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Development of a Solid Sorption Tube for Sampling Hydrogen Fluoride in the Work Atmosphere

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ABSTRACT

The efficiencies of several solid substances in a sorption tube for collecting trace quantities of hydrogen fluoride gas in work atmosphere have been evaluated. Reagent-grade sodium acetate crystals proved to be a very efficient sorbent for hydrogen fluoride. Its solubility in water and pH buffer properties are highly advantageous for subsequent fluoride determination by the ion selective electrode. Experimental results are presented for collection efficiencies of hydrogen fluoride gas at several concentration levels, flow rates, and collection times; the effects of elevated temperatures and humidity; and also breakthrough, bleed-out, storage and shipment studies. Specifications for construction of the sorption tubes are also given.

1. Introduction

This report summarizes work on the development of a sampling procedure and a device for collecting hydrogen fluoride gas in the work atmosphere, and subsequent quantitative determination of the collected gas in the laboratory. The work is part of the program under a Memorandum of Agreement between the National Bureau of Standards and National Institute for Occupational Safety and Health. The program calls for a development of procedures and devices for personal sampling applications, and analytical methods suitable for routine laboratory use. The gas sampling medium should consist of only solid substances.

1.1 Scope of the Work

As stated in the Memorandum of Agreement, the scope of the work includes:

A. Development of sampling procedures and devices for the collection of hydrogen fluoride gas in the industrial atmosphere, including:

    1. Evaluation of various solid sorbent materials.

    2. Selection of an appropriate sorbent based on the following criteria. A suitable sorbent shall:

        a. Be stable upon exposure to air flows, water vapor, temperature extremes, shipping, and storage.

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b. Retain the contaminant quantitatively during sampling, shipment, and storage up until the time of laboratory analysis.

c. Not react or degrade the contaminant in such a way as to prevent identification or change the concentration.

d. Be inexpensive to fabricate and purchase.

e. Be capable of manufacture in a manner so that reproducible collection and desorption properties can be obtained from batch to batch.

f. Be suitable for use in conjunction with personal samplers.

g. Be suitable in all respects for quantitative analysis of the collected materials.

h. Retain the substance of interest in the presence of other substances commonly present in industrial atmospheres.

i. Provide for specificity of measurement of the substance of interest, either by selective collection or by compatibility with selective analytical procedures.

3. Design of a suitable collection device containing the solid sorbent. The collection device should meet the following criteria:

a. The collection device should be as small in size and as light in weight as possible so that it can be attached to a worker's collar or lapel to collect a breathing zone sample.

b. The resistance of the collection device to air flow should not exceed 2.54 cm of mercury pressure drop at a flow rate of one liter per minute through the device, or 6.35 cm of water pressure drop at 200 cm^3 per minute.

c. There should be a method to verify that no breakthrough has occurred during sampling.

d. The collection device should have a sufficient capacity for collection of 4- to 8-hour samples at a flow rate between 50 and 200 cm^3 per minute, and for 15-minute samples at a flow rate of 1 liter per minute, for concentration ranges of

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1/5 to 5 times the threshold limit value (TLV)
concentrations of hydrogen fluoride.

B. Provision of suitable methods for retrieving the contam-
inant from the collection device and for analyzing the level
of contaminant which was collected. The present state-of-
the-art of analytical methods for hydrogen fluoride shall
be investigated. Candidate methods will be experimentally
evaluated for such factors as accuracy, reproducibility,
and criticality of steps. A procedure will be written for
the recommended method suitable for routine laboratory use.

C. Thorough evaluation of the recommended sampling and
analytical methods. The scope of the evaluation shall
include:

   1. Assessment of the collection efficiency of the
       collection device.

   2. Assessment of the effects of temperature and hu-
       midity on the breakthrough characteristics of the
       collection device.

   3. Measurement of the effects of shipping and storage
       of samples in adverse conditions of temperature and
       pressure on percent recovery and analytical accu-
       racy and precision.

   4. Measurement and quantitation of any bleed-out
       effects during extended sampling periods.

   5. Determination of the overall accuracy and precision
       of the recommended sampling and analytical methods,
       compared with known air concentrations.

   6. Assessment of the ruggedness of the recommended
       analytical methods according to the method of
       W. F. Youden given in the Association of Official
       Analytical Chemists paper, "Statistical Procedures
       for Collaborative Tests", where applicable.

   7. Determination of the accuracy and precision of the
       recommended analytical method according to
       American Society for Testing and Materials
       recommended practices.

   8. Determination of the useful range of the recommended
       sampling and analytical methods.

1.2 Method of Approach

For use as a personal sampler, the collection device containing solid sorbent materials should function with high efficiency and possess a large capacity for the contaminant hydrogen fluoride. The contaminant so collected should be completely retrievable for subsequent analysis. These three processes, sorption, retrieval, and analysis, as outlined on p 5 could be either specific or non-specific for hydrogen fluoride. For example, capture of volatile contaminants can be achieved by the mechanisms of physical adsorption/absorption or chemical reaction, each of which may or may not be specific for hydrogen fluoride. The recovery of the contaminant or its reaction product may involve specific or non-specific chemical or physical processes. Finally, analytical methods are available for specific and non-specific determination of hydrogen fluoride. The only necessary condition here is that one of the processes should be specific for hydrogen fluoride.

1.3 Work Coverage

The work in this report involves construction of apparatus for continuous generation of hydrogen fluoride gas at trace levels; construction of apparatus for sampling hydrogen fluoride gas at calibrated flow rates; evaluation and selection of solid sorbents for efficient collection of hydrogen fluoride; development of a sorption tube for personal sampling applications; development of a procedure for collection and subsequent quantitative analysis of hydrogen fluoride; determination of collection efficiencies of the sorption tube at several concentration levels of hydrogen fluoride, flow rates, and collection times; and study of the effects of temperature, humidity, breakthrough, bleed-out, storage, and shipment.

This report also provides specifications for construction of the sorption tube and a recommended procedure for collection and determination of hydrogen fluoride gas.

2. Development of Methodology

This section describes the development of methods for continuous generation and sampling of hydrogen fluoride gas, and of procedures for collection and analysis of the gas. A brief review of the literature on solid sorbents and analytical methods for hydrogen fluoride is also given.

2.1 General Consideration

To approximate the industrial work atmosphere, a relatively concentrated mixture of hydrogen fluoride gas was

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Sorption

Chemical Reaction   Physical Adsorption/Absorption

specific   non-specific   specific   non-specific

Retrieval

Chemical Reaction   Physical Methods

specific   non-specific   specific   non-specific

Analysis

specific   non-specific

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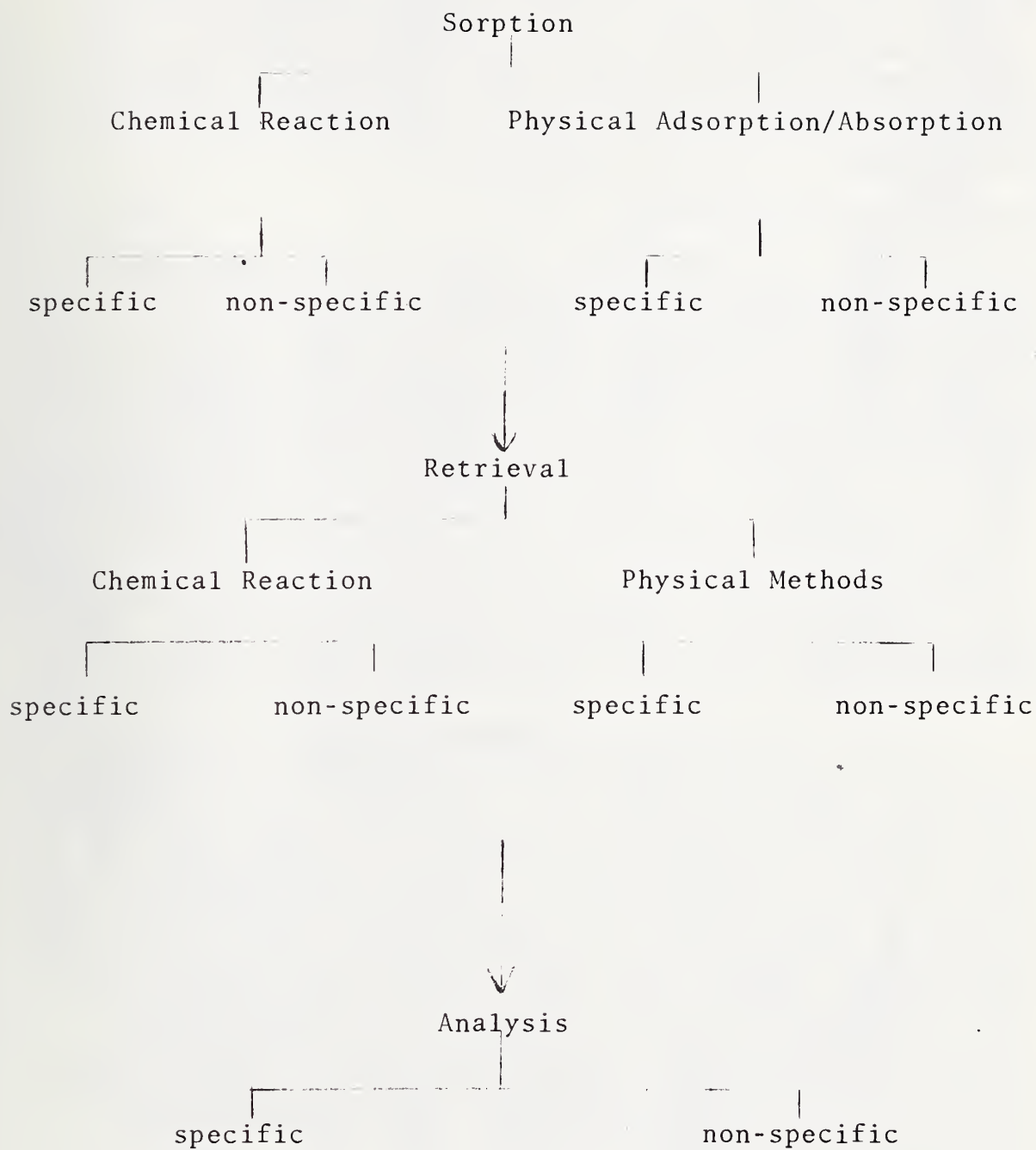
diluted with air rather than pure nitrogen. The hydrogen fluoride gas samples were drawn through sorption tubes by vacuum to simulate sampling by a personal sampler. Consideration was made in the selection of sorbent materials and specification of the sorption tube to conform to the work scope as outlined in Section 1.1. The recommended analytical method was one that required minimal training for efficient performance.

