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FINAL REPORT

DEVELOPMENT AND DEMONSTRATION OF A PERSONAL MONITORING SYSTEM FOR EXPOSURE TO HYDROGEN FLUORIDE

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I. ABSTRACT

A good, functional Hydrogen Fluoride Gasbadge dosimeter has been developed for sampling of airborne HF vapor. The device is small (7.7 cm x 5.4 cm x 1.9 cm) and can easily and conveniently be worn on one's lapel. It consists of polyethylene and polypropylene parts and a triethanolamine-impregnated polypropylene collection element. It is completely self contained, requiring no pumps, impingers, or sampling tubes. Subsequent to sampling, the collection element is analyzed quickly and easily with a fluoride selective-ion electrode. Laboratory tests were conducted to determine precision, linearity, interference effects, influences of temperature and humidity, and collection element stability over time. Results of the tests indicate that the Abcor Gasbadge HF dosimeter is an excellent passive HF monitor for work spaces, and that results obtained with it are accurate within $\pm 25\%$. These results have been corroborated in a field study.

II. INTRODUCTION

This is the final report under grant No. DE-F605-79-EV10249, entitled "Development and Demonstration of a Personal Monitoring System for Exposure to Hydrogen Fluoride", covering the period from October 1979 to December 1980. During this time, developmental work and controlled exposure testing was conducted at Walden's Environmental Engineering Laboratory, Abcor, Inc., Wilmington, MA. Also, field testing was conducted at the Oak Ridge Gaseous Diffusion Plant, Oak Ridge, TN, with the assistance of their industrial hygiene staff.

Hydrogen fluoride, a toxic industrial chemical, is used in the manufacture of most fluorine products and in many other industrial processes. In terms of production volume, it is the most important manufactured compound of fluorine [1]. Aqueous hydrogen fluoride, usually referred to as hydrofluoric acid, has been produced commercially since the late 1800's, while anhydrous hydrogen fluoride has been produced since 1931 [1].

Although it is an extremely useful chemical, significant health hazards are associated with exposure to HF. It has been estimated that 22,000 workers are potentially exposed daily to hydrogen fluoride in the U.S. [2]. Thus, it is important to be able to monitor the ambient workplace concentration of HF, to insure safety and good health.

One of the important industrial uses of hydrogen fluoride is for the gaseous diffusion enrichment of uranium. HF is used to convert uranium oxides to uranium tetrafluoride (UF_4) (reaction 1). HF is also used to produce fluorine gas (F_2) (reaction 2) for the conversion of uranium tetrafluoride to the volatile uranium hexafluoride (UF_6) (reaction 3). Isotopic enrichment is achieved by gaseous diffusion of UF_6 through porous membranes, with the respective isotopes ^{238}U and ^{235}U having different diffusion rates.

Ambient HF levels in workplace air can result from leakage in storage or transfer of anhydrous HF, or from leakage in manufacturing processes. Furthermore, F_2 gas and UF_6 gas (reactions 4,5) react quickly with airborne moisture to produce HF, and therefore, any leakage of these materials is also a potential source of ambient HF.

A. TOXICOLOGICAL ASPECTS OF AIRBORNE EXPOSURE TO HF [2]

Hydrogen fluoride is considered to be the most biologically corrosive of the hydrohalic acids. It produces painful burns of unusual severity due not only to its acid properties, but also because of the mobility of fluoride ion in tissue (including skin), and because of the tendency of fluoride to complex and immobilize calcium.

Acute effects

Exposure to 1% airborne HF produces burns of exposed skin and eyes, and inhalation at this level for only a few minutes produces death from pulmonary edema within hours of exposure. Short exposures at levels from 36 to 120 ppm can produce smarting of the skin with marked eye and respiratory irritation. Exposure to levels above 2.5 ppm produces mild irritation of the skin, eyes, and nose while exposure below 2 ppm usually produces no acute effect.

Chronic Effects

Chronic exposure to over 3 ppm total fluoride can result in osteofluorosis of bones and teeth, calcification of ligament tissue, and at higher levels, kidney and renal damage.

Recommended Limits of Exposure

Based on toxicity data, the recommended workplace environmental limit for exposure to hydrogen fluoride is 2.5 mg/m^3 (3 ppm) for either 8 or 40 hours time weighted average. To preclude acute irritation from HF, the recommended ceiling limit for a 15 minute exposure is 5 mg/m^3 (6 ppm).

B. CURRENT MONITORING METHODS

Several methods are currently available for determining ambient concentrations of HF. However, most of these are cumbersome and/or inconvenient, or require expensive monitoring hardware. The recommended NIOSH analytical procedure for determining ambient levels of HF is bubbler collection in 0.1 M sodium hydroxide solution [3] (See Appendix II). Air is continuously metered through the bubbler by means of a battery operated sampling pump. Other pumped sampling methods have been proposed such as the collection on alkaline-impregnated filters [4], and collection on sodium acetate sampling tubes. Although modern portable sampling pumps are reasonably precise, they must be calibrated with each use, they usually have a working limit of less than 12 hours continuous use, and use of them for 8 hour personal monitoring is often cumbersome. Liquid bubbler methods such as the NIOSH Method are especially difficult for this purpose because normal employee activity can interfere with sample collection, or cause spillage of potentially caustic liquid. Therefore, considerable time must often be spent by the hygienist monitoring the equipment.

The Abcor Gasbadge dosimeter is significantly easier for hygienists to use and for employees to wear. It does not interfere with normal activity, requires no calibration by the hygienist, and has no mechanical parts to wear out or batteries to run down. It can be used for up to 40 hours continuous sampling or for 15 minutes ceiling level sampling, as either an area or personal monitor. The Gasbadge was developed in the early 1970's for monitoring SO_2 and NO_2 , and has been widely used since. Since its introduction, other models have been developed to monitor organic vapors, ammonia, and as described herein, HF.

C. DOSIMETER DESIGN

Figure 1 presents a schematic diagram of the Abcor Gasbadge dosimeter. The components of the dosimeter are:

1. A sliding cover for the diffusion opening. The cover can also serve as a stand if the device is used for area monitoring.
2. Dosimeter front with an opening to allow diffusion of analyte vapor into the device.
3. A draft shield made from non-reactive, porous material, with a protective outer screen.
4. An open grid to define the diffusion geometry and to minimize internal mixing.
5. A replaceable collection element.
6. The caseback with a spring clip for attachment to the individual or area to be monitored.

The current design incorporates an internal blank chamber which is useful in determination of the blank value resulting from handling by the hygienist. (See Appendix 1, "Analysis Method.")

Gasbadge dosimeter sampling and analysis methods have been developed for workplace air sampling of SO_2 and NO_2 [6], for organic vapors [7], and for ammonia [8]. The badge configuration for HF sampling is adapted from the Abcor design for SO_2 monitoring. The front, back, and cover slide are polyethylene, the draft shield and diffusion grid are polypropylene, and the collection element is alkaline-coated polypropylene fabric (See section IV).

FIGURE 1: SCHEMATIC OF DOSIMETER

III. THEORY AND PRINCIPLE OF OPERATION

A. GENERAL [6]

The dosimeter is designed such that the limiting resistance to mass transfer of contaminant to the collection medium is contained in the stagnant air layer within the dosimeter, i.e. between the draft shield and the active collection element. Fick's First Law of Diffusion is the applicable relationship to describe this diffusive transport:

$$N = - DA \frac{dc}{dx} \quad (1)$$

where

- N = diffusive transport rate (moles/sec.)
- D = contaminant diffusivity in air (cm²/sec.)
- A = diffusion path cross-sectional area (cm²)
- x = distance from front of diffusion layer (cm)
- c = contaminant concentration at x (moles/cm³)

Equation (1) may be integrated over the diffusion layer (of thickness λ) to yield the rate of contaminant collection. The boundary conditions for concentration are:

1. The concentration of contaminant at the surface of the collection element is zero (i.e. assume 100% collection efficiency); and
2. The concentration of contaminant at the badge face is the ambient concentration C_{∞} . (This is based on the assumption that all mass transfer resistance is internal to the dosimeter.)

The final result for the rate of contaminant collection is

$$N = \frac{DAC_{\infty}}{\lambda} - \frac{DAC_0}{\lambda} \quad (2)$$

For a given exposure time (seconds), the total mass of contaminant collected becomes

$$Nt = \frac{DAC_{\infty} t}{\lambda} - \frac{DAC_0 t}{\lambda}, \text{ where } t = \text{exposure duration (seconds.)}$$

Nt is thus proportional to the ambient concentration and elapsed time. Chemical analysis of the collection element is used to determine Nt, and C_{∞} may be readily calculated from Equation (3) upon substitution of known geometrical factors, the contaminant diffusivity in air, and exposure time:

$$C_{\infty} = (Nt) \left[\frac{\lambda}{DA t} \right] + C_0 \quad (3)$$

Note that in practice an empirically determined calibration factor may be necessary to account for the influence of parameters such as the efficiency of the collection medium; also C_0 is assumed to be zero.

Sensitivity to Ambient Conditions - Given that the limiting resistance to mass transfer is in the diffusive layer, the only transport parameter sensitive to ambient temperature or pressure is contaminant diffusivity, D, which depends on these parameters as:

$$D \propto \frac{T^{3/2}}{P}$$

The increase in diffusivity with an increase in temperature from 5°C to 35°C would be:

$$\left\{ \left(\frac{308}{278} \right)^{3/2} - 1 \right\} \times 100 = 16.6\%$$

Changes in barometric pressure from 28 to 32 inches Hg would lead to a decrease of 12.5% in the diffusivity.*

* The mass collected by the dosimeter is virtually independent of temperature, and completely independent of pressure. This is because $N \propto DC_{\infty}$. Considering temperature, $D \propto T^{3/2}$; $C_{\infty} \propto T^{-1}$; hence $N \propto T^{1/2}$. Considering pressure, $D \propto P^{-1}$, $C_{\infty} \propto P^1$; hence $N \propto P^0$. Thus, $N \propto T^{1/2} P^0$.

Face Velocity Effects - The dosimeter can be expected to sample accurately so long as all resistance to contaminant transport is contained within the stagnant air layer inside the device. As the velocity of air across the dosimeter surface (face velocity) decreases, the external resistance to mass transfer associated with convection increases. When this latter resistance becomes a significant fraction of the total diffusional resistance, the mass of contaminant collected will become less than that predicted on the basis of Equation (3). Since the external resistance associated with convection is poorly controllable, it is desirable to design the dosimeter such that under the expected conditions of use, this resistance will be negligible.

Convection mass transfer external to the dosimeter is described, for the case of completely boundary layer-dominated transport, by the following relationship:

$$N = kAC_{\infty}^*, \text{ where} \quad (4)$$

k = the convective mass transfer coefficient.

The mass transfer coefficient can be estimated from the correlation for low Reynolds number drag ($10 < Re < 3000$). Using the Chilton-Colburn analogy, which is exact in this case, the mass transfer coefficient is given by:

$$Sh = \frac{kL}{D} = 1.45 (Re_L)^{0.4} (Sc)^{.333} \quad (5)$$

where:

Sh = Sherwood number

Sc = Schmidt number

Re_L = Length Reynolds number

* Compare with $N = \frac{D}{\lambda} AC_{\infty}$, for diffusion-dominated transport.

