



# STANDARD OPERATING PROCEDURES

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## DETERMINATION OF FLUORIDE IN AIR SAMPLES BY ION-SELECTIVE (ISE) METHODS

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### 1.0 SCOPE AND APPLICATION

This method can be used for analyzing particulate and gaseous (soluble) fluoride in air samples that have been collected using filter/treated pad cassettes. The method applies to samples from mining, aluminum reduction, ceramic, glass etching, electroplating, semiconductor, and fluorochemical industries. This Standard Operating Procedure (SOP) only addresses the preparation and analysis of samples for gaseous and particulate fluoride in air.

Detection limits, sensitivity, and optimum ranges for fluoride analysis will vary with the cassette filter material, volume of air sampled, and type of ion-selective electrode (ISE) used. ISEs must be used carefully and results must be interpreted cautiously, since an ISE may be affected by numerous analytical interferences that may either increase or decrease the apparent analyte concentration, or may damage the ISE. Effects of most interferences can be minimized or eliminated by adding appropriate chemical reagents to the sample. ISE manufacturers usually include a list of interferences in the instruction manual accompanying the ISE, along with recommended methods for minimizing or eliminating effects of these interferences.

These are standard (i.e. typically applicable) operating procedures which may be varied or changed as required, depending upon site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (U.S. EPA) endorsement or recommendation for use.

### 2.0 METHOD SUMMARY

Total solubilized fluoride is determined potentiometrically using a fluoride ISE in conjunction with a standard single-junction reference electrode, or a fluoride combination ISE. A pH meter with an expanded millivolt (mV) scale or an ISE meter capable of being calibrated directly in terms of fluoride concentration is also required.

Standards and samples are mixed 1:1 with a total ionic strength activity buffer (TISAB). The TISAB adjusts ionic strength, buffers pH to 5-5.5, and contains a chelating agent to break up metal-fluoride complexes. Calibration is performed by analyzing a series of standards and plotting mV vs. the logarithm of the fluoride concentration or by calibrating the ion meter directly in terms of fluoride concentration.

### 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

All samples must have been collected according to NIOSH method 7902 (Appendix A). After collection, samples must be stored and packed securely for shipment.

### 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

In samples containing cryolite, aluminum is sufficiently concentrated to give erroneous fluoride concentrations. Hydroxide ion concentrations greater than one-tenth of the fluoride level present in the sample gives a positive interference. Polyvalent cations  $\text{Fe}^{+3}$ ,  $\text{Si}^{+4}$ , and  $\text{Al}^{+3}$  give negative interferences. Adding TISAB, which contains a strong chelating agent, suppresses up to 500  $\mu\text{g/mL}$   $\text{Fe}^{+3}$  and up to 90  $\mu\text{g/mL}$   $\text{Si}^{+4}$ .

Sample pH is critical. Hydroxide ion interferes significantly with the electrode response to fluoride when the hydroxide level is greater than one-tenth the fluoride concentration. This interference is avoided by adding TISAB,



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which buffers the sample at a pH of 5-5.5 and prevents the formation of hydrogen complexes of fluoride.

Temperature changes affect electrode potentials; therefore, standards and samples must be equilibrated at the same temperature (+/- 2°C) to achieve accurate results.

### 5.0 EQUIPMENT/APPARATUS

#### 5.1 pH/mV meter

pH/mV meter capable of reading to 0.1 mV and pH electrode. pH paper may also be used to determine pH. Alternatively, an ISE meter may be used.

#### 5.2 Fluoride ISE

Combination fluoride ISE (Orion 9609 or equivalent), or separate fluoride ISE (Orion 9409 or equivalent) and reference electrode (Orion 9001 or equivalent) prepared for use as described in owner's manual.

#### 5.3 Magnetic stirrer

Thermally isolated magnetic stirrer and polytetrafluoroethylene (PTFE) - coated stir bars.

#### 5.4 Glassware

Volumetric flasks, 50-, 100-, and 1,000-mL. Pipettes, appropriate sizes for preparing standards and spiking samples.