2.2 Gas Dilution System

To carry out many tests required for the selection of the solid sorbents, a reliable source of contaminant is needed. The concentration level of hydrogen fluoride required in this work ranges from 0.6 to 15 ppm, i.e., 1/5 to 5 times TLV (1). Although hydrogen fluoride gas mixtures at this concentration range are available commercially, past experience indicated instability of such gas mixtures for extended periods. A cylinder of hydrogen fluoride gas mixture in nitrogen was used as a bulk source of the contaminant. The concentration of the gas at the time of use was found to be 61 ppm. This gas mixture was then dynamically diluted with in-house compressed air to the desired concentrations in a gas dilution system. Several systems of this type have been developed and used successfully for gas dilution (2). This dilution system can also be conveniently used to study the effects of humidity on the collection of the contaminant gas.

Figure 1 is a schematic drawing of the gas dilution system. It consisted essentially of a bubbler containing distilled water to saturate the in-house air, two differential flow controllers (one had a stainless steel diaphram for hydrogen fluoride), two rotameters for measurement of flow rates of air and hydrogen fluoride, and stainless steel mixing and sampling manifolds. Either thick-wall Teflon or stainless steel hardware was used wherever hydrogen fluoride gas passed. Prior to the water saturator, the in-house air was filtered through glass wool. Proper adjustment of the two rotameters R-1 and R-2 by valves V-2 and V-5, respectively, produced hydrogen fluoride gas mixtures of the desired concentrations. The use of valves V-3 and V-4 provided a choice of oil-free dry air and water-saturated air for mixing with hydrogen fluoride. The rotameters were calibrated with a wet test meter.

2.3 Gas Sampling System

The sampling rates required in this work range from 50 cm^3 per minute to 1 liter per minute. These flow rates were obtained with the gas sampling system shown schematically in figure 1. The system consisted essentially of a three-way ball valve, two sorption tubes joined in series
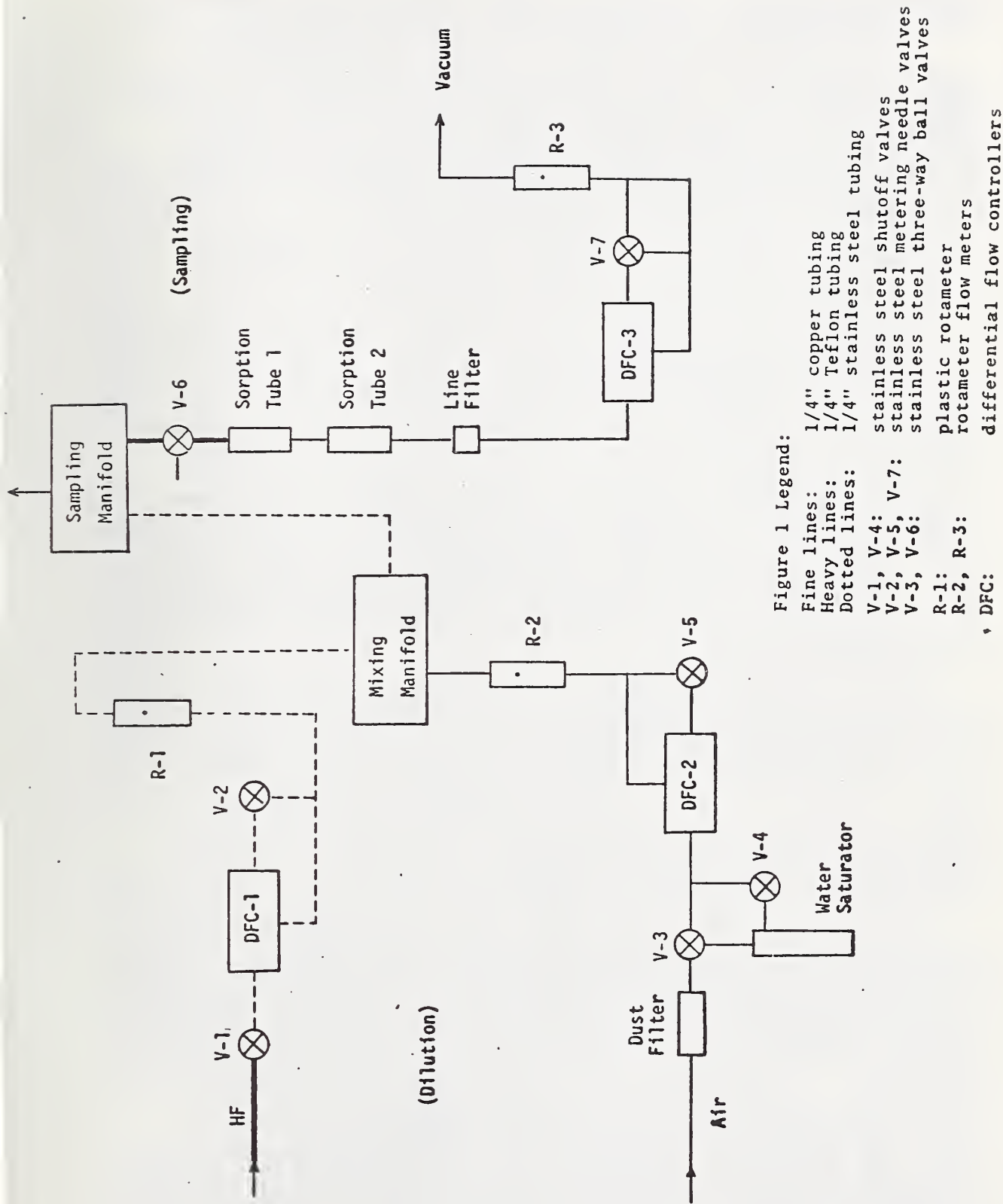
Figure 1. Gas Generating and Sampling Systems for HF

Figure 1 Legend:

Fine lines: 1/4" copper tubing
Heavy lines: 1/4" Teflon tubing
Dotted lines: 1/4" stainless steel tubing

V-1, V-4:   stainless steel shutoff valves
V-2, V-5, V-7:   stainless steel metering needle valves
V-3, V-6:   stainless steel three-way ball valves

R-1:   plastic rotameter
R-2, R-3:   rotameter flow meters

DFC: differential flow controllers

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by Cajon connectors, a brass in-line filter, a differential flow controller, a rotameter, and a vacuum pump.

Gas samples were withdrawn under vacuum from the sampling manifold. When adjusting valve V-7 for the proper sampling rates, the three-way valve V-6 was opened to the atmosphere. The flow rates of the hydrogen fluoride-air mixture in the gas mixing manifold were always maintained at three or more times the gas sampling rates. The rotameter was calibrated with a wet test meter.

2.4 Selection of Solid Sorbents for Hydrogen Fluoride

2.4.1 Literature Survey on Solid Sorbents

Several solid substances have been reported in the literature for sorption of hydrogen fluoride in air. These include sodium bicarbonate (3), sodium carbonate (4-7), limestone (8), alumina (9), sodium formate (10,11), sodium hydroxide-carbonate (12, 13), potassium-sodium carbonates (14,15), potassium hydroxide (16), silica gel (17), and calcium oxide (18). Various collection devices have been developed, such as impregnated filter papers (3, 15, 18-20), fiber filters (7, 14, 21), impregnated polystyrene filters (11), coated tubes or beads (5,6,18,22), and packed towers (8). The Drager detector tube (23) for hydrogen fluoride uses zirconium alizarin lake on silica gel as the sorbent and color indicator.