Simplifying yields:

$$k = 1.45 \frac{D}{L} (Re_L)^{0.4} (Sc)^{.333}$$

To minimize the effects of ambient convection on dosimeter sampling efficiency, the internal diffusive resistance must greatly exceed the external boundary layer resistance. Now

$$R_{\text{diffusive}} = \lambda/D \quad , \text{ and} \quad (6)$$

$$R_{\text{convective}} = 1/k \quad , \text{ so, from (5), (6), and (7):} \quad (7)$$

$$\frac{R_{\text{diffusive}}}{R_{\text{convective}}} = k_1 V^{0.4} \quad , \text{ where} \quad (8)$$

$$k_1 = 1.45 \frac{\lambda}{D^{0.333}} \left(\frac{\rho}{\mu}\right)^{.067} \quad , \text{ and}$$

ρ = gas density

μ = gas viscosity

V = face velocity across the dosimeter

For the dosimeter to accurately sample the pollutant of interest, equation (8) suggests that a minimum air velocity will be required and that once this minimum is achieved, performance will be velocity-insensitive over a wide range. Evaluation of velocity effects both at Abcor and at the Research Triangle Institute indicates no significant effect at face velocities as low as 15 ft./min (0.274 km/hr.) Note that the face velocities encountered

*desire large

in most work places are a minimum of 50-75 ft./min. (0.914-1.37 kph). Thus, for most applications negligible influence of external boundary layer resistance upon accuracy of results is expected, and this has been substantiated in field and laboratory experience to date.

Response Time Considerations - A measure of response time is the average residence time of contaminant within the diffusion zone. Assuming 100% collection efficiency, contaminant concentration at the collecting element surface will be zero. Thus, the average concentration within the diffusion zone is simply $C = C_{\infty}/2$, (assuming a linear concentration profile) and the internal mass hold up is $(C_{\infty}/2)(\lambda A)$. The residence time may be readily calculated, as follows:

$$T_{\text{res}} = \frac{\text{mass hold up}}{\text{diffusive transport rate}} = \frac{(C_{\infty}/2)(\lambda A)}{\frac{D A C_{\infty}}{\lambda}} = \frac{\lambda^2}{2D} \quad (9)$$

For the monitoring of HF the residence time is calculated to be 3.4 seconds for $D = 0.25 \text{ cm}^2/\text{s}$. This short residence time is sufficient for the dosimeter to sample a true time-weighted average HF concentration.

B. MECHANISM FOR HF COLLECTION

The collection medium in the HF dosimeter is an inert substrate coated with triethanolamine (TEA). HF is absorbed at close to 100% efficiency, and reacts with the absorbent to yield the non-volatile fluoride salt (reaction 6.)

The exposed collection element is extracted into a buffer of high ionic strength, and the amount of fluoride present is determined with an ion-selective electrode (see Appendix I, "Analysis Procedures"). Other means of analysis may be adapted to this determination, such as high performance ion exchange chromatography or gas chromatography.

IV. DEVELOPMENT OF HF DOSIMETER CONFIGURATION

A. CASE

Nylon and polyethylene dosimeter cases were available at the start of the project and were tested for reactivity to HF. The comparative test procedure involved spotting the parts with a drop of 50% hydrofluoric acid. The polyethylene was apparently non-reactive but the nylon reacted almost immediately, dissolving the surface nylon within seconds. Therefore, polyethylene was chosen as the case material for the HF badge.

B. GRID

Polypropylene was selected as the HF Gasbadge grid material. Adsorptive effects of the grid toward HF must be minimized if a proper diffusion gradient is to be maintained, especially if very low ambient HF levels are to be monitored. Ideally all collection of HF within the dosimeter should be on the collection medium, although in practice, some adsorption on the grid is unavoidable. Therefore, 3 different grid materials were tested to determine which had the best non-adsorptive characteristics.

Four tests were conducted to compare response of gasbadges that utilized polypropylene or polyethylene grids with that of gasbadges in which conventional polycarbonate grids were used. Gasbadge configuration for all tests was: polyethylene case, PellonTM type FT-2106 polypropylene (Pellon Corp., Lawrence, MA) collection element substrate, 20% triethanolamine in methanol absorbent (dried on pellon substrate), Pellon draftshield, and Vexar screen. Relative humidity was 50% $\pm$ 5%. Face velocity was approximately 65 feet/minute. Exposure levels between 0.6 and 4.0 ppm of HF were generated by bubbling 400 ml/minute of air through a 25% HF solution, and diluting to a total flow rate of approximately 13 liters/minute. Results were:

Test 1. Exposure Time: 50 minutes; Temperature: 26.9°C

<u>Gasbadge No.</u>	<u>Grid Material</u>	<u>Moles of HF Collected*</u>
1	Polypropylene	3.40×10^{-7}
2	Polycarbonate	2.34×10^{-7}
3	Polypropylene	2.22×10^{-7}
4	Polycarbonate	2.14×10^{-7}
5	Polypropylene	1.84×10^{-7}
6	Polycarbonate	1.44×10^{-7}

*Corrected for blank

Test 2. Exposure Time: 81 minutes; Temperature: 26.0°C

<u>Gasbadge No.</u>	<u>Grid Material</u>	<u>Moles of HF Collected*</u>
1	Polypropylene	2.16×10^{-7}
2	Polycarbonate	1.74×10^{-7}
3	Polypropylene	1.64×10^{-7}
4	Polycarbonate	1.50×10^{-7}
5	Polypropylene	1.62×10^{-7}
6	Polycarbonate	1.24×10^{-7}

*Corrected for blank

Test 3. Exposure Time: 93 minutes; Temperature: 26.2°C

<u>Gasbadge No.</u>	<u>Grid Material</u>	<u>Moles of HF Collected*</u>
1	Polypropylene	7.78×10^{-7}
2	Polycarbonate	6.44×10^{-7}
3	Polypropylene	6.60×10^{-7}
4	Polycarbonate	6.12×10^{-7}
5	Polypropylene	5.72×10^{-7}
6	Polycarbonates	5.39×10^{-7}

*Corrected for blank

Test 4. Exposure Time: 60 minutes; Temperature: 24.7°C

<u>Gasbadge No.</u>	<u>Grid Material</u>	<u>Moles of HF Collected*</u>
1	Polypropylene	3.50×10^{-7}
2	Polyethylene	3.24×10^{-7}
3	Polypropylene	2.74×10^{-7}
4	Polyethylene	2.54×10^{-7}
5	Polypropylene	2.46×10^{-7}
6	Polyethylene	2.22×10^{-7}

*Corrected for blank

In comparative testing, no difference in response was detected with Gasbadges using polyethylene, polypropylene, and polycarbonate grids at ambient concentrations between 0.6 and 4 ppm HF. Improper choice of grid material can definitely lower response, as demonstrated in a test in which nylon grids were used. (Nylon is known to react with HF.) The response with nylon grids was forty percent lower than that obtained with the control (polycarbonate).

Because the polyolefins contain only non-polar functional groups, while polycarbonate contains polarized groups such as carbonyl, the polyolefins should be less adsorptive to the polarized HF molecule. Therefore, polyolefins were chosen for the final configuration. It is likely that polypropylene or polyethylene can be used interchangeably, but for the sake of consistency, polypropylene grids were used for both the field study and for the laboratory studies that followed.

C. COLLECTION ELEMENT SUBSTRATE

PellonTM type FT-2106 (Pellon Corp., Lawrence, MA) non-woven polypropylene fabric was judged to be a good mechanical support due to its very low background interference, chemical inertness to HF, mechanical stability in the desorption process, and availability. Subsequent testing (as described in Part D) corroborated its adequacy as a substrate for coating with triethanolamine (TEA) or with a solution of triethanolamine and potassium hydroxide (KOH-TEA).

D. ABSORBENT FOR HF COLLECTION

To obtain good Gasbadge response at all typical conditions, it is necessary to utilize an absorbent that has excellent collection efficiency as well as good mechanical properties. An attempt was made to select 1 or 2 absorbents from the many candidates available. Those investigated were:

1. Potassium Hydroxide (KOH)
2. Sodium Acetate
3. Sodium Carbonate
4. 20% KOH/10% Triethanolamine
5. Triethanolamine

In a National Bureau of Standards study to develop a solid sorption tube for HF, it has been shown [5] that absorbent 4 (20% KOH/10% TEA) has a collection efficiency of 100% at relative humidities greater than 25%. Absorbents 2 and 3 suffered from "powderizing" and subsequent sorbent loss after drying. Absorbent 1 tended to leave caustic residue which could be harmful. Absorbent 4 had similar problems, though less severe. Absorbent 5 gave the best physical characteristics, and was judged suitable if the collection efficiency equals that of absorbent 4. However, it was noted that absorbent 4 displayed undesirable long-term stability effects, absorbing CO_2 from the air and becoming, in effect, a sodium carbonate element within 3 days of exposure to ambient air. Based on this previous research, it was decided to test triethanolamine (TEA) as an absorbent for the HF dosimeter.

Tests at Abcor were performed to determine the optimal triethanolamine (TEA) loading and manufacturing procedure. The Pellon element displaying the best resistance to absorbent loss was prepared by saturating the element with a solution of 15-20% (volume: volume) of TEA in reagent-grade methanol. The element was then dried in a draft oven at 80°C for 15 minutes.

Results of absorbent tests are presented in Table 1 (Runs 1-3). A comparison of runs 1 and 2 indicates that the 20% KOH/10% TEA element gave the same response as the pure TEA element, indicating that both absorbents yield the same collection efficiency. Run 3 corroborates the results with pure TEA.

TABLE 1: PRELIMINARY TESTS - TEA COLLECTION ELEMENT

Run No	Test Date	No. of Impingers	No of Gasbadges	Gasbadge Absorbent	Impinger Conc, ppm	Gasbadge Conc, ppm	(GB Response) (Imp. Response)	Exposure Time (mins)	Test Objective
1	10/19/79	2	3	TEA	153±1.4	55.1±2.1	.360	85	Comparison of Gasbadge response using TEA vs. 20% KOH/10%TEA absorbents
2	10/20/79	2	3	20%KOH 10%TEA	120.8±1.9	45.4±0.93	.376	80	
3	10/22/79	2	3	TEA	105.4±1.13	37.2±1.25	.353	85	
4	10/25/79	2	3	TEA	97.4±1.7	37.0±0.6	.380	80	TEA absorbent check.
5	10/30/79	2	3	TEA	89.6±1.48	33.5±0.4	.374	80	Linearity tests
6	11/2/79	2	3	TEA	18.9±0.35	7.04±0.03	.372	140	
7	11/4/79	2	3	TEA	7.04±0.11	3.1±0.09	.440	150	
8	11/5/79	2	3	TEA	6.05±0.3	2.17±0.06	.359	150	
9	11/6/79	2	3	TEA	2.13±.04	1.07±0.06	.502	100	
10	11/7/79	2	3	TEA	3.18±.19	1.21±.02	.381	60	
11	11/9/79	2	3	TEA	2.15±.01	.90±.08	.419	90	

A preliminary study verified that the selected Pellon/TEA collection element responds linearly in the range 2 to 150 ppm HF. These results are presented in Table 1 and are shown graphically in Figure 2.

E. DRAFT SHIELD

The draftshield must be non-reactive to HF and should be non-adsorptive. It must be permeable to diffusion-controlled transport of HF but must provide a windscreen such that there is a current-free air space inside the gasbadge when outside wind currents are greater than 250 ft/min. Various candidate permeable materials were tested for reactivity to HF by placing a drop of 50% HF on each and noting the reaction. The results of these tests are presented below:

(A "pass" indicates that no noticeable reaction had occurred after 10 minutes.)