#### 5.5 Polyethylene labware

Beakers, 100- or 150-mL; Bottles, 60-, 125-, and 1000-mL.

#### 5.6 Crucibles

Nickel, zirconium, or Inconel, 20- or 30- mL with covers.

#### 5.7 Laboratory furnace

Automatic temperature control, 100 to 700 °C (Thermolyne Type 6000 Furnace or equivalent).

### 6.0 REAGENTS

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

#### 6.1 Reagent Water



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All references to water in this method refer to reagent water (Type I Water, ASTM D1193)

6.2 Sodium Hydroxide Solution (NaOH), 20% (w/v) or 5M

Dissolve 200 g of NaOH in reagent water to make 1-L NaOH solution. Store in a tightly sealed polyethylene bottle. Alternatively, 20% NaOH solution is commercially available (VWR VW3216-1 or equivalent).

CAUTION: This solution is extremely corrosive.

6.3 Potassium Chloride (KCl)

6.4 Sodium Acetate ( $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ )

6.5 Cyclohexylene Diamine Tetra-Acetic Acid (CDTA)

6.6 Hydrochloric Acid (HCl), 1:1 (v/v)

Carefully add an equal amount of concentrated HCl to reagent water, cool, and store in a polyethylene bottle.

6.7 Sodium Fluoride (NaF)

6.8 TISAB Solution

To approximately 500 mL of reagent water add 37 g KCl, 68 g sodium acetate, and 346 g CDTA. Stir to dissolve and adjust the solution pH to 5.5 +/- 0.2 with 1:1 HCl. Transfer the solution to a 1,000 mL volumetric flask and dilute to the mark with reagent water. Transfer and store the solution in a polyethylene bottle. Alternatively, TISAB solution is available commercially (VWR VW3492-1 or equivalent).

6.9 Fluoride Calibration Stock Solution, 100 mg/L  $\text{F}^-$

Dissolve 0.2211 g of sodium fluoride (NaF, dried two hours at 105 °C and stored in a desiccator) in reagent water and dilute to 1000 mL in a volumetric flask. Store in a clean polyethylene bottle. Alternatively, fluoride stock solution is available commercially (CPI International, 4400-01002, 100 mg/L, or equivalent).

6.10 Fluoride Reagent Blank Solutions

6.10.1 Gaseous Fluoride

Add 500-mL reagent water to 500-mL TISAB in a polyethylene bottle, store tightly capped.

6.10.2 Particulate Fluoride

Add 100-mL 20% NaOH to 500-mL TISAB, stir and adjust pH to 5.5 +/- 0.2 with 1:1 HCl.



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Transfer to 1-L volumetric flask and dilute to the mark with reagent water. Transfer and store in a tightly capped polyethylene bottle.

### 6.11 Fluoride Calibration Standards

Prepare a minimum of seven calibration standards (50 mL each) by diluting the 100 mg/L fluoride standard (section 6.9) with the appropriate reagent blank solution (particulate or gaseous fluoride, section 6.10) in 50-mL volumetric flasks.

To provide better accuracy and precision at low  $F^-$  concentrations, use calibration standards from 0.001 to 0.100 mg  $F^-$  per 50 mL sample (0.02 to 2.0 mg/L) for gaseous (soluble) fluoride, and 0.0025 to 0.250 mg  $F^-$  per 50 mL sample (0.05 to 5.0 mg/L) for particulate fluoride. The linear range can be verified with a linear analytical range (LAR) standard at 10.0 mg/L.

Transfer standards to 60-mL polyethylene bottles for storage. Working standards are stable at least one month in polyethylene bottles at 4 °C.

## 7.0 PROCEDURES

### 7.1 Cellulose Ester Membrane Filter (particulate fluoride)

Water-soluble particulate fluorides may be extracted by the procedure for gaseous fluorides (section 7.2). Insoluble particles require fusion.