The Intersociety Committee (18) described the use of filter papers impregnated with calcium-based fixative agents such as calcium oxide or other soluble alkalies, and cautioned that gaseous fluorides collected on glass fiber filters cannot be quantitatively removed by leaching with water. Thompson et al. at the Environmental Protection Agency (21) employed fiber filters to collect gaseous and particulate water-soluble fluorides from ambient air and recovered the fluorides by reflux with water.

Bourbon and Alary (3) found that filter papers impregnated with 1 percent sodium bicarbonate gave better recovery of fluoride than lime papers. Okita et al. (5) found that the collection efficiency for gaseous fluorides was best in a glass spiral coated with dried sodium carbonate. Hermann (6) used silver balls coated with a thin layer of sodium carbonate. A two-stage filter consisting of a membrane filter and a second membrane filter impregnated with 1 percent sodium carbonate was developed in Japan (7). Naoi (13) removed acidic gases by filters impregnated with a mixture of sodium hydroxide and carbonate. Okita (14) obtained 100 percent collection efficiency for particulate fluoride compounds by membrane filters impregnated with

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sodium and potassium carbonates. Okita et al. (15) collected gaseous hydrogen fluoride on filter papers impregnated with 1 percent sodium and potassium carbonates. At 0.05 to 1.0 ppm level, the collection efficiency was 94 percent at 40 percent relative humidity.

Gilbert et al. (8) investigated the effects of different types of limestone, gas velocity and temperature, size of packing, and hydrogen fluoride concentrations on the absorption coefficient. Lobos et al. (9) used a heated alumina desiccator to absorb hydrogen fluoride, and found that the gamma-type alumina absorbed over 2 percent fluoride in a fraction of a second. Jahr (10) employed two successive filters, the first untreated and the second impregnated with sodium formate. Particulate fluorides were collected quantitatively on the first filter whereas hydrogen fluoride was found on both. However, the hydrogen fluoride on the first filter could be completely transferred to the second by heating.

Biheller and Resch (11) were able to trap more than 99 percent of hydrogen fluoride with polystyrene filters which were impregnated with 10 percent sodium formate in 50 percent alcohol. Huygen (16) compared the efficiencies of filter papers impregnated with 20 percent potassium hydroxide-10 percent glycerol, filter papers impregnated with 20 percent potassium hydroxide-10 percent triethanolamine, and bubblers containing 0.1 N sodium hydroxide solution. The freshly prepared filter papers had 100 percent collection efficiency at humidities greater than 25 percent, and 87 percent at zero humidity. Guilbault (20) described paper tapes impregnated with Mg-8-hydroxylquinoline to give ppb detection capability by quenching of fluorescence.

2.4.2 General Considerations

As hydrogen fluoride is chemically a very reactive species and also a very strong acid when ionized, sorption by chemical reaction received more consideration than physical adsorption/absorption (see Section 1.2). Many inorganic fluorides are soluble in water. If the reaction product in sorption is a water-soluble fluoride, retrieval of hydrogen fluoride as a fluoride can be complete and quite convenient. Furthermore, if the final chemical analysis should be specific for fluoride, then the sorption reaction need not be specific.

For personal sampler applications, the collection device must be compact in size with high efficiency and large capacity. It follows that packed columns or tubes are more desirable than impregnated papers, tapes, membrane filters and coated tubes.

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2.4.3 Collection Efficiencies

In a preliminary screening of solid sorbents, the collection efficiencies of sodium bicarbonate powders, activated charcoal (roasted coconut shells), activated charcoal soaked with saturated sodium bicarbonate solution, firebrick soaked with saturated sodium bicarbonate solution, sodium citrate crystals, and sodium acetate crystals were evaluated. These substances in granular form were packed in glass tubings of 6 mm outside diameter so that the pressure drop did not exceed 2.54 cm of mercury at the air flow rate of 1 liter/minute.

Two tubes, connected in series, were used to evaluate collection efficiency. After sampling a given hydrogen fluoride gas mixture at a flow rate for a period, the amounts of fluoride collected in the first and second sorption tubes were determined by the method to be described in Section 2.6. The collection efficiency, E, defined as

$$E = \frac{(A_1 - B_1)}{(A_1 - B_1) + (A_2 - B_2)} \times 100$$

where A_1 = amount of fluoride collected in the first sorption tube,

A_2 = amount of fluoride collected in the second sorption tube,

B_1 = blank for the first sorption tube,

B_2 = blank for the second sorption tube,

was calculated. Blanks were obtained under identical conditions but using the ambient air of the laboratory.

Table 1 is a summary of the collection efficiencies of the solid sorbent systems studied. Although sodium bicarbonate showed a relatively high collection efficiency, it had the disadvantage that it was available only in the powder form, and the pressure drop of sorption tubes generally exceeded 2.5 cm mercury. Also, its efficiency of collection at the flow rate of 50 cm^3/min was rather low.

It was difficult to leach sodium fluoride, the reaction product of sodium salts with hydrogen fluoride, from activated charcoal and firebrick substrates. The fine particulates of the substrates in the resultant solutions had to be filtered off before analysis. No attempt was made to determine the recovery of fluoride in the leaching process.

Table 1.   Collection Efficiencies of Various Sorbents for
3 ppm Hydrogen Fluoride Gas

Sorbent	Collection Time	Flow Rate cm^3/min	Collection Efficiency
$NaHCO_3$	15 min	1050	98.7-99.8[a]
	4 h	211	96.8
	6 h	211	95.8
	8 h	211	99.8
	8 h	50	73.3
Activated charcoal	15 min	1050	93.1, 97.4
	6 h	211	90.7
	4 h	41	82.8
	8 h	50	52.5
Firebricks soaked with sat'd $NaHCO_3$ sol'n	15 min	1050	70.6
Charcoal soaked with sat'd $NaHCO_3$ sol'n	15 min	1050	61.0, 85.0
Charcoal soaked with sat'd $NaHCO_3$ sol'n + 5 percent glycerine	15 min	1050	89.0, 90.3
Na citrate crystals	15 min	1050	12.9
	4 h	211	11.8
Na citrate in urethane + 5 percent glycerine solution	15 min	1050	31.5
Na acetate crystals	15 min	1050	93.9-97.5[b]

[a] A total of 9 runs.

[b] A total of 6 runs.

There was evidence that water was desirable for the reaction of sodium in the solid sorbents with hydrogen fluoride, as shown by the higher collection efficiency (31.5 percent) of sodium citrate plus 5 percent glycerine in water over the dry salt. Activated charcoal soaked with saturated sodium bicarbonate solution also gave higher collection efficiencies when 5 percent glycerine was present.

Sodium acetate was selected as the sorbent for hydrogen fluoride on the following basis:

1. high collection efficiency,

2. acetate acts as a pH buffer in the fluoride selective electrode method of analysis,

3. readily available as reagent grade in the 20-40 mesh size,

4. relatively inexpensive,

5. chemical stability of both sodium acetate and the reaction product sodium fluoride under normal conditions,

6. presence of three molecules of water of hydration per formula weight, highly desirable for the reaction with hydrogen fluoride in air,

7. non-toxic, non-irritating, non-corrosive, non-obnoxious,

8. high solubilities of both sodium acetate and sodium fluoride in water,

9. high melting points of sodium acetate and sodium fluoride, 58°C and 992°C, respectively.

2.5   Construction of Sorption Tubes for Hydrogen Fluoride

The sorption tubes were constructed according to the procedure given below. The reagent-grade sodium acetate used was pooled from bottles from three different suppliers. Crystals of 20 to 40 mesh were separated from the bulk in the reagent bottles by sieving. The only apparent difference among these three sources of sodium acetate was in the distribution of particle size. An average of 10 percent of the sodium acetate in the bulk was of 20 to 40 mesh. No attempt was made to determine the distribution of particle size in the 20 to 40 mesh crystals.

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Figure 2 is a drawing of the sorption tube. Although the specifications call for Pyrex glass tubing, polyethylene tubing should be preferable to avoid reaction of hydrogen fluoride with the glass surfaces. Subsequent studies showed a slight loss of hydrogen fluoride when Pyrex tubes were used.

For use as a personal sampler, two sorption tubes may be joined in series with a piece of polyethylene tubing so that the second sorption tube acts as a breakthrough indicator. However, the high capacity of the collection tube makes this virtually unnecessary.

2.5.1 Specifications of Sorption Tubes

1. Join two Pyrex glass tubings of 6 mm outside diameter and 3 cm long to a Pyrex glass tube of 13 mm outside diameter and 4 cm long. Make very slight constrictions at the joints.