<u>Material</u>	<u>Result</u>
Remay (a white, resilient polyester material, manufactured by DuPont)	Passed
Pellon (non-woven polypropylene, Type FT-2106)	Passed
Gelman Versapore (1.5 μ m pore size filter paper)	Failed
Gelman Type AE (glass fibre filter)	Failed

Because of availability, the Pellon material was chosen for preliminary testing. Subsequent exposure runs showed that this material was acceptable at a face velocity of up to 300 ft/min (1.52 m/s); it was thus chosen for the final configuration. Data from the 2 runs at 300 ft/min are presented in Table 2.

F. FINAL GASBADGE CONFIGURATION

In summary, the final gasbadge configuration chosen for field and laboratory validation was as follows:

FIGURE 2: PRELIMINARY LINEARITY PLOT

HF GASBADGE DATA - IMPINGER RESPONSE VS. GASBADGE RESPONSE

TABLE 2:

GASBADGE RESPONSE AT 300 FEET/MINUTE FACE VELOCITY

<u>Monitor</u>	<u>PPM Measured</u>	<u>Average PPM</u>
Impinger 1	18.1	17.6 ± 0.6
Impinger 2	17.0	
Gasbadge 1	8.57	8.37 ± 0.94
Gasbadge 2	8.40	
Gasbadge 3	9.31	
Gasbadge 4	7.83	
Gasbadge 5	7.74	

$$\text{Response Factor} = \frac{8.37}{17.6} = 0.48$$

<u>Monitor</u>	<u>PPM Measured</u>	<u>Average PPM</u>
Impinger 1	28.2	27.9 ± 0.3
Impinger 2	27.6	
Gasbadge 1	14.1	13.8 ± 0.3
Gasbadge 2	13.8	
Gasbadge 3	13.6	
Gasbadge 4	13.6	
Gasbadge 5	13.8	

$$\text{Response Factor} = \frac{13.8}{27.9} = 0.49$$

The average value, 48.5% theoretical response, compares well with other preliminary runs at 70 feet/min face velocity. That value is approximately 45% ±10%.

Case - Polyethylene

Grid - Polypropylene

Draftshield - Pellon FT2106 with polypropylene screen (vexar)

Collection element - Pellon FT-2106 coated with TEA

This configuration was subsequently shown to be acceptable in both laboratory testing (Section V-B) and in actual industrial exposure in the field (Section VI). Although this configuration is a very good one, further refinements and improvements may be possible.

V. EXPERIMENTAL SECTION

A. EQUIPMENT AND PROCEDURES

1. Analytical Equipment

All fluoride analysis was accomplished with a fluoride ion-selective electrode (Orion Model 94-06). Potential was measured to the nearest 0.1 mv using a digital readout PH-MV meter (Orion Model 701). Analytical procedures are detailed in Appendices I and II.

2. Contaminant Air Generation and Exposure Systems

Two different exposure systems were utilized; a preliminary system, and an improved final system. Figure 3 shows the general configuration for both systems.

a. Preliminary System

(1) Manifold - Preliminary testing was done with the Abcor Development Corporation controlled exposure system. Airflow was regulated with calibrated flowmeters (Fisher & Porter models #10A1338N32AX (10 l/min) and could be delivered at up to 24 l/min for 50% relative humidity, and up to 12 l/min for 0% or 100% relative humidity. Dry air (Linde Breathing Grade) was saturated by bubbling it through gas dispersion bottles containing distilled water. The resulting saturated air could be mixed in any proportion with dry air to yield the desired humidity. Air temperature was controlled with a thermostated water bath (Superior Electric Co., Model 116B) and a recirculating pump (March, Model U21).

(2) HF Source - HF was generally introduced by metering air @ 400 ml/min through a solution of hydrofluoric acid, with subsequent dilution to 15 l/min. The desired HF output was adjusted by varying the HF concentration of the aqueous generating solution. It had been intended to use a calibrated tank of 1000 ppm HF in nitrogen as the HF source, but such a tank could not be procured. On one occasion a calibrated HF tank was obtained from Synthatron, Inc., 50 Intervale Road, Parsippany, NJ 07054; however,

FIGURE 3a: HF MANIFOLD + EXPOSURE SYSTEM

FIGURE 3b: - HF SOURCES

I. PRELIMINARY HF SOURCE

II. LOW LEVEL HF SOURCE, FINAL SYSTEM

III. HIGH LEVEL HF SOURCE, FINAL SYSTEM

although this tank was analyzed by the manufacturer and guaranteed stable at 1000 ppm, upon arrival at Abcor it was found to contain 20-40 ppm of HF and the observed HF concentration was dropping with time. Although some preliminary testing was accomplished with this tank, only a stable mixture (with predictable output) is acceptable for precise testing. Another tank from Synthatron, and one from Scott (each purporting to be a stable 1000 ppm HF mixture) contained no detectible HF at all. After obtaining three unsatisfactory tanks, it was decided to use a different HF source for the final configuration.

(3) Exposure Chamber - The exposure chamber for the preliminary system was usually a polycarbonate linear design of 51 cm x 3.3 cm x 6.5 cm internal dimensions, which could house up to 5 badges. A circular polycarbonate chamber of internal dimensions 30 cm depth x 30 cm diameter was employed for some preliminary testing. Although this chamber could house up to 20 badges, it proved too large for the airflow capacity of the manifold. Further, the development of concentration gradients within the chamber could not be avoided.

b. Final System

Although the first system was useful in the development of dosimeter configuration (Section IV), consistent agreement between intended and actual output could not always be achieved. The system incorporated much glass and PVC, materials that are reactive with HF. Because of this, long conditioning of the system was necessary; this wasted materials and time. Consequently, a new system was constructed from less reactive materials and with increased output airflow capacity.

(1) Manifold - As in the first system, flow rate was controlled with calibrated flowmeters (Dwyer Model RMA-22). The larger capacity of these rotameters (25 l/min) increased the output capacity of the system to 50 l/min for 50% relative humidity. Humidity and temperature were controlled as in the first system but the water bath capacity was increased to allow for a diffusion tube holder. A 30 cm x 30 cm diameter polycarbonate tank (Nalgene) was employed as the water bath container for this final system. The capacity of this bath was about 5 times the volume of the first water bath. The water was

heated with a thermostated heater (Technilab Instruments, Model 94-10) and circulated with a magnetic drive pump (March Model MPX-3). All tubing was polypropylene or polyethylene to minimize adsorptive effects, and was 0.95 cm O.D. to minimize pressure drop.

(2) HF Source - The HF source, for output levels below 15 ppm, was a set of 30 cm. permeation tubes (Metronics Model 110-300-0040) housed in a submersible holder (Metronics Model 19X-430). The desired HF output could be adjusted by varying the number of tubes (from 1 to 5) or by varying the permeation temperature (from 20°C to 80°C). The tubes were not calibrated but were observed to yield consistently reproducible levels of HF. For a typical application, 300 ml/min of air were metered past (5) 30 cm permeation tubes maintained at $43 \pm 1^\circ\text{C}$. The resulting contaminant air was diluted to 30 l/min to yield a final output concentration of 2.1 ± 0.1 ppm HF @ 25°C.

A double dilution system of pure anhydrous HF vapor (Matheson) was utilized to generate [HF] levels in excess of 100 ppm. Each dilution was accomplished using a 30 cm x 30 gauge teflon syringe needle (Hamilton) as a flow restrictor. This high-level HF generation system was only partly successful and was quite dangerous to operate; therefore, only 3 tests were performed with this set-up.

Based on the knowledge gained in the year of laboratory testing, we strongly recommend the use of permeation tubes as the source of HF when generating atmospheric test gas at the low ppm level or below. Both in terms of safety and convenience, and in terms of predictable output and quick equilibration, no other source was as successful.

(3) Exposure Chamber - For the second system a linear chamber of 61 cm x 3.2 cm x 7.0 cm internal dimensions was constructed of polypropylene (See Figure 4). This chamber could house up to 6 badges and had ports for up to 5 external sampling systems. For a typical run, 3 or 4 dosimeters were placed in the chamber, approximately 7 cm. apart. They were exposed for approximately 4 hours to 30 l/min of contaminant air. The chamber air was independently sampled to determine the "true" concentration as described below.

FIGURE 4 : SKETCH OF COMPLETED CHAMBER (all dimensions O.D.)

3. External Sampling Train

For both exposure systems the true exposure concentration was determined by collection of the HF in 0.1 M NaOH as specified by NIOSH Method S-176 (See Appendix II). One l/min of contaminant air was bubbled through 15 ml of absorbing solution and the resulting solution was analyzed for fluoride. Flow was controlled with calibrated critical orifices (1.0 l/min, Millipore) and the required pressure drop was generated by a vacuum pump (Welch Model 1600). For the 1.0 l/min orifice to operate as a "critical" orifice, the required pressure drop is 280 mm Hg; the vacuum system employed generated 630 mm Hg pressure drop, thus insuring that the orifice was critical.

B. PERFORMANCE TESTING

1. Linearity

The HF gasbadge was shown to exhibit linear response to ambient HF in the range of .05 - 212.5 ppm over an 8 hour exposure. Table 3 gives data for these linearity runs and Figure 4 shows the linearity plot.

Gasbadge data were reduced by using the Gasbadge formula (see Appendix I). The diffusion coefficient D used in the data reduction was calculated using the formula of Fuller and Giddings [9], which yields $D_0 = 0.25 \text{ cm}^2/\text{s}$ at 25°C and 760 mm Hg. (See Appendix V). This value of the diffusion coefficient was then corrected for exposure temperature as indicated by the formula $[D/D_0 = (T/T_0)^{1.5}]$ (See Section III-A - Temperature Effect on D). Impinger data were reduced following the procedures described in NIOSH Method S-176 (See Appendix II).

A linear regression on the 20 data points yields the following relationship:

$$(1) \quad [\text{HF}]_{\text{Gasbadge}} = 1.10 [\text{HF}]_{\text{Impingers}} - 3.42, \text{ where} \quad (10)$$

$[\text{HF}]_{\text{Gasbadge}}$ = indicated HF concentration (ppm) from Gasbadge

$[\text{HF}]_{\text{Impingers}}$ = indicated HF concentration (ppm) from NIOSH Method S-176

The coefficient of determination (r^2) for this relationship is

$$r^2 = 0.988.$$

The closeness of this value to 1.00 is an indication of how well the data are fit by the linear regression.