Transfer the membrane filter to a crucible containing 5-mL of 20% NaOH. Evaporate to dryness. Cover and place the crucibles in the laboratory furnace, ramp the temperature to 600 °C, and heat the residue at 600 °C for 30-minutes. Cool the crucibles and dissolve in approximately 5-mL reagent water. Transfer the sample into a 100-mL plastic beaker. Rinse the crucible with 25-mL of TISAB, then with a few drops of 1:1 HCl. Adjust to pH 5.5 +/- 0.2 using 1:1 HCl. Transfer to a 50-mL volumetric flask and dilute to volume with reagent water. The sample may be transferred and stored in a 60-mL polyethylene bottle prior to analysis.

NOTE: Fluorides are extremely corrosive to skin, eyes, and mucous membranes. Perform all fusions in a fume hood.

### 7.2 Treated Pad (gaseous fluoride)

Transfer the treated pad to a 100-mL plastic beaker. Add 50-mL of gaseous fluoride blank solution (section 6.10.1). Soak the pad for at least 30-min with sufficient stirring to reduce it to a pulp. The sample may be transferred and stored in a 125-mL wide-mouth polyethylene bottle prior to analysis.

### 7.3 Media Blank

Prepare the media blank using blank filter media from the same lot as the unknown samples. Prepare the media blank using the procedure outlined in Section 7.1 or 7.2 at the same time the samples are prepared. A minimum of one media blank per batch of samples (not to exceed 20 samples) must be prepared. If a lot blank is provided with the samples, it may be used as the media blank and an additional lot blank does



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not need to be prepared.

### 7.4 Media Blank Spike/Blank Spike Duplicate

Prepare the media blank spike (BS) and blank spike duplicate (BSD) samples by spiking blank filter media with known amounts of fluoride (5 to 10 times the detection limit). Spike blank filter media with appropriate amounts of fluoride and prepare the BS/BSD samples using the procedure outlined in Section 7.1 or 7.2. BS/BSD samples are prepared in the laboratory to monitor the precision and accuracy of the method. Use the BS/BSD samples delivered to the laboratory with the unknown samples, or blank filter cassettes from the same lot, if none are provided with the samples.

### 7.5 Reagent Blank Spike/Blank Spike Duplicate

Prepare the reagent blank spike and blank spike duplicate samples by spiking reagent blank with known amounts of fluoride (5 to 10 times the detection limit). Reagent blank spike/spike duplicate samples are prepared in the laboratory to monitor reagent contamination, and the precision and accuracy of the method.

### 7.6 Calibration

If using a fluoride combination ISE, ensure that the ISE is filled with the solution recommended by the manufacturer. Change the solution if the ISE has not been used for an extended period. If using a fluoride ISE and a separate reference electrode, ensure that the reference electrode is filled with the solution recommended by the manufacturer. Equilibrate the electrode in the solution recommended by the manufacturer before use. Prepare separate calibration curves for particulate and gaseous fluorides.

Allow standard solutions to equilibrate to room temperature prior to calibration and analysis. The standards must be at the same temperature (within  $\pm 2$  °C) for accurate results. Prior to and between analyses, rinse the electrode thoroughly with reagent water and gently shake off excess water. Low level measurements are faster if the electrode tips are first immersed for five minutes in reagent water.

Calibrate the fluoride ISE using standards that bracket the expected sample concentration. Pour approximately 20 to 25 mL of each standard into plastic beakers. Add a PTFE coated magnetic stir bar, place the beaker on a magnetic stir plate, and stir at slow speed. Immerse the electrode tips to just above the rotating stir bar. If using an ISE meter, calibrate the meter in terms of fluoride concentration following the manufacturer's instructions. If using a pH/mV meter, record the meter (mV) as soon as the reading is stable (typically after 2 min), but not more than five minutes after immersing the electrode tips.

Prepare a calibration curve by plotting measured potential (mV) as a function of the logarithm of fluoride concentration. The slope must indicate a 54-60 mV change per 10-fold change in fluoride concentration. If the slope is not acceptable, the ISE may not be working properly. For corrective action, consult the ISE operating manual (Reference 1).

NOTE: Use only plasticware (polyethylene) when preparing and analyzing fluoride samples.