2. Introduce a wad of loose surgical cotton, about 5 mg, inside the tube.

3. Blow dry air inside the tube to arrest the cotton at the "groin" of the tube.

4. With the aid of a small funnel and a piece of Tygon tubing, fill the tube with 20 to 40 mesh reagent-grade sodium acetate crystals, $NaC_2H_3O_2 \cdot 3H_2O$, (about 3 g) up to the "neck". Gently tap the tube to help the crystals settle. Do not use crystals that are lumped together.

5. Insert a wad of loose surgical cotton, about 4 mg, on top of the sodium acetate crystals.

6. Mark an arrow on the outside wall of the tube to indicate the air flow direction, i.e., the same direction as the air that was used in blowing the cotton.

7. Connect the sorption tube to an orifice which has an opening to pass air at 1 l/min. Connect the orifice to a manometer and vacuum with a tee. Figure 3 is a drawing of the pressure drop measurement apparatus.

8. Turn the vacuum on to check the pressure drop. Reject sorption tubes with a pressure drop over 2.54 cm Hg.

9. When not in use, tightly seal both ends of the sorption tube with plastic end caps. Do not store tubes at temperatures above 40°C.
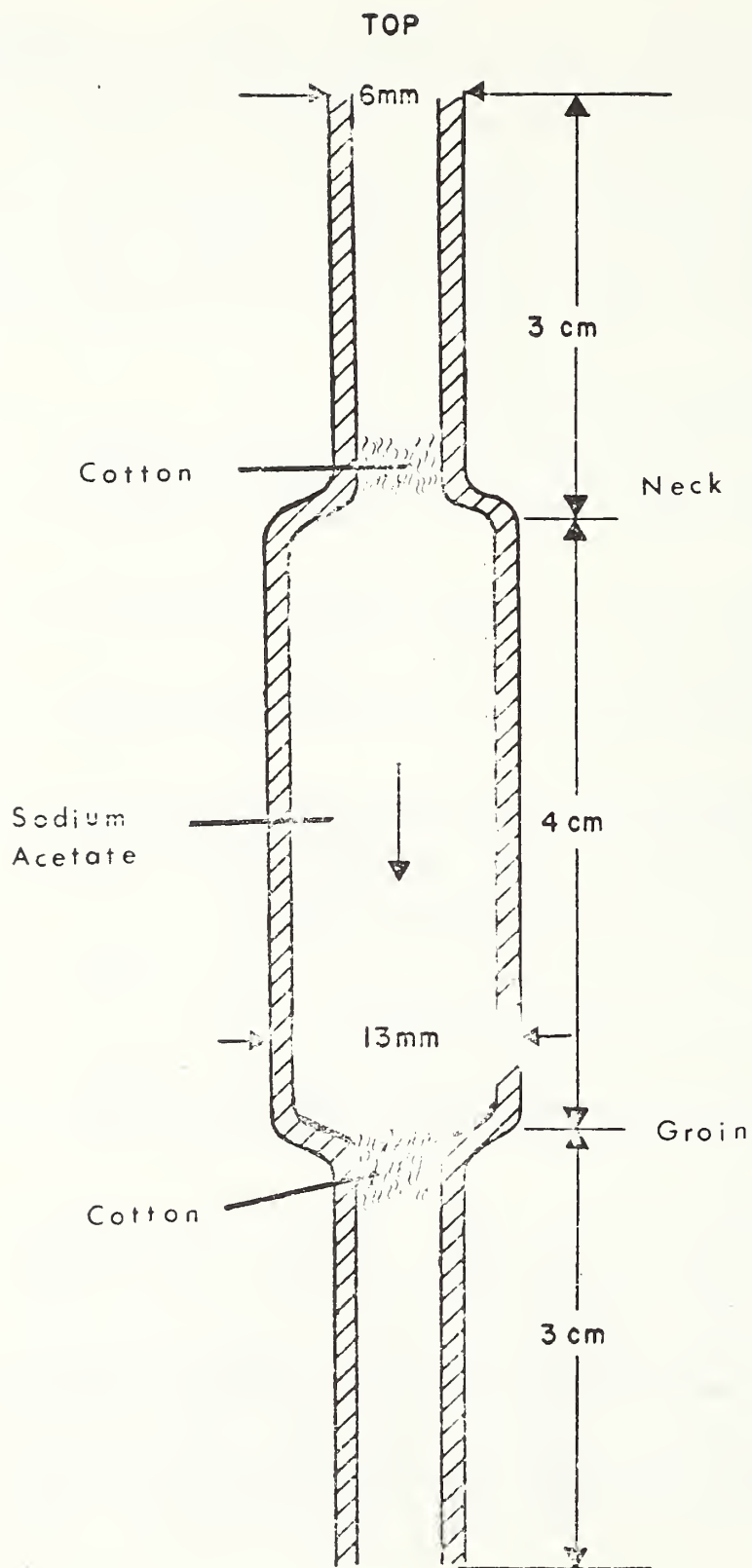
13

TOP

6mm

3 cm

Cotton

Neck

Sodium
Acetate

4 cm

13mm

Cotton

Groin
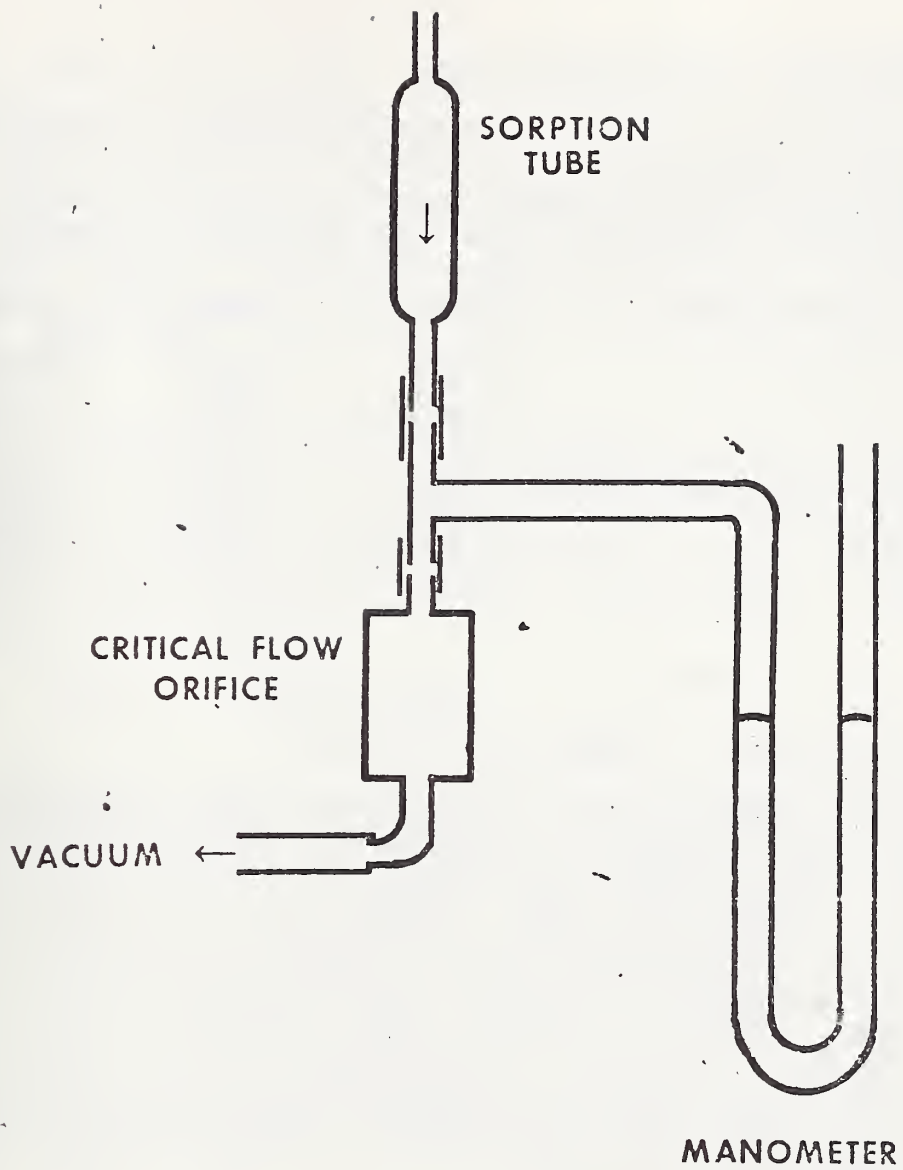
3 cm

Figure 2.   Sorption Tube for HF

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Figure 3. Pressure Drop Measurement Apparatus

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2.5.2 Impurities in Sodium Acetate

The sodium acetate used in the experiments contained the following impurities, as listed on the labels of the reagent bottles. None of these impurities is expected to interfere with the fluoride selective electrode analysis.