TABLE 3. RESULTS OF PRECISION/LINEARITY TESTS

Run #	Exposure Date	Exposure Time (min)	Exposure Temp (K)	(X) [HF] Impingers (ppm)	(Y) [HF] Badges (ppm)	Badge Deviation From Impingers (%)	Percent of Theoretical Response *
1	Oct 23	199.2	297.0	0.46±0.005	0.32±0.02	-30	68.0
2	" 24	244.07	295.3	0.45±.01	0.42±.02	-6.6	93.2
3	" 29	236.5	295.3	0.13±.002	0.15±.01	+15.4	115.2
4	" 30	261.0	294.5	0.10±0	0.073±.006	-27.0	70.0
5	Nov 3	177.33	294.8	0.099±.01	0.117±.02	+18.2	118.0
6	" 4	246.92	293.4	0.41±.009	0.30±.02	-26.8	73.2
7	" 5	240.0	295.8	1.09(1 run)	0.82±.03	-24.8	76.0
8	" 5	224.33	296.2	1.18±0.002	0.98±.05	-16.9	83.2
9	" 6	211.50	295.6	1.22±.02	1.21±.06	-0.8	99.2
10	" 7	249.25	296.0	4.58±.14	2.84±.11	-38.0	62.0
11	" 10	260.0	295.4	3.33±.05	2.42±.06	-27.3	72.8
12	" 11	248.11	295.3	3.03±.04	2.53±.10	-16.5	83.6
13	" 12	244.0	295.8	3.13±.007	2.51±.10	-19.7	80.4
14	" 13	80.28	294.4	203±5.4	183±9.0	-9.9	90.0
15	" 14	130.0	295.7	132±0.6	120±2.6	-9.1	90.8
16	" 17	248.88	295.7	387±9.2	450±6.1	+16.3	116.4
17	Dec 4	256.5	296.4	10.4±1.3	7.40±.12	-28.8	71.2
18	" 5	256.5	296.7	10.6±1.4	7.88±0.31	-25.7	74.4
19	" 8	256.5	297.2	11.1±0.30	7.53±0.37	-32.2	68.0
20	" 9	256.5	296.6	10.7±.09	6.84±0.19	-36.0	64.0

* Mean value of response factor 83.6% (R=0.836)

$$(\text{Response factor} = \frac{[\text{HF}]_{\text{Gasbadge}}}{[\text{HF}]_{\text{Impingers}}})$$

FIGURE 5. HF DOSIMETER PRECISION/LINEARITY TESTS

12/12/80

Also presented in Table 3 are values showing percent of theoretical response for each run. The overall response for the badge was taken to be the average of the badge response shown for all 20 runs. The average response was 83.6% of theoretical, which compares well with other Gasbadge calibration factors.

2. Precision and Accuracy

It is recommended by NIOSH that the overall accuracy of a sampling method for an environmental contaminant should be ± 25 percent for 95 percent of the samples taken between 0.5 and 2 times the accepted standard [10]. Equation 11 is an overall accuracy statement corresponding to that criterion [11].

$$\text{Overall accuracy} = \pm \left[\text{absolute mean bias} + 2 \left(\text{mean relative standard deviation} \right) \right] \quad (11)$$

To determine overall accuracy, several terms must be defined.

- Definitions:
- (1) i = run number
 - (2) m = badge number
 - (3) n_i = total number of badges in run i
 - (4) j = total number of runs
 - (5) $[HF]_{i,m}$ = HF concentration of badge m in run i
 - (6) Mean HF concentration of all n_i badges in run i , $\overline{[HF]_i}$

$$\overline{[HF]_i} = \frac{\sum_{m=1}^{n_i} [HF]_{i,m}}{n_i}$$

(7) Standard deviation for run i, S_i :

$$(S_i) = \sqrt{\frac{n_i}{n_i - 1} \left[\frac{\sum_{m=1}^{n_i} [HF]_{i,m}^2}{n_i} - \frac{\left(\sum_{m=1}^{n_i} [HF]_{i,m} \right)^2}{n_i^2} \right]}$$

(8) Relative standard deviation for run i, RS_i :

$$(RS_i) = \frac{S_i}{[HF]_i} \times 100\%$$

(9) Mean Relative Standard Deviation (MRS)

$$= \sqrt{\frac{(n_1 - 1)(RS_1)^2 + \dots + (n_i - 1)(RS_i)^2}{\sum_{i=1}^j (n_i - 1)}}$$

(10) Percent bias, (B) = $\frac{\text{Ave ppm (sample)} - \text{Ave ppm (true)}}{\text{Ave ppm (true)}} \times 100\%$

(11) Mean Bias, $\overline{(B)} = \frac{B_1 n_1 + B_2 n_2 + \dots + B_i n_i}{\sum_{i=1}^j n_i}$

For the HF Gasbadge to meet the acceptable accuracy requirement, the overall accuracy as defined above in Equation 11 should not exceed 25 percent for samples in the action range (approximately 0.5 to 2 x TLV).

Data in Table 4 are the linearity study results taken from Table 3 and divided by the overall response factor ($R = 0.836$). The overall accuracy in the action range was $\pm 17.3\%$, well within the $\pm 25\%$ limit. This estimate of accuracy should be conservative because it assumes no error in the precision of the true HF concentration (impinger sampling). In reality, the average precision for both the badges and impingers was very good, about $\pm 3.5\%$.

The overall accuracy for all 20 runs including those in the action range, as defined by Equation 11 was $\pm 10.4\%$.

TABLE 4 : ACCURACY + PRECISION - STATISTICAL SUMMARY

Run No.	[HF] ppm (Impingers)	[HF] ppm (Badges) (with R = 0.836) ^{1/}	No. of Badges	RS (Badges)%	% Bias
1	0.46	0.38	4	6.25	-17.4
2	0.45	0.50	4	4.76	11.1
3	0.13	0.18	4	6.67	38.5
4	0.10	0.087	4	8.22	-13.0
5	0.099	0.14	4	14.5	41.4
6	0.41	0.36	4	6.67	-12.2
7*	1.09	0.98	4	3.66	-10.1
8*	1.18	1.17	4	5.10	-0.8
9*	1.22	1.45	4	4.95	18.9
10*	4.58	3.40	4	3.87	-26.0
11*	3.33	2.89	4	2.48	-13.2
12*	3.03	3.02	4	3.97	- 0.3
13*	3.13	3.00	4	3.98	- 4.2
14	203	219	3	4.92	7.8
15	132	144	3	2.17	11.5
16	387	538	3	1.36	39.1
17*	10.4	8.85	3	1.62	-14.9
18*	10.6	9.42	3	3.93	-11.1
19*	11.1	9.00	3	4.91	-18.9
20*	10.7	8.18	3	2.78	-23.6

Action Range

MRS = $\pm 4.27\%$

Mean Bias = -8.71%

Overall Accuracy = $\pm 17.3\%$

Overall

MRS = $\pm 5.07\%$

Mean Bias = $+0.28\%$

Overall Accuracy = $\pm 10.42\%$

*Runs within "Action Range" (0.5 to 2.0 x TLV.)

^{1/}Values presented here are raw data (ppm) divided by the response factor of 0.836.

3. Temperature Effects

Performance of the HF Gasbadge was shown to vary with temperature in a manner consistent with theory. Temperature changes apparently had no effect on the collection efficiency of the absorbent, or on the stability of the collected HF. The observed increase in the sampling rate of HF with increasing temperature was shown to agree with the expected increase in the diffusivity of HF.

According to theory, the only badge parameter affected by temperature should be the diffusion coefficient (D) as discussed in Section III(A). The following temperature dependence should be shown by D (Equation 12):

$$D(T) = D_0(T/T_0)^{3/2}, \text{ where} \quad (12)$$

D_0 = diffusion coefficient at standard temperature and pressure
(298 K, 1 atm) (cm^2/s)

$D(T)$ = diffusion coefficient at temperature T (cm^2/s)

T = absolute temperature (K)

T_0 = standard temperature = 298 K

Preliminary testing showed reasonable agreement with theory, but the data showed too much scatter to be considered conclusive (See Figure 6 and Table 5.)

A second study was done more accurately to show the temperature effect at approximately 38°C, a temperature typical of the field study (See Section VI.) This study was done with the final exposure system. The data for these runs are presented in Table 6. For each run, 3 badges and 2 impingers (Runs 5 and 6) or 3 impingers (Runs 1-4) were used. HF concentrations near 2.2 ppm were generated with permeation tubes.

PRELIMINARY STUDY

3/25/80

FIGURE 6: GASBADGE RESPONSE AS A FUNCTION OF TEMPERATURE

TABLE 5

PRELIMINARY GASBADGE TEMPERATURE DEPENDENCY TEST RESULTS

Run No.	Temp.(K)	Exposure Duration (mins)	HF Concen- tration from Badges(ppm)*	HF Concen- tration from Impingers(ppm)**	Response* Factor R(T)
1	314.6	180	0.26±0.02	0.72±0.02	0.361
2	315.3	273	0.47±0.02	1.33±0.06	0.353
3	316.5	83	0.42±0.04	1.38±0.10	0.304
4	316.5	180	0.61±0.02	1.54±0.06	0.396
5	315.4	73	3.7±0.14	11.2±0.01	0.330
6	315.1	155	3.7±0.07	8.99±0.06	0.412
7	315.4	85	5.01±0.10	12.4±0.07	0.404
8	304.9	105	3.36±0.06	8.17±0.03	0.411
9	305.1	117	4.69±0.09	11.8±0.20	0.397
10	287.6	90	0.36±0.01	2.11±0.02	0.171
11	287.6	130	1.70±0.03	7.45±0.24	0.228
12	288.8	174	1.47±0.05	4.84±0.03	0.304

*Mean value of 5 badges

**Mean value of 2 impingers, corrected to standard conditions of 298K and 1 atmosphere.

TABLE 6: TEMPERATURE EFFECTS

RESULTS OF 311K TESTS								
Run No.	Date	Exposure Duration (Minutes)	T(K)	[HF](ppm)		Theoretical Diffusion Coefficient at 298K, D_0 (cm ² /s)	Observed Diffusion* Coefficient D' (cm ² /s)	Response Factor $R=D'/D_0$
				Impingers	Badges			
1	12/17/80	265.9	310.5	2.25±.02	1.88±.19	.250	.209	.836
2	12/19/80	270.2	311.0	2.10±.05	1.73±.14	.250	.206	.824
3	12/22/80	270.0	311.0	2.24±.04	1.88±.02	.250	.210	.840
4	12/23/80	270.0	311.4	2.21±.04	2.02±.02	.250	.229	.916
5	12/30/80	272.0	311.5	2.27±.006	1.94±.06	.250	.214	.856
6	12/31/80	267.0	311.2	2.31±.04	1.84±.15	.250	.199	.796
Mean		269.2	311.1	2.23	1.88	.250	.211	.844

*The value of D required to make the Gasbadge results agree precisely with the impinger results, corrected to 298K (assuming a $T^{1.5}$ dependence.)

The observed average response factor agrees within 1% of the value predicted assuming a $T^{3/2}$ dependence of D. Therefore, all badge calculations should employ this temperature correction for D.

4. Humidity Effects

The HF gasbadge response was shown to be insensitive to ambient moisture at levels below 90% relative humidity. Deviation at higher humidity levels may reflect bias introduced by the exposure system and not actual bias in the sampling device.

Preliminary studies were run using the aqueous bubbler system for HF generation. These results (Table 7 - Part A) seem to indicate a noticeable humidity effect. However, subsequent testing, (Part B), using a calibrated 25 ppm HF in N₂ tank as the HF source, suggests that there is little effect of humidity on response. The seven runs in Part B represent the only testing accomplished with the preliminary exposure system in which the correlation between badges and impingers consistently approaches the level observed later with the new exposure system. Since all other conditions were identical, it seems reasonable that the aqueous HF generation system caused the lower response; the generating system was probably affected by the humidity changes.