### 7.7 Analysis

Allow samples to equilibrate to room temperature (within  $\pm 2$  °C). Prior to and between analyses, rinse



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the electrode thoroughly with reagent water and gently shake off excess water. Low-level measurements are faster if the electrode tips are first immersed for five minutes in reagent water.

Pour approximately 20 to 25 mL of the sample into a plastic beaker. Add a PTFE-coated magnetic stir bar. Place the beaker on a magnetic stir plate and stir at a slow speed. Immerse the electrode tips to just above the rotating stir bar. Record the meter reading (mV or concentration) as soon as the reading is stable (typically after 2 min), but not more than five minutes after immersing the electrode tips. If reading mV, determine fluoride concentration from the calibration curve.

When analyses have been completed, rinse the electrodes thoroughly and store them in an appropriate fluoride standard solution (per manufacturer's instructions). If the electrodes will non extended time, drain the internal filling solution, rinse with reagent water, and store dry (per manufacturers instructions).

If the measured concentration is higher than the calibration range, dilute with the appropriate blank solution (section 6.10), re-analyze, and apply the dilution factor in calculations.

When the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition may be used.

#### 8.0 CALCULATIONS

If using an ISE meter, read the fluoride concentration in mg/L directly from the read-out system. If using a pH/mV meter, record the meter reading (mV) and then, interpolate the fluoride concentration (mg/L) from the calibration using a linear regression of mV versus the logarithm of the fluoride concentration. Calculate the fluoride concentration in the sample (A) as follows:

$$A = \text{mg/L fluoride sample} = B \times \frac{D + C}{D}$$

where:

- B = Concentration of fluoride (mg/L)
- C = Amount of blank matrix used for dilution (mL)
- D = Sample aliquot used for dilution (mL)

Note: If a dilution was not required, C = 0, and A = B.

Calculate the amount of fluoride (W) for each filter (or pad):

$$W = \text{mg/filter fluoride} = A \times \frac{FV}{1000}$$

where:

- A = Concentration of fluoride in the sample (mg/L)
- FV = Final solution volume (mL)





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Calculate the concentration ( $\text{mg}/\text{m}^3$ ) of fluoride in the air volume sampled:

$$\text{mg}/\text{m}^3 \text{ fluoride} = 000 \times \frac{W - \text{BLK}}{V}$$

where:

- W = Concentration of fluoride in each filter/pad ( $\text{mg}/\text{filter}$ )
- BLK = Concentration of fluoride present in the media blank ( $\text{mg}/\text{filter}$ )
- V = Volume of air sampled ( $\text{L}/\text{filter}$ )

NOTE: If one media blank is analyzed, do not subtract if the value is  $<\text{MDL}$ . If more than one media blank is analyzed, BLK is the average media blank concentration. For values  $<\text{MDL}$ , substitute zero (0) for the raw data prior to calculating the average. The calculated average is then subtracted from each sample even if the average is  $<\text{MDL}$ .

NOTE: Report  $\text{mg}/\text{filter}$  results for lot blank, trip blank, field blank(s), and BS/BSD samples because no air volume is collected for these samples.

All final results and MDLs must be reported to two significant figures.

### 9.0 QUALITY ASSURANCE/QUALITY CONTROL

All quality control data should be maintained and available for easy reference or inspection.

#### 9.1 Initial Calibration Verification Standard (ICV)

After performing the calibration step (7.6), verify the calibration by analyzing an ICV. The ICV contains a known fluoride concentration near the mid-range of the calibration standards and should be from an independent source. ICV recovery must be within 90-110%. If not, the error source must be found and corrected. An acceptable ICV must be analyzed prior to sample analysis. The ICV also serves as a laboratory control sample.

#### 9.2 Continuing Calibration Verification Standard (CCV)

After every 10 samples, and after the final sample, a CCV must be analyzed. The CCV contains a known fluoride concentration near the mid-range of the calibration. CCV recovery must be within 90-110%. If not, the error source must be found and corrected. If ISE calibration has changed, all samples analyzed since the last acceptable CCV must be re-analyzed. All samples must be bracketed between two acceptable calibration verifications.