Impurities (in percent)	Supplier A	Supplier B	Supplier C
Insoluble matter	0.003	0.005	0.001
Chloride	0.0004	0.001	0.0003
Phosphate	0.0003	0.0005	0.0002
Sulfate	0.001	0.002	0.0004
Ca, Mg, and R_2O_3 precipitates	0.005	0.010	0.003
Heavy metals as Pb	0.0002	0.0005	0.0002
Iron	0.0002	0.0005	0.0001
Potassium	0.001	0.005	0.005
Ammonium		0.001	

2.6 Analytical Methods for Hydrogen Fluoride

2.6.1 Brief Review of Analytical Methods

Many analytical methods for hydrogen fluoride are now available. As the number of references on fluoride determination is quite large, only a few representatives are cited here. In general, these methods may be classified as ion selective electrode (21,24), colorimetry (18,23,24), titrimetry (18), spectrophotometry (18,25), photometry (6,22,24), fluorimetry (20,25,26), gas ionization (27), bioassay (28), spot test (29,30), and nuclear activation analysis (31,32). The first four methods are more applicable to the present work than the others. Below is a brief description of their basic principles, interferences, and range or limits of detection.

The fluoride selective electrode gives Nerstian response to fluoride ion concentrations from above 1 M to 10^{-5} M, and only hydroxide ion seems to interfere with this response. With the pH of the sample solution maintained between 5 to 7 by a pH buffer and the presence of a polyvalent anion to break up any complexing agent, selectivity is excellent. The limit of detection is 100 µg/l.

The colorimetric method measures the change of color intensity of a dye lake by the reaction of fluoride ions, using either a color comparator or a photometer. In the SPADNS method, sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3, 6-naphthalene disulfonate, also called 4,5-dihydroxy-3-(parasulfophenylazo)-2,7-naphthalene disulfonic acid trisodium salt, combine with zirconyl chloride to form the dye lake. Sodium alizarinsulfonate, also known as alizarin

red S, may also be used. The range of applicability is 0.05-1.4 mg/l. Interferences include alkalinity, aluminum, chloride, iron, hexametaphosphate, phosphate, and sulfate.

In titrimetry, the sample solution containing fluoride and sodium alizarinsulfonate is titrated against thorium nitrate. Interferences are aluminum, barium, calcium, iron, thorium, titanic, vanadyl, zirconium, phosphate and sulfate ions. The range and sensitivity are 5-50 µg in the total sample for titration.

In spectrophotometry, the change in absorbance of the solution containing a metal dye complex, such as zirconium-eriochrome cyanine R or zirconium-SPADNS, by fluoride is measured. The range of applicability is 0.02-1.4 mg/l. Lanthanum alizarin complexone, commonly called alizarin fluorine blue, may also be used, and the range is lowered: 0.015-0.5 mg/l. Interferences include aluminum, iron, phosphate, and sulfate.

2.6.2 General Considerations

The ion selective electrode method for fluoride determination was chosen on the basis of its excellent selectivity for fluoride and simplicity in operation. The necessary equipment in this method includes a fluoride selective electrode, a calomel reference electrode, a pH meter with millivolt mode, and a magnetic stirrer. The concentration of fluoride in a sample solution is obtained from the millivolt reading and a calibration curve. The latter is established from a plot of millivolt response versus fluoride concentrations of sodium fluoride standard solutions. The standard solutions are prepared from known weights of dried sodium fluoride dissolved in 0.88 M sodium acetate solution containing 0.3 g sodium citrate per liter. The procedure for operation of the fluoride selective electrode instrument is given in the next section.

At the conclusion of gas sampling, the amount of fluoride collected in the sorption tube may be determined according to the procedure given in Section 2.6.4. In the preliminary screening of solid sorbents, the sorbents sodium bicarbonate and citrate were dissolved in sodium nitrate solution to give the same ionic strength as the standard solutions. For charcoal and firebricks, the sodium fluoride was leached out from the substrates with 25 ml water, and the proper amounts of sodium acetate and citrate were added to the solutions.

The amount of fluoride collected, in moles of fluorine, was calculated from the following equation:

$$A = \frac{25\ C}{1000}$$

where   A = amount of fluoride collected in the sorption tube, and

       C = molar concentration of fluoride.

The concentration of hydrogen fluoride, in parts per million (ppm), in the gas samples was calculated from the following equation:

$$\text{ppm HF} = \frac{A \times 24.5 \times 10^6}{T \times R}$$

where T = total collection time in minutes, and

       R = flow rate of gas sample in liters per minute at standard temperature-pressure condition.

     To study the effects of sodium acetate concentration on millivolt response, a series of sodium fluoride standards in 0.55 M sodium acetate solutions was prepared. Figure 4 shows the calibration curves of the standard solutions in both 0.88 M and 0.55 M sodium acetate solutions. The effect of sodium acetate concentration was negligible.

2.6.3   Operation of Fluoride Selective Electrode Instrument

     The following directions apply to the use of the ion selective electrode:

1.   Connect the fluoride and the reference electrodes to the pH meter. Set the meter to "standby" position.

2.   Transfer the sample solution to a 50-ml polyethylene beaker. Add 2 drops of 0.5N HNO_3 to adjust the pH of the solution to 6.8.

3.   Place the electrodes in the sample solution.

4.   Place a Teflon coated magnetic stirrer in the beaker and turn on the variable transformer to provide gentle stirring of the solution.

5.   At the end of 15 minutes, set the meter to millivolt mode and record the millivolt reading.

6.   Set the meter back to "standby" position.
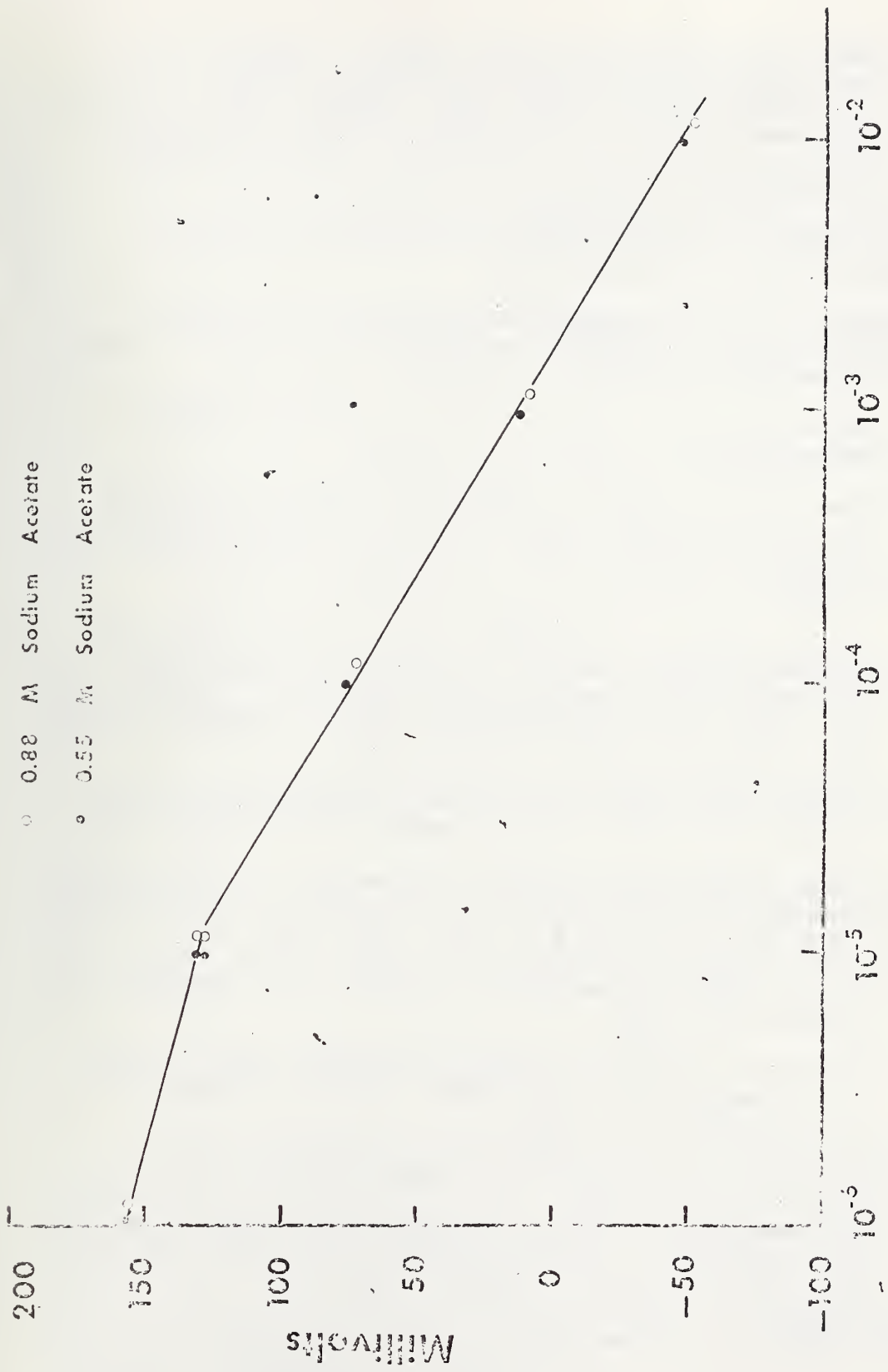
Figure 4. Calibration Curve of Fluoride Standard Solutions

o   0.88   M   Sodium   Acetate

•   0.55   M   Sodium   Acetate

Molar Concentration of Fluoride

Millivolts

200
150
100
50
0
-50
-100

10^{-5} 10^{-4} 10^{-3} 10^{-2}

10^{-6}

7.   Empty the contents of the beaker. Rinse the
     electrodes thoroughly with distilled water. Wipe
     the electrodes dry with soft tissue. The electrodes
     are now ready for measurement of another sample.
     When not in use, the electrodes should be immersed
     in distilled water.