TABLE 7: HUMIDITY EFFECTS

PART A (Aqueous HF Generation System)

st te	Relative Humidity (%)	Test Duration (Minutes)	Gas Flow Rate (liters/ min)	No. of Gasbadges	Impinger Response (ppm HF)	Gasbadge Response (ppm HF)	Response Factor R*	Diffusion Coeff. D, assum. R=1.0 (cm ² /S)
2/80	90	307	13	5	1.91±0.01	0.66±0.22	0.35	0.085
3/80	90	279	13	3	3.11±0.02	1.28±0.33	0.41	0.102
5/80	90	312	13	3	1.84±0.04	0.84±0.19	0.46	0.113
6/80	90	188	13	3	2.00±0.06	0.72±0.16	0.36	0.089
9/80	70	150	13	3	9.24±0.08	4.81±0.34	0.52	0.129
0/80	70	120	13	3	4.43±0.05	2.02±0.14	0.46	0.113
1/80	4	240	13	3	7.09±0.04	4.50±0.13	0.63	0.157
1/80	30	144	13	3	4.22±0.07	2.83±0.07	0.67	0.166

PART B (Gaseous HF Generation System)

23/80	47	146	12.7	3	2.60±0.06	1.71±0.05	0.66	0.162
27/80	87	243	13	3	2.55±0.08	1.56±0.03	0.61	0.151
28/80	92	250	13	3	1.72±0.04	0.94±0.03	0.55	0.135
28/80	70	338	13	3	1.65±0.04	1.10±0.09	0.67	0.165
29/80	70	214	13	3	2.85**	1.96±0.08	0.69	0.170
29/80	30	245	13	3	2.04±0.04	1.34±0.04	0.66	0.162
30/80	30	285	13	3	3.20±0.06	2.23±0.05	0.70	0.172

$$*R = \frac{\text{Gasbadge Response}}{\text{Impinger Response}}$$

** 1 sample only

Unfortunately, corroborative humidity testing could not be done with the new system before the end of the contract. There are several plausible explanations concerning the effect of humidity on the diffusion of HF and thus upon gasbadge response:

HF is known to dimerize or polymerize in the vapor state, with the degree of association dependent on the partial pressure of HF [12]. At levels above 20% HF, the diffusivity of HF may measurably decrease as the association factor increases (See Section VII for a further discussion of HF polymerization). It has been shown that in the vapor state the hydrogen bond in the $\text{HF} \cdot \text{H}_2\text{O}$ complex is "slightly stronger than in the $(\text{HF})_2$ dimer" [13]. Therefore, due to the strong interaction between HF and H_2O (similar to that between HF and HF,) the diffusivity of HF in air may decrease with increasing H_2O concentration. However, this effect should not be measurable at less than about 20% H_2O by volume in air. Also, it is highly unlikely that the HF badge will ever be used in air monitoring at such a high humidity level. Therefore, there should be no measurable effect of humidity on the diffusivity of HF under typical monitoring conditions.

However, if actual condensation of water occurs on the draftshield or diffusion grid (or if the draftshield is moistened), the response of the badge will be lowered. The moistened draftshield would become a collector and would no longer be inert. Therefore, monitoring at humidity levels above 95-100% should be avoided.

5. Interference Effects

The response* of the HF gasbadge was shown to be insensitive to competing SO_2 vapors at 10 times the HF concentration. In addition, a covalent fluoride compound (chlorodifluoromethane) was not collected with measurable efficiency, did not yield any ionized fluoride, and therefore, did not interfere with badge response to HF. Thus, interference effects are expected to be negligible in the course of conventional monitoring with the HF dosimeter.

$$\text{*Response} = \frac{[\text{HF}]_{\text{Badge}}}{[\text{HF}]_{\text{Impinger}}} \times 100\%$$

Interference effects of sulfur dioxide (SO_2) and chlorodifluoromethane (Freon-22, ClCHF_2) were studied using the preliminary exposure system and the large chamber. Usually 10 badges were exposed on the lower chamber level and compared with 2 impinger samples. For this system, the Gasbadge response with no interferent present was approximately 40-50% of that achieved with the final system. If the badge response with interferent present matched the expected response, then the effect of the interferent was judged to be insignificant.

Sulfur dioxide (SO_2) and Freon 22 were tested as potential interferents in the HF gasbadge dosimeter. SO_2 was tested as a potential interferent because it may compete with HF for active sites on the Gasbadge collection element. If this were true, SO_2 would be a negative interferent, decreasing the ability of the badge to collect HF; this would tend to decrease the Gasbadge response factor R.

Freon 22 was selected as a potential interferent because the fluorine contained therein might constitute a positive interference in the Gasbadge detection system. Freon 22 has the following structure:

If OH^- ions substitute for F^- ions, the liberated F^- would be desorbed during analysis and would constitute a positive interference.

Four tests were conducted to determine interference effects of SO_2 and Freon 22. Data from these tests are presented below:

Test 1: (SO₂ Interference):

[HF] set at 1.5 ppm

[SO₂] set at 20 ppm

Gasbadges 1-10 on lower level of chamber

Impingers sampling at middle of chamber

<u>Sampling Device</u>	<u>ppm of HF measured</u>	
Gasbadge 1	0.62	} $\overline{[HF]} = 0.61 \pm 0.02 \text{ ppm}$
2	0.62	
3	0.63	
4	0.61	
5	0.62	
6	0.61	
7	0.61	
8	0.60	
9	0.59	
10	0.61	
Impinger 1	1.50	} $\overline{[HF]} = 1.53 \pm 0.03 \text{ ppm}$
2	1.55	

$$\text{Response Factor} = \frac{0.61}{1.53} = \boxed{0.399}$$

This compared very well with the expected HF response, of 0.4-0.5.

Test 2 (SO₂ Interference):

[HF] set at 0 ppm

[SO₂] set at 20 ppm

Gasbadges 1-9 on lower level of chamber

Impinger sampling at middle of chamber

<u>Sampling Device</u>	<u>ppm of HF measured</u>	
Gasbadge 1	0.034	} $\overline{[HF]} = 0.034 \pm 0.001 \text{ ppm}$
2	0.034	
3	0.035	
4	0.034	
5	0.034	
6	0.034	
7	0.034	
8	0.034	
9	0.034	
Impinger 1	0.091	} $\overline{[HF]} = 0.091$

$$\text{Response Factor} = \frac{0.034}{0.091} = \boxed{0.374}$$

Again, the response factor of 0.374 compares very well with the expected values. Thus, there appears to be negligible interference due to SO_2^* .

Test 3 (Freon Interference):

[HF] set at 0 ppm

[Freon 22] set at ~400 ppm

Gasbadges 1-10 on lower level of chamber

No impingers used

Exposure duration of 3 hrs. 0 mins.

* Several brief tests were conducted to determine the suitability of the present Gasbadge as an SO_2 monitor. From these tests, it appears that the badge may indeed be suitable as an SO_2 monitor. In fact, the current Gasbadge configuration may be suitable for simultaneous detection of several acidic gaseous pollutants, such as SO_2 , NO_2 , HF, and HCl. See Section VII-B.

<u>Sampling Device</u>	<u>ppm of HF measured</u>	
Gasbadge 1	0.03	} $\overline{[HF]} = 0.03 \pm 0 \text{ ppm}$
2	0.03	
3	0.03	
4	0.03	
5	0.03	
6	0.03	
7	0.03	
8	0.03	
9	0.03	
10	0.03	

$$[HF]_{\text{actual}} = [HF]_{\text{measured}}/R$$

$$[HF]_{\text{actual}} = (0.03 \text{ ppm})/0.40 = \boxed{0.075 \text{ ppm}}$$

Since this value was close to zero, it was concluded that Freon 22 was not a positive interferent on this run.

Test 4 (Freon Interference):

[HF] set at ~3 ppm

[Freon 22] set at ~400 ppm (verified by GC analysis to be 342 ppm)

Gasbadges 1-10 on lower level of chamber

Impingers sampling at middle of chamber

Exposure duration 3 hrs. 54 mins.

<u>Sampling Device</u>	<u>ppm of HF measured</u>	
Gasbadge 1	1.07	} $\overline{[HF]} = 1.08 \pm 0.02 \text{ ppm}$
2	1.07	
3	1.07	
4	1.07	
5	analyzed for Freon 22 by GC*	
6	1.10	
7	1.08	
8	1.07	
9	1.07	
10	1.10	

Impinger 1	2.87	}	[HF] = 2.86 ± 0.02 ppm
2	2.84		

* Gasbadge #5 was desorbed with 4.0 ml of methanol, and this extract was analyzed for Freon 22 with a gas chromatograph. No Freon 22 was detected.

$$\text{Response Factor } R = \frac{1.08}{2.86} = \boxed{0.378}$$

This acceptable response factor, coupled with the lack of any detectable Freon on the collection element and the results of Test 7, indicated that Freon 22 was not an interferent for the HF Gasbadge dosimeter. This study suggests that other covalent fluorides, such as SF₆, should not interfere as long as they do not react with the TEA to form ionized fluoride.

Other Potential Interferents

1) Particulate Fluorides

Particulate fluorides, such as CaF₂ or UF₄ are potential interferents. No means of testing this sort of material could be devised within the time allotted for this research. The badge should show little response, even to water-soluble particulates, because these materials should not be transported by diffusion to the collection element. It seems unlikely that a solid particle could migrate across a current-free air space, however, permeable the draft shield may be to that particle. However, proper testing of particulate fluoride interferents would be a useful study for the future.

2) Uranium Hexafluoride (UF₆)

This is a special case, and testing for the interference effect of this material would require extreme precaution in that UF₆ is a volatile

radioactive substance.

UF₆ has been shown to be reactive with airborne water (Reaction 4, Section I-A). However, any airborne UF₆ which does not react could be collected by the gasbadge. UF₆ vapor at room temperature should have a diffusion coefficient of approximately 0.05 cm²/s in air, sufficient for the UF₆ to be collected by a suitable gasbadge. Absorption of 1 molecule of UF₆ could yield up to 6 fluoride ions; a significant source of interference. Therefore, proper testing of UF₆ interference effects would be another useful study for the future.

3) Competing Acid Vapors

The effect of competing acid vapors (in addition to SO₂) could be a useful future study. The effects of ambient levels of other strong acids could be measured in terms of the effect on HF response. Alternatively, the usefulness of the present badge for monitoring mixtures of other acids could be investigated. A study of 5 competing organic vapors collected on the organic vapor dosimeter yielded important information not only on the suitability of the badge for monitoring each of the vapors, but also on the negative interference effects of each of the competing vapors [7]. A similar study on the current HF badge might include SO₂, NO₂, HF, HCl, and formic acid (HCOOH). The results of such a study may be the validation of the HF gasbadge as a general acid vapor dosimeter.

