should rarely exceed 0.3 µg of fluoride.

## 13. Preparation of Samples for Fluoride Analysis

13.1 Carry analysis out in a work area with an atmosphere free of contamination by fluorides.

13.2 Preparation of the tapes used to collect acidic gaseous fluoride for fluoride analysis.

13.2.1 *For Potentiometric Analysis:*

13.2.1.1 Cut out individual sample spots and place in clean 15 by 150-mm test tubes. Add 5 mL of 1 + 1 TISAB solution (8.8) and mix for several seconds with a vortex mixer. Decant into a clean high-pressure linear polyethylene (or polypropylene or TFE-fluorocarbon) beaker.

13.2.1.2 Analyze using the potentiometric method given in Test Methods D 3269.

13.2.2 *For Semiautomated Analysis:*

13.2.2.1 Cut out individual sample spots and place in clean 15 by 150-mm test tubes. Add 5.0 mL of deionized water and mix for several seconds with a vortex mixer. Filter samples (to remove cellulose fibers) into 8.5-mL sample cups by a semimicro filtration method.

13.2.2.2 Analyze using the semiautomated method given in Test Methods D 3270.

13.3 *Preparation of the Prefilter Tapes Used to Collect Particulate Matter for Fluoride Analysis:*

13.3.1 *For Potentiometric Analysis:*

13.3.1.1 Cut out individual sample spots and place in 15 by 150-mm test tubes. Add 5.0 mL of 1 *N* H<sub>2</sub>SO<sub>4</sub> (8.9), mix for several seconds with a vortex mixer, and allow to stand for 5 min.

13.3.1.2 Add an equal volume of 1 *N* NaOH solution (8.10). Decant into a clean high-pressure linear polyethylene (or polypropylene or TFE-fluorocarbon) beaker and add 10.0 mL of TISAB solution (8.8). See Note 2.

NOTE 2—In any specific sampling program, the quantitative recovery of the fluoride content of the tape by 1 *N* H<sub>2</sub>SO<sub>4</sub> extraction shall be confirmed. (See Test Methods D 3269).

13.3.1.3 Analyze using the potentiometric method given in Test Methods D 3269.

13.3.2 *For Semiautomated Analysis:*

13.3.2.1 Cut out individual sample spots and place in clean 15 by 150-mm test tubes. Add 5.0 mL of 1 *N* H<sub>2</sub>SO<sub>4</sub> (8.9), mix for several seconds with a vortex mixer, and allow to stand for 5 min. Filter samples (to remove cellulose fibers) into 8.5-mL sample cups by a semimicro filtration method.

13.3.2.2 Analyze the sample using the semiautomated method given in Test Methods D 3269.

13.4 *Calibration and Standards*—None required.

#### 14. Calculation

14.1 Calculate the volume of air sampled as follows:

$$C = (R \times 10^{-3}) (t_s) (n_s) \quad (1)$$

where:

$C$  = sample volume at 25°C [77°F] and 101.3 kPa (760 mm Hg), m<sup>3</sup>

$R$  = sampling rate at 25°C [77°F] and 101.3 kPa (760 mm Hg), L/min obtained from the calibration curve prepared for the draft gauge,

$t_s$  = minutes sampled per spot, and

$n_s$  = number of spots used for one analytical sample.

14.2 Calculate the results for either the prefilter tape or the acidic gaseous fluoride tape.

$$S = (A - B)/C \quad (2)$$

where:

$S$  = concentration of fluoride, µg/m<sup>3</sup>,

$A$  = mass of fluoride in the spots,  $n_s$ , µg, and

$B$  = mass of fluoride in the blank of  $n_s$  spots, µg.

#### 15. Quality Assurance

15.1 Establish a Quality Assurance Program for ambient HF measurement systems in accordance with Guide D 3614. It shall include the use of the HF calibrator and HF permeation tube to determine the efficiency of sample collection, at a frequency determined by the results of the QA program.

#### 16. Precision and Bias <sup>9</sup>

16.1 *Precision:*

16.1.1 With 1-h samples, the relative standard deviation of the fluoride measurements (including collection efficiency) was found to be 5 % in the range of 1 to 3 µg/m<sup>3</sup>, and <1 % at higher concentrations (10 to 20 µg/m<sup>3</sup>). With a probe heated at 70°C, relative humidities of 45 to 90 % had no effect on precision in the range of 1 to 20 µg/m<sup>3</sup>.

16.1.2 For potentiometric measurements of concentrations in air less than 3 µg/m<sup>3</sup>, the temperature of eluted samples must be maintained to ±1°C during the measurement. Each degree Celsius differential results in a 2 to 3 % error.

16.2 *Bias*—Fluoride recovery was >95 % for known amounts of fluoride in the range 2 to 20 µg/m<sup>3</sup> and sampling times of 20 to 120 min. Negligible amounts of gaseous fluoride were removed by the prefilter at relative humidities of 45 to 95 % when the sample air passing through the inlet tube was heated to 54°C. Since the studies showed that dust can effect bias significantly, the inlet probe must be cleaned regularly under dusty conditions.

#### 17. Keywords

17.1 acidic gaseous fluoride; ambient atmospheres; double paper tape sampler; fluoride; particulate fluoride; tape sampler

<sup>9</sup> Supporting data available from ASTM Headquarters, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959. Request RR:D22-1020.

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