#### 9.3 Initial/Continuing Calibration Blank (ICB/CCB)

After the ICV and after every CCV, an ICB or CCB must be analyzed using the reagent blanks prepared in section 6.10. The ICB or CCB concentration must be less than the fluoride detection limit. If not, the contamination source must be found and corrected. All samples analyzed since the last acceptable reagent blank must be re-analyzed. All samples must be bracketed by two acceptable calibration blanks.

#### 9.4 Media Blank Spike



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At least one media BS and BSD must be run with each batch of samples (not to exceed 20 samples), or with each sample matrix type to verify the accuracy and precision of the method. The spike concentration should be 5 - 10 times the detection limit and the volume added must be negligible.

Media Blank Spike percent recovery (%R) must be within 75-125% and calculated as:

$$\text{Matrix Spike Recovery}(\%R) = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = spiked sample result, mg/filter  
SR = media blank result, mg/filter  
SA = spike added, mg/filter

The Relative Percent Difference (RPD) of the media BS and BSD samples should be within  $\pm 20\%$  and calculated as:

$$RPD = \frac{[SR - BSR]}{(BSR + MSBR)/2} \times 100$$

where,

BSR = %R for the media spike sample (BS)  
MSBR = %R for the media spike duplicate sample (BSD)

### 9.5 Other QC Requirements

A linear analytical range (LAR) standard may be analyzed after calibration standards (before ICV) to determine maximum linear range of the calibration. Recovery must be within 85 - 115%. If the recovery is outside these limits, the maximum standard concentration defines the linear range.

The reagent blank spike/spike duplicate recoveries must be within 75 - 125%. If recovery is outside acceptable limits, prepare and analyze an additional reagent blank spike. If the additional spike fails, investigate the source of error prior to continuing the analysis.

### 10.0 DATA VALIDATION

Data validation will be performed by the Data Validation & Report Writing Group. Data will be assessed in accordance with the guidelines set forth in the most current version of ERT/REAC SOP #1017, *Data Validation Procedures for Routine Inorganic Analysis*. However, data is considered satisfactory for submission purposes if all procedures for analyzing fluoride in air samples are followed and QA/QC criteria are met.

### 11.0 HEALTH AND SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for following the chemical hygiene plan and laboratory safety program regarding the safe handling of the chemicals specified in this



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method.

When working with potentially hazardous materials, refer to U.S. EPA, OSHA and corporate health and safety practices. More specifically, refer to ERT/REAC SOP #3013, *REAC Laboratory Safety Program*.

#### 12.0 REFERENCES

Orion Research Incorporated. 1991. *Instruction Manual*. Model 94-09 and 96-09 Fluoride/Combination Fluoride Electrodes. Rev. C.

#### 13.0 APPENDICES

A - NIOSH Method 7902. Fluorides, Aerosol and Gas.



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APPENDIX A  
NIOSH Method 7902. Fluorides, Aerosol And Gas  
SOP #1812  
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### FLUORIDES, aerosol and gas by ISE 7902

F<sup>-</sup> MW: 18.998 CAS: (HF) 7664-39-3 RTECS: (HF) MW7875000

METHOD: 7902, Issue 2 EVALUATION: PARTIAL Issue 1: 15 February 1984  
 Issue 2: 15 August 1994

OSHA : 2.5 mg/m<sup>3</sup> (fluorides); 3 ppm (HF)  
 NIOSH: 2.5 mg/m<sup>3</sup> (fluorides); 3 ppm (HF); STEL 6 ppm (HF)  
 ACGIH: 2.5 mg/m<sup>3</sup> (fluorides); C 3 ppm (HF) (1 ppm HF = 0.818 mg/m<sup>3</sup> @ NTP)

PROPERTIES: HF: liquid; BP 19.5 °C; fluoride salts liberate HF in presence of acids

SYNONYMS: sodium fluoride (CAS #7681-49-4); hydrogen fluoride; hydrofluoric acid; cryolite; sodium hexafluoroaluminate (CAS #13775-53-6).