6. Post-Exposure Stability Tests

Tests were conducted to determine the chemical stability over time of Gasbadge elements that have been exposed to HF. For these tests, elements were not exposed to gaseous HF over several hours, but liquid HF was injected directly onto the elements. The quantities of liquid injected corresponded roughly to badge loadings that would obtain from a 4-hour exposure to gaseous

HF concentrations of 1/2, 1, 2, and 5 times the threshold limit value (TLV) of 3 ppm. (See Appendix III for solution preparation technique.) Four elements were prepared at each badge loading on 17 April 1980. Half of these were refrigerated, and half were not. Eight elements (4 refrigerated, 4 not) were analyzed on 18 April 1980; this analysis was repeated for the remaining elements on 25 April, 2 May, 9 May, and 16 May 1980. Any change over time in measured HF concentration (or equivalently in quantity of HF recovered from the badge elements) was noted. Results were:

<u>Quantity of HF (Fraction of TLV)</u>	<u>Sample Age</u>	<u>Refrigerated ug of HF present*</u>	<u>Unrefrigerated ug of HF present*</u>
0.5	2 days	10.8	11.0
0.5	"	10.7	11.0
0.5	"	11.0	11.0
0.5	"	10.7	10.7
Blank	"	0	0
Mean		10.8	10.9
0.5	1 week	10.7	10.5
0.5	"	10.7	10.7
0.5	"	10.5	10.5
0.5	"	10.7	10.5
Blank	"	1.5	1.5
Mean		10.7	10.6
0.5	2 weeks	11.3	11.7
0.5	"	12.0	12.2
0.5	"	11.7	12.2
0.5	"	11.7	12.3
Blank	"	2.0	2.0
Mean		11.7	12.1

*Corrected for Blanks

<u>Quantity of HF (Fraction of TLV)</u>	<u>Sample Age</u>	<u>Refrigerated µg of HF present*</u>	<u>Unrefrigerated µg of HF present*</u>
0.5	3 weeks	12.3	12.1
0.5	"	12.5	12.8
0.5	"	12.3	12.9
0.5	"	11.5	12.3
Blank	"	2.9	3.3
Mean		12.2	12.5
0.5	4 weeks	11.6	11.6
0.5	"	11.6	11.2
0.5	"	11.0	11.2
0.5	"	10.9	10.6
Blank	"	4.4	4.4
Mean		11.3	11.2
1	2 days	21.5	21.5
1	"	21.8	21.8
1	"	22.1	21.8
1	"	22.1	21.5
Blank	"	0	0
Mean	"	21.9	21.7
1	1 week	21.6	21.6
1	"	21.9	21.6
1	"	21.9	20.8
1	"	20.7	21.6
Blank	"	1.5	1.5
Mean	"	21.5	21.4
1	2 weeks	22.4	22.4
1	"	22.0	22.4
1	"	22.4	22.0
1	"	22.0	22.4
Blank	"	2.0	2.0
Mean	"	22.2	22.3

*Corrected for Blanks

<u>Quantity of HF</u> <u>(Fraction of TLV)</u>	<u>Sample Age</u>	<u>Refrigerated</u> <u>ug of HF present*</u>	<u>Unrefrigerated</u> <u>ug of HF present*</u>
1	3 weeks	23.9	23.7
1	"	24.4	23.5
1	"	23.9	24.0
1	"	24.1	(lost)
Blank	"	2.9	3.3
Mean	"	24.1	23.7
1	4 weeks	20.5	20.5
1	"	21.2	20.7
1	"	20.5	20.5
1	"	21.5	21.3
Blank	"	4.4	4.4
Mean	"	20.9	20.8
2	2 days	42.5	42.0
2	"	41.5	42.5
2	"	42.0	42.0
2	"	42.5	42.5
Blank	"	0	0
Mean	"	42.1	42.3
2	1 week	44.0	44.0
2	"	44.0	43.3
2	"	44.7	43.1
2	"	43.1	43.3
Blank	"	1.5	1.5
Mean	"	44.0	43.4
2	2 weeks	44.7	45.5
2	"	44.5	44.5
2	"	45.5	44.5
2	"	45.5	46.2
Blank	"	2.0	2.0
Mean	"	45.1	45.2
2	3 weeks	46.7	44.9
2	"	48.7	44.2

*Corrected for Blanks

<u>Quantity of HF (Fraction of TLV)</u>	<u>Sample Age</u>	<u>Refrigerated ug of HF present*</u>	<u>Unrefrigerated ug of HF present*</u>
2	3 weeks	45.3	46.3
2	"	45.7	46.3
Blank	"	2.9	3.3
Mean	"	46.6	45.4
2	4 weeks	42.1	41.8
2	"	42.3	42.3
2	"	41.2	43.1
2	"	42.3	42.1
Blank	"	4.4	4.4
Mean	"	42.0	42.3
5	2 days	103	99.3
5	"	105	101
5	"	103	99.3
5	"	103	99.0
Blank	"	0	0
Mean	"	103.5	99.7
5	2 days	102	97.0
5	"	100	99.5
5	"	105	100
5	"	97.0	100
Blank	"	1.5	1.5
Mean	"	101.0	99.1
5	2 weeks	105	105
5	"	100	103
5	"	100	105
5	"	105	105
Blank	"	2.0	2.0
Mean	"	102.5	104.5
5	3 weeks	100	104
5	"	104	105
5	"	102	103

<u>Quantity of HF</u> <u>(Fraction of TLV)</u>	<u>Sample</u>	<u>Refrigerated</u> <u>ug of HF present*</u>	<u>Unrefrigerated</u> <u>ug of HF present*</u>
5	3 weeks	104	105
Blank	"	2.9	3.3
Mean	"	102.5	104.3
5	4 weeks	97.6	97.6
5	"	98.6	97.6
5	"	97.6	98.6
5	"	97.6	98.0
Blank	"	4.4	4.4
Mean	"	97.9	98.0

TABLE 8: POST EXPOSURE STABILITY TEST DATA SUMMARY (MEAN VALUES):

<div> <div>Age (weeks)</div> <div>raction of TLV</div> </div>	0.3		1		2		3		4	
	Ref.	Non-Ref.	Ref.	Non-Ref.	Ref.	Non-Ref.	Ref.	Non-Ref.	Ref.	Non-Ref.
0.5	10.8	10.9	10.7	10.6	11.7	12.1	12.2	12.5	11.3	11.2
1.0	21.9	21.7	21.5	21.4	22.2	22.3	24.1	23.7	20.9	20.8
2.0	42.1	42.3	44.0	43.4	45.1	45.2	46.6	45.4	42.0	42.3
5.0	103.5	99.7	101.0	99.1	102.5	104.5	102.5	104.3	97.9	98.0

Test results are summarized above and in Figure 6. The results indicate that HF shows good retentivity and stability with respect to time, whether elements are refrigerated or not, for at least 1 month after exposure. The results also show that transfer of exposed HF elements to vials and subsequent mail shipment (as is done for other gasbadge elements) is practical for this badge element.

These test results also indicate that the blank values were apparently increasing with time. Investigation showed that this was not the case, but that F⁻ electrode response was changing. Purchase of a new electrode overcame this potential problem.

6/4/80

FIGURE 7: POST EXPOSURE STABILITY TEST RESULTS

7. Pre-Exposure Stability

Collection elements were shown to be stable for at least one year after preparation. Two exposure chamber runs were executed to measure the long term stability of properly packaged HF collection elements. For these studies 3 badges were exposed to approximately 2 ppm HF, and their response was compared with the values obtained from 2 impinger sampling trains. Two of the 3 badges in each case (badges 1 and 3) contained collection elements that were about a year old (prepared 1/15/80.) Badge 2 contained elements prepared recently (within the last few months) and served as a control. To measure the long-term stability of these collection elements, the average response of the old elements was compared with that of the new:

<u>Test Date</u>	<u>Run No.</u>	<u>[HF]_{old elements} (ppm)</u>	<u>[HF]_{new elements} (ppm)</u>	<u>% Difference</u>
12/30/80	5	1.95 ± 0.08	1.94	0.5%
12/31/80	6	1.86 ± 0.20	1.80	3.2%

The very good agreement between old elements and new elements indicates excellent stability of collection elements over at least 1 year.

Further corroboration of collection element stability over time was obtained by directly measuring the triethanolamine (TEA) concentrations of the elements. This is easily accomplished with a conventional glass pH electrode after extracting the TEA in water. Two old elements were compared for TEA content with a control element, using this technique:

<u>Element Preparation Date</u>	<u>ml of TEA Found (per element)</u>
1/15/80	0.088
1/15/80	0.089
9/1/80 (control)	0.083

These values compare favorably, again indicating excellent chemical stability of the collection elements.

It is felt that if HF elements are prepared and packaged properly, their shelf life is on the order of several years, since the packaging material contains no fluoride, the package is hermetically sealed, and TEA is stable when kept from air and light.

VI. FIELD DEMONSTRATION

A. GENERAL METHODOLOGY

Field Monitoring was conducted in buildings K-402-9, K-1131, and K-1132 of the Oak Ridge Gaseous Diffusion Plant, Oak Ridge National Laboratories, Oak Ridge, Tennessee, from 28 July 1980 through 19 August 1980. In general, area monitoring was conducted, wherein approximately 5 HF Gasbadges were exposed simultaneously with an impinger sampling train as per NIOSH Standard Method S-176 (See Appendix II). Exposure durations were approximately 320 minutes at 300K and 750 mm Hg pressure. Gasbadges and impingers were located near each other, in the same room. In one case, a personnel sample was obtained, wherein Gasbadges and an impinger were worn by an individual during the course of his daily work.

Gasbadges and impinger sampling trains were prepared and distributed each morning of testing, and pertinent data (test location, ambient temperature, ambient pressure, impinger pump flow rate, badge identification) were recorded. Impinger pump flow rates were checked several times each day. At the end of each day, Gasbadges and impinger trains were retrieved. End times, end pump flow rates, temperatures, and pressures were recorded. Samples were recovered and analyzed as per NIOSH standard Method S-176 for impingers, and as per the HF Gasbadge Method for Gasbadges. (See Appendices I and II for details.)

Samples were analyzed within 1 work day of exposure. All glassware was washed with 1 Molar HCl and rinsed with de-ionized water prior to use. All F⁻ measurements were done in disposable 50 ml polypropylene beakers.

B. SCHEDULE AND TEST TYPE

The following schedule was used for field testing:

<u>Dates</u>	<u>No. of Gasbadges Tested</u>	<u>Test Type</u>
7/28/80	10	Determination of background level on blank Gasbadge elements
7/28/80	10	Micro-Climate Variability Tests
7/30/80 - 7/31/80	25	Area Sampling
7/31/80	5	Area Sampling, Overnight Test
8/1/80 - 8/5/80	31	Area Sampling
8/5/80	15	Area Sampling; comparison of impinger with pre-filter with impinger without prefilter
8/6/80 - 8/19/80	123	Area Sampling
8/19/80	2	Personnel Sample
8/20/80	5	Area Sampling, 3 impinger trains in same location as Gasbadges

Total Gasbadges Tested: 226

C. EQUIPMENT UTILIZED

The following equipment was utilized for field testing:

<u>Equipment</u>	<u>Purpose</u>
(3) Bendix Model BDX 103 Personal Monitoring Systems	Impinger Train Sample Pumps for HF, ff NIOSH Method S-176
(226) Abcor HF Gasbadge Dosimeters	Testing
(1) SKC 1.0 liter soap bubble meter	Calibration of Bendix Pumps
(1) Kurz Model 540 S hot-wire calibrated flow meter	Calibration of Bendix Pumps
(1) Orion Model 701 A digital pH meter	F ⁻ Gasbadge Analyses
(1) Orion Model 76-09 combination fluoride electrode	F ⁻ Gasbadge analyses
(1) Water Deionizer	De-ionizing water for analyses

D. RESULTS

Results of the 47 field study experiments are presented in Table 9 and in Figure 8. The data indicate a reasonably good correlation between the Gasbadge results and the impinger results (NIOSH Standard Method S-176). It is estimated that the Gasbadge results give an accurate indication of the true time-weighted average HF concentration within $\pm 25\%$.

A linear regression on the 47 data points yields the following relationship:

$$[\text{HF}]_{\text{Gasbadge}} = 1.202 [\text{HF}]_{\text{Impingers}} - .0133, \text{ where} \quad (13)$$

$[\text{HF}]_{\text{Gasbadge}}$ = indicated HF concentration (ppm) from Gasbadge

$[\text{HF}]_{\text{Impingers}}$ = indicated HF concentration (ppm) from NIOSH Method S-176

The coefficient of determination (r^2) for this relationship is

$$r^2 = 0.995.$$

The closeness of this value to 1.00 is an indication of how well the data are fit by the linear regression.

E. CONCLUSIONS

It appears from this study that the Abcor HF Gasbadge dosimeter provides a reasonably accurate measurement of the HF time-weighted average when used as an area monitor in actual in-field situations. Low level data suggest that the detectability limits are due to limitations in the accuracy of the F^- electrode used in analysis, and in limitations on blank element cleanliness, rather than any Gasbadge design or performance limitation.