2.6.4   Procedure for Measurement of Amount of Fluoride
        Collected in Sorption Tubes

     Prepare a stock solution containing 0.3 g sodium
citrate per liter in distilled water, and use it for dissolu-
tion of the sodium acetate.

1.   Disconnect the sorption tube from the sampling
     apparatus.

2.   Use a stiff wire or a pair of straight corrugated
     forceps to remove the top wad of cotton in the
     sorption tube and place the cotton in a polyethylene
     beaker.

3.   Insert the top end of the sorption tube into the
     neck of a 25-ml volumetric flask, and empty the
     sodium acetate crystals into the flask. Gently tap
     the tube against the flask to get as many as possi-
     ble of the crystals into the flask.

4.   With a stiff wire, break loose the bottom wad of
     cotton. Keep the cotton inside the sorption tube.

5.   Rinse the inside walls of the sorption tube and the
     cotton with 15-18 ml stock citrate solution. Make
     sure all the rinse goes into the flask.

6.   Remove the sorption tube from the neck of the
     volumetric flask.

7.   Rinse the cotton in the polyethylene beaker with
     5 ml stock citrate solution. Add the rinse to the
     25-ml volumetric flask.

8.   Dissolve the sodium salts completely.

9.   Add enough stock citrate solution to make 25 ml.
     Mix thoroughly. The solution is now ready for fluo-
     ride concentration determination.

2.6.5   Calibration of Fluoride Selective Electrode

     Prepare a series of sodium fluoride standard solutions
as follows:

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1. Prepare a stock solution containing 120 g sodium acetate and 0.3 g sodium citrate per liter in distilled water. Use this stock solution for dissolution and dilution of the sodium fluoride below.

2. Dissolve 420 mg, weighted to the accuracy of ±0.1 mg, of dried sodium fluoride and dilute it to 100.0 ml in a volumetric flask. This makes the 10^{-1} M solution.

3. Dissolve 420 mg, weighted to the accuracy of ±0.1 mg, of dried sodium fluoride, and dilute it to 1.000 liter in a volumetric flask. This makes the 10^{-2} M solution.

4. Pipette 10.0 ml of the 10^{-1} M solution and dilute it to 1.000 liter in a volumetric flask. This makes the 10^{-3} M solution.

5. Pipette 10.0 ml of the 10^{-2} M solution and dilute it to 1.000 liter in a volumetric flask. This makes the 10^{-4} M solution.

6. Pipette 1.00 ml of the 10^{-2} M solution and dilute it to 1.000 liter in a volumetric flask. This makes the 10^{-5} M solution.

7. Pipette 1.00 ml of the 10^{-3} M solution and dilute it to 1.000 liter in a volumetric flask. This makes the 10^{-6} M solution.

Store all the sodium fluoride standard solutions in polyethylene bottles. Use 25 ml of each of these solutions for calibration periodically. Follow the procedure given in Section 2.6.3. Plot the millivolt response against the calculated concentrations of sodium fluoride.

3. Experimental Results

3.1 Collection Efficiencies of Sodium Acetate

Table 2 summarizes the collection efficiencies of sodium acetate crystals for hydrogen fluoride at room temperatures (23.9° to 25.5°C). These experimental runs were made in random order and not in the sequence as shown in table 2. It appears that 3 g of sodium acetate in 20 to 40 mesh was sufficient to remove completely hydrogen fluoride from air having concentration of hydrogen fluoride ranging from 0.5 to 16 ppm for the collection times and flow rates specified in Section 1.1.

Table 2. Collection Efficiencies of Sodium Acetate for Hydrogen Fluoride Gas

Collection Time	Flow rate cm³/min	ppm HF	g. NaAc	Collection Efficiency
15 min	916	4.90	1.87	94.8
15 min	916	5.08	1.87	94.7
15 min	916	3.70	3.0	100
15 min	916	4.64	3.0	100
15 min	916	5.57	3.0	99.7
15 min	1010	0.48	3.0	100
15 min	1010	0.51	3.0	100
15 min	1010	0.57	3.0	100
15 min	1010	0.63	3.0	100
15 min	1010	0.70	3.0	100
15 min	1010	3.54	3.0	100
15 min	1010	15.8	3.0	100
4 h	52	0.69	3.0	100
4 h	52	0.74	3.0	100
4 h	52	0.81	3.0	100
4 h	52	5.00	3.0	100
4 h	52	15.2	3.0	100
4 h	188	4.93	1.87	99.3
4 h	188	5.11	3.0	100
4 h	198	0.57	3.0	100
4 h	198	3.09	3.0	100
4 h	198	15.4	3.0	100
8 h	52	0.74	3.0	100
8 h	52	2.21	3.0	100
8 h	52	4.64	3.0	100
8 h	52	16.4	3.0	100
8 h	188	5.43	3.0	100
8 h	198	0.57	3.0	100
8 h	198	4.37	3.0	100
8 h	198	15.8	3.0	100

3.2   Breakthrough and Capacity of the Sorption Tube

A gas mixture of 15 ppm hydrogen fluoride was passed continuously through two sorption tubes at a flow rate of 1.01 l/min. At 15 minute intervals, the second tube was replaced with another sorption tube and its fluoride content analyzed. A total of 32 second sorption tubes was thus obtained and analyzed. The first sorption tube had collected 5.89 mg hydrogen fluoride. No fluoride was found in any of the 32 second sorption tubes in the 8 hours of collection.

In another similar experiment, the hydrogen fluoride from the cylinder was fed without dilution through two sorption tubes in series, at the flow rate of 1.01 l/min. Every 4 hours, the second tube was replaced and analyzed. Again, no breakthrough was detected in the second tubes after collection of a total of 46 mg hydrogen fluoride in the first sorption tube. However, the inside walls of the first sorption tube above the sodium acetate crystals were etched at the end of the 16 hour run, indicating reaction of hydrogen fluoride with the glass surfaces.

The capacity of two smaller sorption tubes was also studied. Hydrogen fluoride gas, without dilution, was passed through two sorption tubes in series, each of which was 4 cm long with 10 mm outside diameter and contained 1.4 g sodium acetate. The sample flow rate was 1.01 l/min. At the end of 15 minutes, the fluoride contents of these two tubes were determined. The experiment was repeated with two sorption tubes of the same length but of 8 mm outside diameter, each of which contained 0.8 g sodium acetate. The sample flow rate was 198 cm^3/min and collection time was 5 hours. The results are tabulated in table 3.

These smaller sorption tubes also possessed 100 percent collection efficiency, and no breakthrough was observed after collecting more than 5 mg of hydrogen fluoride in the 10 mm tube and more than 17 mg in the 8 mm tube. However, these tubes exhibited a pressure drop far higher than the 2.54 cm mercury specified in Section 1.1.

The amount of fluoride collected, column 6 of table 3, was computed from the fluoride analysis results, and not from the sample flow rate, collection time, and concentration of the hydrogen fluoride gas. When the last two experiments were performed, the pressure inside the hydrogen fluoride cylinder was below 203×10^3 pascal (15 pounds per square inch above atmosphere), and the concentration of hydrogen fluoride was much higher than the original value of 61 ppm.

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Table 3. Capacity of Sorption Tubes of Different Sizes

Outside diameter of tube (mm)	Amount of sodium acetate (g)	Pressure drop (cm Hg) at 1 l/min	Sample flow rate (l/min)	Collection time (h)	Total fluoride collected (mg)	Collection efficiency (%)
13	3.0	2.5	1.01	8	5.89	100
13	3.0	2.5	1.01	16	46.0	100
10	1.4	3.8	.1.01	0.25	5.75	100
8	0.8	5.0	0.198	5	17.5	100

3.3 Effects of Elevated Temperatures

A Pyrex glass tube of 13 mm outside diameter and 25 cm long was placed in front of two sorption tubes, all in series and all wrapped with a heating tape. Heat was generated at a constant rate, and the temperature inside the 25 cm tube was measured by a thermometer with air flowing at 52 cm^3/min. A hydrogen fluoride gas sample was withdrawn through this assembly at a flow rate of 52 cm^3/min. The experiment was repeated with the heating tape removed and with two new sorption tubes.