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER + TREATED PAD (0.8-µm cellulose ester membrane + Na <sub>2</sub> CO <sub>3</sub> -treated cellulose pad)	TECHNIQUE:	ION-SPECIFIC ELECTRODE
FLOW RATE:	1 to 2 L/min	ANALYTE:	fluoride ion (F <sup>-</sup> )
VOL-MIN:	12 L @ 2.5 mg/m <sup>3</sup>	FILTER (particulate F <sup>-</sup> ):	fuse in NaOH, dissolve in 50 mL water + TISAB
-MAX:	800 L	TREATED FILTER (gaseous F <sup>-</sup> ):	extract in 50 mL water + TISAB
SHIPMENT:	routine	CALIBRATION:	standard F <sup>-</sup> solutions in TISAB
SAMPLE STABILITY:	stable	RANGE:	0.03 to 1.2 mg F <sup>-</sup> per sample
BLANKS:	2 to 10 field blanks per set	ESTIMATED LOD:	3 µg F <sup>-</sup> per sample [1]
<b>ACCURACY</b>		PRECISION (S <sub>r</sub> ):	0.017 @ 55 to 220 µg per sample [2]
RANGE STUDIED:	not studied		
BIAS:	not determined		
OVERALL PRECISION (S <sub>r</sub> ):	not determined		
ACCURACY:	not determined		

**APPLICABILITY:** The working range is 0.12 to 8 mg/m<sup>3</sup> for a 250-L air sample. The method applies to mining samples, and samples from the aluminum reduction, ceramic, glass etching, electroplating, semi-conductor, and fluorochemical industries. If other aerosols are present, gaseous fluoride may be underestimated owing to sorption on collected particles, with concurrent overestimation of particulate/gaseous fluoride ratio [3-8].

**INTERFERENCES:** In samples containing cryolite, aluminum is sufficiently concentrated to give erroneous fluoride concentrations [3]. Hydroxide ion greater than 1/10 of the fluoride level will interfere positively. Fe<sup>3+</sup>, Si<sup>4+</sup>, and Al<sup>3+</sup> give a negative interference. Concentrations >8 µg/mL of these elements cannot be suppressed [9]. The TISAB suppresses up to 500 µg/mL Fe<sup>3+</sup> and up to 90 µg/mL Si<sup>4+</sup>.

**OTHER METHODS:** This revises method 7902 [10] which was withdrawn on 5/15/89. The method was originally based on a method by Eifers and Decker [11], and NIOSH method S176 for HF [2]. Method 7903 (Acids, Inorganic) is an alternative method for HF. Method 7906 (Fluorides by IC) employs the same sampling procedure, but uses ion chromatography for measurement.



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### REAGENTS:

1. Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ).
2. Glycerol.
3. Potassium chloride (KCl).
4. Sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ ).
5. Cyclohexylene diamine tetraacetic acid (CDTA).
6. Hydrochloric acid, 1:1 (v/v).
7. Sodium fluoride (NaF).\*
8. Deionized water.
9. Fixative solution. Dissolve 25 g  $\text{Na}_2\text{CO}_3$  in deionized water. Add 20 mL glycerol. Dilute to 1 L.
10. Total ionic strength activity buffer (TISAB), pH 5.5. Dissolve 37 g KCl, 68 g sodium acetate and 36 g CDTA in  $\text{H}_2\text{O}$ . Adjust to pH  $5.5 \pm 0.2$  with 1:1 HCl. Dilute to 1 L.
11. Calibration stock solution, 100  $\mu\text{g}/\text{mL}$ : Dissolve 0.2211 g NaF (dried at  $105^\circ\text{C}$  for 2 h) in deionized water; dilute to 1 L.
12. Sodium hydroxide, 20% (w/v). Dissolve 200 g NaOH in deionized water to make 1 L solution.

\* See SPECIAL PRECAUTIONS.

### EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 37-mm, 0.8- $\mu\text{m}$  pore size, with porous plastic backup pad (Nuclepore #220800, or equivalent), treated cellulose pad (Moisten with 0.8 mL fixative solution and dry at  $105^\circ\text{C}$  for 30 to 45 minutes. Discard if charred.) in a 3-piece cassette with a 1/2" extension. Assembly of sampler: Place treated pad in rear (outlet) piece of cassette, insert 1/2-inch extension, place porous plastic pad and membrane filter in upper part of extension, and insert top piece (inlet) of cassette. Press tightly together and seal with shrink band or tape.  
NOTE: Leak test with hand vacuum pump.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Crucibles, nickel, zirconium, or Inconel, 20- or 30-mL.
4. Bunsen or Meaker burner.
5. Tripod.
6. Triangle, ceramic-covered.
7. Volumetric flasks, 50- and 100-mL, and 1-L.
8. Pipets, appropriate sizes for standards.
9. Beakers, plastic, 100-mL or 150-mL.
10. Magnetic stirrer.
11. PTFE-coated stirring bars.
12. Fluoride ion selective electrode (ISE), NaF combination or with calomel-type reference electrode.
13. pH/ion meter with millivolt readout and pH electrode.
14. Hand vacuum pump.

### SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 2 L/min for a total sample size of 12 to 800 L. Do not exceed 2 mg total dust loading on the filter.
3. Pack securely for shipment.

**SPECIAL PRECAUTIONS:** Fluorides are extremely corrosive to skin, eyes and mucous membranes [12]. Perform all fusions in fume hood.

### SAMPLE PREPARATION:

4. **Cellulose ester membrane filter** (particulate fluoride).  
NOTE: Water-soluble particulate fluorides may be extracted by the procedure for gaseous fluorides. Insoluble particles require fusion.
  - a. Transfer the membrane filter to a crucible containing 5 mL 20% NaOH.
  - b. Evaporate to dryness.
  - c. Heat residue to fusion temperature, 1 to 2 min, cool and dissolve in ca. 5 mL deionized water.



# STANDARD OPERATING PROCEDURES

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- d. Transfer sample into 100-mL plastic beakers.
- e. Rinse crucible with 25 mL of TISAB then with a few drops of 1:1 HCl.
- f. Adjust to pH  $5.5 \pm 0.2$  using 1:1 HCl.
- g. Transfer to 50 mL volumetric flask; dilute to volume with deionized water.
5. **Treated pad** (gaseous fluoride).
  - a. Transfer treated pads to 100-mL plastic beakers.
  - b. Add 25 mL TISAB and 25 mL deionized water.
  - c. Soak pad for 30 min with sufficient stirring to reduce it to pulp.

### CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards over the range 3 to 1200  $\mu\text{g F}^-$  per sample.
  - a. Add known amounts of calibration stock solution to 25 mL TISAB and 5 mL 20% NaOH (particulate fluoride) or 25 mL TISAB (gaseous fluoride) in 100-mL beakers.
  - b. Adjust pH to  $5.5 \pm 0.2$  with 1:1 HCl.
  - c. Transfer to 50-mL volumetric flasks. Dilute to the mark with deionized water.  
NOTE: Working standards are stable at least one month in polyethylene bottles at 4 °C.
  - d. Analyze together with samples and blanks (steps 7 through 10).
  - e. Prepare separate calibration graphs (mV vs.  $\log \text{F}^-$  concentration) for particulate and gaseous fluorides.  
NOTE: Calibration curve is not linear below 0.1  $\mu\text{g/mL}$  or above 25  $\mu\text{g/mL}$ .

### MEASUREMENT:

7. Bring sample and standard solutions to room temperature.

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### EVALUATION OF METHOD:

Measurement precision,  $\bar{S}_p$ , in the range 0.055 to 0.22 mg HF per sample averaged 0.017 with average recovery 100.0% [2]. Analytical results on field samples report detection limits of 3  $\mu\text{g}$  per sample for both gaseous and particulate fluorides [1]. Reported collection ranges for gaseous fluoride and particulate fluorides were 4 to 61  $\mu\text{g}$  per sample and 4 to 410  $\mu\text{g}$  per sample, respectively [10].

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