This is the first Gasbadge study to show significant correlation between Gasbadge and impinger results at concentrations below 100 ppb.

TABLE 9: HF GASBADGE FIELD STUDY RESULTS

C-064

Test No.	Test Date	Gas badge			Impingers (Method S-176)				Test Location	[HF] Imp.		Comments
		No. of Gas-badges	[HF] (1) (ppm)	Gas badge Exposure Duration (mins)	Ambient Temp (K)	Ambient P (mm Hg)	Pump Flow Rate (l/min)	Impinger Sampling Duration (mins)	[HF] (2) (ppm)	[HF] Imp.	[HF] Imp.	
1	7/28/80	10	.004 ± .006	301	302	746	.943	301	.005	0.76	0.76	Micro Climate Variability Tests
2	7/28/80	10	.004 ± .006	301	302	746	.939	301	.005	0.76	0.76	Area Sampling
3	7/28/80	10	.004 ± .006	301	302	746	.924	301	.005	2.17	2.17	"
4	7/30/80 (3)	5	.013 ± .001	331	305	747	.956	331	.006	1.86	1.86	"
5	7/30/80	5	.013 ± .001	328	305	747	1.025	329	.007	1.50	1.50	"
6	7/30/80	5	.009 ± .002	326	305	747	.963	327	.006	1.00	1.00	"
7	7/31/80	5	.413 ± .043	343	311	745	.926	342	.413	1.41	1.41	Area Sampling Overnight test
8	7/31/80	5	.380 ± .049	328	311	745	.620	329	.270	1.06	1.06	Area Sampling
9	7/31/80	5	.018 ± .002	1073	--	--	.730	1073	.017	1.55	1.55	"
10	8/1/80	5	.048 ± .009	358	312	745	1.022	358	.031	1.68	1.68	"
11	8/1/80	4	.047 ± .004	354	312	745	.984	354	.028	.97	.97	"
12	8/4/80	5	.060 ± .009	342	310	744	.975	342	.062	.90	.90	"
13	8/4/80	5	.451 ± .006	343	310	744	.777	343	.499	.57	.57	"
14	8/4/80	5	.004 ± .004	327	306	744	.488	327	.007	.86	.86	"
15	8/5/80	7	.084 ± .009	330	308	747	1.004	330	.098	.82	.82	Pump had pre-filter
16	8/5/80	8	.053 ± .011	323	308	747	.960	323	.065	.87	.87	Pump had no prefilter
17	8/5/80	8	.053 ± .011	323	308	747	1.046	323	.061	1.03	1.03	Area Sampling
18	8/6/80	5	2.07 ± .160	329	311	749	.975	329	2.01	1.22	1.22	"
19	8/6/80	5	6.26 ± .028	327	311	749	.968	327	5.14	1.20	1.20	"
20	8/6/80	5	.963 ± .061	320	312	749	.090	320	.689	1.62	1.62	"
21	8/7/80	5	.103 ± .004	366	312	749	1.004	366	.086	1.21	1.21	"
22	8/7/80	5	.152 ± .012	366	311	749	.703	366	.094	1.04	1.04	"
23	8/7/80	5	.087 ± .007	364	311	749	.944	364	.072	1.27	1.27	"
24	8/8/80	5	.050 ± .008	313	313	747	1.030	313	.048	.92	.92	"
25	8/8/80	5	.062 ± .006	313	313	747	.939	313	.049	.62	.62	"
26	8/8/80	5	.045 ± .003	312	313	747	1.030	313	.049	.75	.75	"
27	8/11/80	5	.024 ± .004	321	314	745	.964	321	.039			"
28	8/11/80	5	.021 ± .004	322	313	745	.738	322	.028			"

(1) Average of all Gasbadges

(2) From Method S-176

(3) New, cleaner batch of collection elements used from this date on.

(Continued on Page 2)

TABLE 9: HF GASBADGE FIELD STUDY RESULTS (Continued)

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C-064

Test No.	Test Date	Gasbadge		Impingers (Method S-176)				Test Location	[HF] Imp.		Comments
		No. of Gasbadges	[HF] (1) (ppm)	Gasbadge Exposure Duration (mins)	Ambient T (K)	Ambient P (mm Hg)	Pump Flow Rate (l/min)	Impinger Sampling Duration (mins)	[HF] (2) (ppm)	[HF] Imp.	
29	8/11/80	4	.0371.004	319	313	745	1.020	319	.046	.00	Area Sampling
30	8/12/80	5	.0311.005	325	303	745	.994	324	.031	1.00	"
31	8/12/80	5	.0161.009	323	309	745	1.020	322	.033	.48	"
32	8/12/80	5	.0301.013	322	309	745	.976	321	.057	.53	"
33	8/13/80	5	.1261.025	180	301	746	1.060	181	.109	1.16	"
34	8/13/80	5	.0641.007	179	308	746	1.020	180	.056	1.14	"
35	8/13/80	5	.0601.013	178	309	746	.994	178	.045	1.51	"
36	8/13/80	4	.1651.019	198	307	746	1.010	198	.100	.92	"
37	8/13/80	4	.1351.015	198	312	746	.982	198	.098	1.38	"
38	8/13/89	4	.1061.020	198	312	746	1.010	198	.079	1.34	"
39	8/14/80	5	.1761.017	230	309	744	1.020	321	.159	1.11	"
40	8/14/80	5	.0881.036	227	309	744	1.030	227	.047	1.87	"
41	8/18/80	5	.0131.006	316	302	747	1.030	317	.013	1.00	"
42	8/18/80	5	.0651.013	316	308	747	.976	316	.184	.35	"
43	8/19/80	2	.0171.005	226	308	747	.952	226	.022	.77	"
44	8/20/80	5	.0371.007	304	310	745	.997	304	.019	1.95	3 pumps in same location with 5 gasbadges
45	8/20/80	5	.0371.007	304	310	745	1.030	304	.027	1.37	
46	8/20/80	5	.0371.007	304	310	745	.976	304	.017	2.18	
47	8/19/80	2	.0341.008	231	308	747	.980	231	.041	.83	Personnel Sample

(1) Average of all Gasbadges
 (2) From Method S-176

FIGURE 8: FIELD STUDY RESULTS FOR HIF DOSIMETER

VII. DISCUSSION

A. DISCREPANCY BETWEEN AQUEOUS AND ANHYDROUS HF GENERATION SYSTEM RESULTS

In the experiments conducted with the preliminary exposure system, the typical observed badge response was about $45\% \pm 10\%$ of theoretically ideal response. For these preliminary experiments, aqueous hydrofluoric acid was employed as the HF source. For the last ten experiments using the preliminary system, the aqueous generating system was replaced with a tank of 25 ppm HF in anhydrous nitrogen. The observed badge response for these runs was about $70\% \pm 10\%$, a response level much more consistent with response shown using the final exposure system, about $84\% \pm 10\%$. The question arises, why was there dramatic improvement when the aqueous generating system was replaced with an anhydrous HF-source? Several plausible arguments may be presented to explain this.

1. H₂O·HF Complexing

If HF exists primarily as either dimer (HF)₂ or as H₂O·HF complex when it is sampled by the gasbadge, the mass collected per unit time should be less than if HF exists in the non-associated state because of a difference in the diffusion rate. It was shown in Section III-A that the sampling rate was proportional to the diffusion coefficient and the ambient concentration. Changes in the degree of association for very dilute HF systems do not change the HF concentration expressed as mg HF/M³ air. However, the estimated diffusion coefficients for the (HF)₂ dimer and the H₂O·HF complex are approximately 0.17 cm²/s compared with 0.25 cm²/s for the non-associated HF. Clearly, the diffusivity of any associated HF will be lower than for non-associated HF, and since the mass collected by the badge is proportional to the diffusivity, the response should also be lower.

The equilibrium constant for the formation of the vapor state H₂O·HF complex is 0.0024 kPa⁻¹ (0.24 atm⁻¹) at 315K [14]. From this constant the equilibrium concentration of H₂O·HF complex is determined to be approximately 0.4 to 0.6% of the total HF concentration under most test conditions. Therefore,

if the badges sample air which is truly at equilibrium, there should be no measurable effect on badge response due to the existence of this complex. However, if there is a significant time of existence for the associated species, the eventual equilibrium state may not be reached by the time sampling is completed in a dynamic exposure system. If this be the case, then there may be substantial associated molecules ($\text{H}_2\text{O}\cdot\text{HF}$) that are sampled by the Gasbadge, which would lead to a lower apparent badge response.

When the aqueous HF system was used for preliminary runs, the badges sampled air about 30 seconds after the HF was added to the diluent flow. If the HF was in an associated form when diluted, and if a significant amount of the associated form exists for at least 30 seconds when diluted to percent levels, then a lowering effect on the diffusivity may become noticeable.

The data suggest that significant amounts of $\text{H}_2\text{O}\cdot\text{HF}$ complex may exist for 30 seconds or more in an atmosphere of about 2% HF and 2% H_2O , typical of the air space atmosphere above a 40% wt/wt solution of HF in H_2O . Most of the 30 second residence time for generated HF molecules in the exposure system was in the 200 ml of head space above the HF solution (see Figure 3b). After leaving that head space, the further residence time in the system was only a few seconds.

After the aqueous system was abandoned, 3 other sources of HF were employed (see Figure 3b). Source 1, the 25 ppm HF in anhydrous nitrogen, could not be a source of associated HF. Only the dimer $(\text{HF})_2$ or other homopolymers could exist in anhydrous conditions. In the dilute state of 25 ppm, the equilibrium concentration on polymerized HF is essentially zero.

In source 2, the teflon permeation tubes, the rate of permeation is proportional to the diffusivity of HF through the teflon tube and also proportional to the solubility of HF in the teflon [15]. The residence time of the HF in the teflon material is probably on the order of an hour or more, assuming an HF diffusion coefficient in teflon of about 10^{-6} to 10^{-7} cm^2/sec (our best estimate to date.) It seems probable that the molecules of HF diffusing out of the teflon into the dry diluent air are in the non-associated state. The observed badge response was consistent with non-associated HF.

In source 3, pure anhydrous HF vapor, the HF should exist almost exclusively in the associated state, with an average association factor of about 3 [12]. The residence time in the exposure system of HF from this source is estimated to be about 20-40 seconds, based on flow rates and tubing dimensions. The observed response suggested no association in the HF sampled by the gas-badges using pure HF vapor as the HF source. Apparently, equilibrium had been reached by the time sampling was done. Since the equilibration time was of the same magnitude as for the aqueous HF source, and a much higher badge response was observed than with the aqueous HF source, it may be hypothesized that equilibrium had not been reached for the aqueous system.

The equilibrium reactions are summarized below for the $(\text{HF})_2$ dimer and $\text{H}_2\text{O}\cdot\text{HF}$ complex:

The hydrogen bond in $\text{H}_2\text{O}\cdot\text{HF}$ has been shown elsewhere to be stronger than for the $(\text{HF})_2$ dimer in the vapor state [13]. Our observations suggest that the $\text{H}_2\text{O}\cdot\text{HF}$ complex may have a significantly longer lifetime when equilibrium is shifted to extreme dilute state, than does the $(\text{HF})_2$ dimer. It follows that the vapor state dissociation energy for the dimer should be less than that for the $\text{H}_2\text{O}\cdot\text{HF}$ complex.