Table 4 is a summary of the experimental results for two different collection times. Together with the experimental data presented in table 2, it is concluded that the collection efficiency of sodium acetate for hydrogen fluoride was 100 percent at temperatures ranging from 23.9°C to 38.0°C. However, there was a loss of 9 percent of hydrogen fluoride at the elevated temperatures, as shown in the last column in table 4. Possibly, part of the hydrogen fluoride reacted with the inside walls of the Pyrex tubes with a higher kinetic rate at the elevated temperatures than at the room temperatures.

3.4 Effects of Humidity

With the water saturator turned on (see Figure 1), it was possible to generate air-hydrogen fluoride mixtures with various relative humidities by adjusting valves V-2 and V-5. The samples were withdrawn through two sorption tubes in series at a flow rate of 1.01 1/min for 15 minutes. The experiment was repeated with the water saturator turned off and with two new sorption tubes. The amount of fluoride in the sorption tubes was determined after the collection.

The collection efficiencies in both the wet and dry cases were 100 percent. However, the collection efficiency as defined in Section 2.4.3 is a relative quantity. When comparing the absolute amounts (A_1-B_1), of fluoride collected, it was found that the fluoride collected from the wet air was only 76.7 percent of that from the dry mixture.

In the next experiment, the stainless steel mixing and sampling manifolds and tubings were replaced by polyethylene manifolds and tubings. Again, the collection efficiencies were 100 percent in all cases. But the amount of fluoride collected from the wet air was now 96 percent of that from the dry mixture. Finally, sorption tubes were constructed from polyethylene tubing, and the experiments were repeated at three relative humidities. The results are summarized in table 5.

Table 4. Effects of Temperature on Collection
of Hydrogen Fluoride

Temperature (°C)	Collection time (h)	Collection efficiency	ppm HF	Net moles F collected $\times 10^{-6}$	Ratio of moles F collected (elevated temp/ room temp)
36.0	1	100	5.2	0.60	0.91
25.0	1	100	5.2	0.66	
38.0	3	100	22.9	7.98	0.914
25.4	3	100	22.9	8.73	

Table 5. Effects of Humidity on Collection of
Hydrogen Fluoride

Humidity (%water saturation)	Mixing and Sampling Manifolds	Sorption Tubes	Collection efficiency	Ratio of HF collected (wet/dry)
59.8	stainless steel	Pyrex	100	0.767
59.8	polyethylene	Pyrex	100	0.963
59.8	polyethylene	polyethylene	100	1.00
79.3	polyethylene	polyethylene	100	1.00
18.4	polyethylene	polyethylene	100	1.00

Apparently, part of hydrogen fluoride reacted with water vapor, and the product(s) then reacted with the stainless steel walls of the gas dilution and sampling systems. There was indication that hydrogen fluoride also reacted with the glass surfaces of the sorption tubes to the extent of 3.7 percent.

3.5 Precision, Bleed-out, Storage, and Shipment Studies

A total of 20 collections of hydrogen fluoride gas was made under identical experimental conditions, i.e., 15 minutes of collection time at a flow rate of 1.01 l/min and hydrogen fluoride concentration of 3 ppm. The 20 sorption tubes so obtained were distributed, in random order, for the following studies.

Four were analyzed for the fluoride content immediately. Four were stored for 35 days at room temperature and then analyzed for fluoride content. Four were stored for 70 days at room temperature and then analyzed.

Four days after the collection, four sorption tubes were sent to the National Institute for Occupational Safety and Health. Two were returned immediately and the other two were returned one week later.

Two sorption tubes were kept in a water-saturated atmosphere at room temperature for 70 days, and then analyzed.

One sorption tube was flushed with ambient air for 6 hours with a second tube in series. Another was flushed in the same manner for 24 hours. The fluoride contents in the first and the second tubes were analyzed.

The results are summarized in table 6, together with the history of the sorption tubes. The samples were collected in the alphabetical order of the sample labels, but they were analyzed in random order. The solution resulting from each sample was measured 7 times, and the average and estimated standard deviation are listed in the second and third columns respectively. For each group of samples receiving the same or similar treatment, the average and standard deviation are also computed and listed in table 6.

A statistical analysis of the data shows no significant correlation among these 20 samples. A slight but inconclusive trend is observed with storage. One sample (T) has a low value, but the overall average of 75.2 includes this value.

Table 6.   Precision, Bleed-out, Storage, and
Shipment Studies

Sample label	Average mv reading	Standard deviation (mv)	History
A	75.4	0.4	Analyzed immediately
C	75.3	0.4	
H	74.8	0.3	
T	73.2	0.6	
	74.7 ± 1.0		
D	76.9	0.3	Stored for 35 days at room
L	75.0	0.7	temperature
O	75.6	0.8	
R	74.7	0.7	
	75.6 ± 1.0		
B	76.4	0.5	Stored for 70 days at room
E	75.9	0.7	temperature
J	76.4	0.7	
M	75.3	0.7	
	76.0 ± 0.5		
K	75.1	0.7	Sent to NIOSH, returned
P	74.3	1.0	immediately
G	75.5	1.0	Sent to NIOSH, returned one week
Q	74.4	0.7	later
	74.8 ± 0.6		
I	75.6	0.5	Flushed with air for 24 hours
N	74.2	0.9	Flushed with air for 6 hours
	74.9 ± 1.0		
F	74.5	0.6	Stored in water-saturated
S	74.8	0.9	atmosphere
	74.6 ± 1.0		

Average of   75.2 ± 0.87
20 samples

The overall standard deviation of ±0.87 mv corresponds to a relative standard deviation of ±3.4 percent in fluoride concentration. This is a measure of the sample variability.

No bleed-out was obtained in the sorption tubes that were flushed with ambient air.

3.6 Glass versus Polyethylene Tubes

As mentioned in Sections 3.2, 3.3, and 3.4, there was evidence that hydrogen fluoride reacted with the glass surfaces of the sorption tubes. To determine the extent of the reaction more precisely, hydrogen fluoride gas, without dilution, was passed directly from the gas cylinder through Teflon tubings into two sorption tubes in series. The flow rate was 198 cm³/min and the collection time was 15 minutes. The experiment was repeated alternatively using Pyrex glass and polyethylene tubes. After collection, the fluoride content in the sorption tubes was determined. The results are presented in table 7.

The difference of 0.7 mv (44.8 - 44.1), corresponds to a loss of 3 percent of hydrogen fluoride in the glass tubes, assuming no loss of hydrogen fluoride in the polyethylene tubes. However, this may not be significant in view of the relatively large standard deviations in the measurements.

4. Summary and Conclusions

A collection device consisting of 3 g sodium acetate crystals of 20 to 40 mesh packed in a 13-mm OD tube has a very high efficiency and capacity for removing gaseous hydrogen fluoride from air. This device collects hydrogen fluoride at the 1/5 to 5 times the TLV with 100 percent efficiency, at air flow rates ranging from 50 cm³/min to 1 l/min. The capacity of the device is at least 46 mg of hydrogen fluoride. The recovery of the fluoride from the tube is expected to be quantitative, although no determination was made on the recovery.

This collection device is not specific for hydrogen fluoride. It will probably trap particulate fluorides and fluorine gas with high efficiency, and the recovery may also be complete for water-soluble fluorides. The analytical method, however, is specific for fluoride. Therefore, any water-soluble compound that ionizes to fluoride and is trapped by this device will give a high analytical result for hydrogen fluoride, to the extent of the collection efficiency of such compound. On the other hand, no interference is expected from any substance that will not form ionizable fluoride.

Table 7. Glass versus Polyethylene Tubes

Tube	mv reading	
Glass	44.0	
	45.5	
	45.3	
Polyethylene		43.6
		44.3
		44.3
Glass	45.0	
	44.8	
	44.3	
Average	44.8 ± 0.6	44.1 ± 0.4

Although no accuracy has been established for this collection device, it is expected that the high collection efficiency of sodium acetate for hydrogen fluoride, solubility of sodium fluoride in water, and the specificity of the fluoride electrode all contribute to a high degree of reliability. The sources of error include fluctuation in air flow rates, inaccuracy in recording collection time, error in volumetric dilution, instability of the instrument response, and inaccuracy in weighing the sodium fluoride standards.

At elevated temperatures such as 36° to 38°C, there is a loss of 9 percent hydrogen fluoride, possibly resulting from reaction of hydrogen fluoride with the glass surfaces of the sorption tube. Even at room temperature, a loss of hydrogen fluoride to the extent of 3.7 percent may be realized at a 60 percent relative humidity. Such problems are eliminated if the tubes were constructed of polyethylene.

The device is stable under normal conditions. No significant deterioration was observed after storage for 70 days, shipment via air freight, and purging with air for 24 hours. The precision of the sampling and analysis is ±3.4 percent relative standard deviation at 3 ppm hydrogen fluoride concentration.

The 3 grams of sodium acetate crystals must be packed in a 13-mm outside diameter tube, so that the pressure drop across the tube will be below 2.54 cm mercury at an air flow rate of 1 l/min. A smaller diameter tube of the same length (4 cm) exhibits a higher pressure drop for the same flow rate. A shorter tube of the same 13 mm outside diameter containing less than 3 g sodium acetate has less than 100 percent collection efficiency.

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APPENDIX A

HYDROGEN FLUORIDE IN THE ATMOSPHERE

Tentative Method of the
Physical and Chemical Analysis Branch
and Engineering Branch

Analyte: Hydrogen Fluoride   Method No.   P&CAM

Matrix: Air   Range: 0.03 to 5000 ppm

Procedure: Ion selective   Precision: Relative standard
             electrode   deviation ±3.4 %

Date Issued: Collaboratively Tested: No

Date Revised:

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1.   Principle of the Method

   1.1   Hydrogen fluoride in air is collected by a sorption
         tube containing sodium acetate crystals.

   1.2   The fluoride, together with the sodium acetate, is
         dissolved in water.

   1.3   The fluoride content in the resultant solution is
         measured by a fluoride ion selective electrode.

   1.4   The amount of fluoride in the sample solution is
         obtained from a calibration curve established with
         sodium fluoride standards.

2.   Range and Sensitivity

   2.1   At an air flow rate of $50\,cm^3$/min and a collection
         time of 4 hours, the upper range of detection is
         5000 ppm.

   2.2   At an air flow rate of $200\,cm^3$/min and a collection
         time of 8 hours, the lower range of detection is
         0.03 ppm.

   2.3   The sensitivity is 2.5 µg of fluorine.

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3. Interferences

3.1 In the presence of a pH buffer, such as sodium acetate, and a polyvalent anion, such as citrate, there is no interference in the analytical method.

3.2 Elemental fluorine is a positive interferrant, to the extent of its collection efficiency on sodium acetate and hydrolysis to form hydrogen fluoride.

4. Precision and Accuracy

4.1 The relative standard deviation, computed from the results of 20 samples, each with 7 determinations, is ±3.4% at 3 ppm hydrogen fluoride.

4.2 The accuracy has not been determined. No collaborative tests have been performed on this method. However, the sodium acetate sorption tubes have been shown to be 100% efficient in collecting hydrogen fluoride, up to a total capacity of 46 mg. The accuracy of the analytical method is dependent upon the reliability of the sodium fluoride standards.

5. Advantages and Disadvantages of the Method

5.1 Advantages: This method is highly selective for fluoride ions and very simple in operation. It involves few steps and requires a minimal amount of training. The instrument is readily available commercially and is relatively inexpensive. No special chemical reagents are needed.

5.2 Disadvantages: This method requires a minimum of 20 minutes per run. This includes times for emptying the sorption tube (2 minutes), dissolution of the sodium acetate (3 minutes), and stabilization of the electrode (15 minutes).

6. Apparatus

6.1 Fluoride ion selective electrode.

6.2 Calomel reference electrode.

6.3 pH meter with millivolt mode.

6.4 Magnetic stirrer with a variable transformer.

6.5 Analytical balance.

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6.6 Polyethylene beakers, 50 ml.

6.7 Plastic coated forceps.

6.8 Straight corrugated forceps.

6.9 Triple beam balance.

6.10 1-liter polyethylene bottles, narrow mouth.

6.11 25-ml volumetric flasks.

6.12 Wash bottles.

6.13 Stiff wires.

6.14 Sampling apparatus.

    6.14.1 Sorption tube for hydrogen fluoride.

    6.14.2 Personal sampling pump.

7. Reagents

7.1 Sodium acetate.

7.2 Stock citrate solution: 0.3 g sodium citrate dissolved in one liter of distilled water.

7.3 Sodium fluoride, dried at 110°C for 24 hours and kept in a desiccator.

7.4 0.5 N nitric acid.

8. Procedure

8.1 Collection of samples: hydrogen fluoride in air is collected by the sorption tube with a personal sampling pump. Plastic end caps are placed on the sorption tube after sample is collected.

8.2 Analysis of samples.

    8.2.1 The plastic end caps are removed from the sorption tube.

    8.2.2 Using a stiff wire, suitably bent, or a pair of straight corrugated forceps, the top wad of cotton in the sorption tube is removed and placed in a polyethylene beaker.

8.2.3 The top end of the sorption tube is inserted into the neck of a 25-ml volumetric flask, and the sodium acetate crystals are emptied into the flask. The sorption tube may be gently tapped to get as many crystals as possible into the flask.

8.2.4 Using a stiff wire, the bottom wad of cotton is broken loose. The cotton should stay inside the sorption tube.

8.2.5 The inside walls of the sorption tube and the cotton are rinsed with 15-18 ml stock citrate solution. Care must be taken that all the rinse go into the volumetric flask.

8.2.6 The sorption tube is removed from the neck of the volumetric flask.

8.2.7 The cotton in the polyethylene beaker is rinsed with 5 ml stock citrate solution. The rinse is added to the 25-ml volumetric flask.

8.2.8 The solids in the volumetric flask are dissolved completely.

8.2.9 Stock citrate solution is added to the 25-ml mark in the volumetric flask, and the solution is mixed thoroughly.

8.2.10 The sample solution is transferred to a 50-ml polyethylene beaker, and 2 drops of 0.5 N nitric acid are added.

8.2.11 The fluoride selective electrode and the calomel reference electrode are brought to the sample solution.

8.2.12 The magnetic stirrer is placed in the beaker containing the sample solution, and the variable transformer is turned on to provide gentle stirring of the solution.

8.2.13 At the end of 15 minutes, the pH meter is set to the millivolt mode and the reading is recorded.

8.2.14 The pH meter is set to "standby" mode.

8.2.15 The sample solution is removed from the elec-
trodes. The electrodes are rinsed with dis-
tilled water thoroughly and then wiped dry
with soft tissues. The electrodes are
immersed in distilled water when not in use.

9. Calibration and Standards

9.1 Standards

9.1.1 A stock solution is prepared by dissolving
120 g sodium acetate and 0.3 g sodium citrate
in one liter of distilled water. This stock
solution is used for dissolution and dilu-
tion of the sodium fluoride standards.

9.1.2 Sodium fluoride, 420 mg weighed to the
accuracy of ±0.1 mg, is dissolved and diluted
to 100.0 ml in a volumetric flask. This
makes the 10^{-1} M standard solution.

9.1.3 Sodium fluoride, 420 mg weighed to the
accuracy of ±0.1 mg, is dissolved and diluted
to 1.000 liter in a volumetric flask. This
makes the 10^{-2} M standard solution.

9.1.4 10.0 ml of the 10^{-1} M standard solution is
transferred into a volumetric flask and
diluted to 1.000 liter. This makes the 10^{-3}
standard solution.

9.1.5 10.0 ml of the 10^{-2} M standard solution is
transferred into a volumetric flask and
diluted to 1.000 liter. This makes the 10^{-4}
M standard solution.

9.1.6 1.00 ml of the 10^{-2} M standard solution is
transferred into a volumetric flask and
diluted to 1.000 liter. This makes the 10^{-5}
M standard solution.

9.1.7 1.00 ml of the 10^{-3} M standard solution is
transferred into a volumetric flask and
diluted to 1.000 liter. This makes the 10^{-6}
M standard solution.

9.2 Calibration Curve

9.2.1 A 25-ml sample of each of the standard solu-
tions is used to obtain the millivolt read-
ing for the fluoride concentration.

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9.2.2 A plot is made of the millivolt reading versus fluoride concentration. The latter is plotted on logarithmic scale. The plot should give a straight line down to $10^{-5}M$.

10. Calculations

10.1 The molar concentration of fluoride is read from the calibration curve corresponding to the millivolt reading of the sample solution.

10.2 The amount of fluoride collected in the sorption tube, in mg hydrogen fluoride, is calculated as follows:

mg HF = 500 x molar concentration of fluoride.

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16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

The efficiencies of several solid substances in a sorption tube for collecting trace quantities of hydrogen fluoride gas in work atmosphere have been evaluated. Reagent-grade sodium acetate crystals proved to be a very efficient sorbent for hydrogen fluoride. Its solubility in water and pH buffer properties are highly advantageous for subsequent fluoride determination by the ion selective electrode. Experimental results are presented for collection efficiencies of hydrogen fluoride gas at several concentration levels, flow rates, and collection times, the effects of elevated temperatures and humidity, and also break-through, bleed-out, storage and shipment studies. Specifications for construction of the sorption tubes are also given.

17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)

Air analysis; air sampling; gas analysis; hydrogen fluoride; industrial hygiene; sodium acetate; sorber; solid; work atmosphere.

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