If the existence time of the $\text{H}_2\text{O}\cdot\text{HF}$ complex is as long as the preliminary data suggest, then under certain field conditions the existence of this complex could constitute a negative interference. This interference could not exist when monitoring those industrial operations in which anhydrous HF is the contaminant source. The complex could only exist in air which is close to an open source of aqueous hydrofluoric acid. (Note, ambient HF at Oak Ridge mostly arose from leaks in anhydrous sources. However, some of the ambient level arose from leaks in an aqueous KOH scrubber system, which could be a source of complexed HF.)

Time did not allow a check(using the new exposure system) of the gasbadge response factor with an aqueous HF source. A few short runs would indicate whether or not the apparent bias seen with the old aqueous system was caused by the exposure system configuration or was caused by molecular interactions.

If a measurable time of existence were detected, a series of very careful experiments could actually measure the magnitude of the existence time. Such a study would employ the novel approach of using a diffusion controlled sampler to measure the molecular weight of the diffusing species.

2. Hydrofluoric Acid Aerosol

Another possible explanation for the apparent lower Gasbadge response when aqueous HF is used as the contaminant source may have been the existence of hydrofluoric acid aerosol (condensed microdroplets of aqueous hydrogen fluoride). The gasbadge is designed to sample HF in the vapor phase. Condensed HF aerosol would not be collected by a diffusion-based sampling method such as the HF Gasbadge. The limiting factor for this phenomenon would be the time of existence for the droplets of condensed $\text{HF} \cdot \text{H}_2\text{O}$.

The magnetic stirrer employed in the aqueous system (Figure 3b) caused the HF solution to warm to about 40°C over the first half hour of exposure chamber operation. Since the temperature of operation was ambient ($\approx 20\text{-}25^\circ\text{C}$), considerable condensation occurred in all tubing leading from the hydrofluoric acid vessel to the main diluent air flow, after this warm-up time.

Since the final diluted test air contained ppm levels of HF in 50% relative humidity air, any condensed droplets should quickly evaporate. The badges sampled air approximately 3 seconds after the HF was added to the diluent air (based on average flow rate and tubing dimensions.) Therefore, if the hypothetical HF aerosol did not equilibrate in 3 to 4 seconds, then the existence of this aerosol could significantly lower gasbadge

response relative to impinger response. (The NaOH sampling train used to determine the "true" HF concentration would not discriminate between vaporized and condensed HF.)

* * * * *

It is very possible that the actual observed discrepancy between results obtained using aqueous HF as the contaminant source versus the anhydrous HF sources was a combination of the two effects discussed herein with the possible added wall effects of the more adsorptive polycarbonate exposure chamber. For either of the two hypothetical explanations, the existence of complexed HF or HF aerosol, the effect should be strongly humidity-dependent. In controlled testing, only when the aqueous HF source was employed was there a noticeable effect on badge response at higher humidities (see Table 7.) Furthermore, those tests run below 30% relative humidity with the aqueous system showed considerably higher response than was typically observed at 50% relative humidity. These low-humidity runs yielded responses that were very consistent with those values obtained using the 25 ppm anhydrous HF source with the preliminary system (Table 7.)

B. USE OF HF BADGE FOR OTHER ACID VAPORS

In Section V-B, it was shown that the HF badge sampling of HF vapor was not affected by competing SO_2 vapors. A preliminary analysis suggested that the SO_2 is collected with nearly complete efficiency by the HF badge. The badge should respond to all acid vapors that complex or react with the TEA and do not react with polyolefin materials of badge construction. For those materials collected at near complete efficiency, the badge should respond independently to each individual acid vapor in a mixture, unless or until the collection element is saturated. This saturation level will vary for each acid vapor and may be influenced by the presence of 1 or more competing acids. At near saturation levels, weaker acids may be displaced by

stronger acids, those with a lower pKa value. Thus, the HF Gasbadge should be useful as a monitor for many acid vapors other than SO₂.

Currently there are 10 acid vapors for which NIOSH sampling and analysis methods have been established. All these vapors have diffusivities adequate for diffusion-controlled sampling. A list of these vapors is presented in Table 10; the pKa values are given as a measure of relative acid strength. Although these actually show the acid strength in water solution, they should be roughly equivalent to the acid strength in TEA. The polyolefin materials used in the present badge construction are not incompatible with any of the vapors in the table.

The present configuration is likely to be effective for HNO₃, HCl, and HBr (all strong acids) provided that the TEA does not interfere with the ion-analysis. Formic and especially acetic acids, being somewhat weaker, may need a stronger base (such as KOH) as the collection medium. (Acetic acid may be more easily monitored with the organic vapor dosimeter, a method consistent with the NIOSH recommended method for this vapor.) The TEA collection medium should not appreciably interfere with the derivitization procedure recommended for the determination of formic acid.

SO₂ and NO₂ have been monitored with a gasbadge dosimeter in the past [6], using TEA as the collection medium. Some discrepancies in response were observed which were possibly caused by interactions between the acid vapor and the fiberglass draftshield and/or the collection element substrate employed in that badge design. Because all fiberglass or other material containing polar functionalities has been eliminated in the present HF badge design, it is felt that this design is at least as good as the old design for NO₂ and SO₂ monitoring and most likely is superior. In a preliminary test, an HF gasbadge was exposed to 21.8 ppm SO₂ as determined by NIOSH Method P + CAM 160 [3]. The HF gasbadge yielded 22.7 ppm SO₂ (assuming a 100% collection efficiency and that D₀ for SO₂ equals 0.126 cm²/sec; see Appendix V .) This demonstrates that the current configuration of the HF Gasbadge may be very good, as is, for monitoring SO₂.

TABLE 10: NIOSH ACID VAPOR METHODS

ACID GAS	8 Hour TLV (ppm)	NIOSH METHOD[3]	COLLECTION MEDIUM	ANALYSIS PROCEDURE	pKa*	SUITABILITY OF PRESENT BADGE
Hydrogen Fluoride (HF)	3	S-176	0.1 M NaOH	ISE ¹	3.45	yes - calibrated
Nitrogen Dioxide (NO ₂)	5	S-320	TEA ⁵ -molecular sieve	SP ²	3.37	yes - not calibrated.
Sulfur Dioxide (SO ₂)	5	1)S-308 2)P+CAM 160	0.3 M H ₂ O ₂ ⁴ 0.04 M TCM ⁴	Titrimetry SP ²	1.81 1.81	yes - not calibrated yes - not calibrated
Hydrogen Bromide (HBr)	3	S-175	0.01 M NaOH	ISE ¹	<0	Probable
Hydrogen Chloride (HCl)	5	S-246	0.5 M NaAC ⁶	ISE ¹	<0	Probable
Nitric Acid (HNO ₃)	2	S-2	H ₂ O	ISE ¹	<0	Probable
Formic Acid (HCOOH)	5	P+CAM 232	0.1 M NaOH	1)Derivitize 2)GC ³	3.75	Possible
Acetic Acid (CH ₃ COOH)	10	S-169	Activated Carbon	GC ³	4.75	Possible **
Hydrogen Sulfide (H ₂ S)	10	S-4	Cd(OH) ₂ slurry	SP ²	7.04	Not probable
Hydrogen Cyanide (HCN)	10	P+CAM 116	0.1 M NaOH	ISE ¹	9.31	Not probable

Abbreviations:

- 1) ISE - Ion Selective Electrode
- 2) SP - Spectrophotometry or colorimetry
- 3) GC - Gas Chromatography
- 4) TCM - Potassium Tetrachloromercurate
- 5) TEA - Triethanolamine
- 6) NaAC- Sodium Acetate

* From Handbook of Chemistry & Physics, 51st ed., 1971, CRC Publishing Co., Cleveland

** Suitability of Organic Vapor (activated carbon) Gasbadge - Probable.

For the strong acids, especially those stronger than HF, the current badge could be calibrated using a mixture of 4 or 5 acid vapors. Recent developments in high performance ion-exchange chromatography make possible the simultaneous determination of most of the substances listed in Table 10. The development of the HF dosimeter, coupled with these advances in analytic procedure, may make the simultaneous determination of many airborne acid vapors straightforward.

As for the weak acid vapors, HCN and H₂S, each of these materials may require significant badge modification. Individual calibration would be necessary for these acids.

VIII. SUMMARY AND CONCLUSIONS

A diffusion-controlled passive dosimeter has been developed for monitoring airborne hydrogen fluoride vapor. The device can be conveniently worn on one's lapel or pocket; it consists of polyethylene and polypropylene parts and a triethanolamine-impregnated Pellon collection element. It is completely self-contained. Overall accuracy in controlled laboratory exposure testing was $\pm 10.3\%$ and the badge response was linear from 0.1 to 387 ppm over approximately 4 hour exposures. Overall response was 84% of theoretical ideal response; this observed response is consistent with monomeric HF behavior. These results were corroborated in field tests during which a high degree of correlation was shown between HF levels determined by the HF gasbadge and levels determined by NIOSH method S-176 (Appendix II) at ambient levels between 0.007 and 6.0 ppm HF.

In addition, the following specific conclusions may be drawn regarding badge performance:

1. Badge response is not affected by temperature changes except for the expected variation of the diffusivity with temperature. This variation was shown to be very close to a $T^{3/2}$ dependence, as predicted by theory.
2. Badge response is independent of relative humidity except possibly at levels approaching 100% relative or under such conditions that condensation of water occurs on badge parts.
3. Competing acid vapors are not expected to interfere with badge response unless saturation of the collection element occurs, a situation that is very unlikely to occur in the field. Covalent fluoride compounds are not collected by the HF gasbadge, do not yield any ionized fluoride, and therefore are not interferents. Specific interference effects of SO_2 and chloro-difluoromethane were measured and were found to be negligible.

4. Exposed collection elements are stable for at least one month if kept from heat and light. A desorbed sample is stable for at least one month the solution is kept in polyolefin or teflon containers and is kept from heat and light.
5. Properly prepared and packaged collection elements are stable for at least one year prior to use.
6. Overall accuracy of the Gasbadge HF sampling method in the action range was $\pm 17.3\%$. This easily meets NIOSH criteria requiring that overall accuracy be within $\pm 25\%$ for 95% of the samples taken between 0.5 and 2 times the accepted standard.

* * * * *

The HF dosimeter that has been developed is an excellent, convenient, accurate means of monitoring workplace exposure to airborne HF vapor in the range 0.1 to 387 ppm.

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APPENDIX I - HF GASBADGE ANALYSIS METHOD

I. Principle

1.1. HF vapors diffuse across permeable draft-shield, through diffusion grid, and are collected on TEA or KOH-TEA impregnated collection medium.

1.2. The collected Fluoride ion is eluted with 20.0 ml of 1/2 strength TISAB buffer solution.

1.3. The resulting solution is analyzed for Fluoride ion with ion-sepcific electrode.

II. Range and Sensitivity

1.1. The ion-electrode is sensitive to molar fluoride concentrations to below $1 \times 10^{-6}M$. This corresponds to a lower detection limit of about 0.1 ppm hrs.

1.2. The sensitivity can be increased by using a smaller elution volume and a combination electrode.

1.3. The upper limit is defined by the loading capacity of the element to HF vapors. Tests indicate that 1200 ppm hrs. is well within this capacity limit.

III. Interferences

3.1. For solutions buffered to pH 5.0-5.5, the known interferents for the fluoride selective electrode are those metal ions which complex F^- , such as Ca^{++} , Al^{+3} , Fe^{+3} .

3.2. Collection efficiency interference effects of competing acid vapors (such as HCl , SO_2 , NO_2) are currently under investigation.

3.3. Interference of particulate fluorides is currently under investigation.

IV. Precision, Accuracy, and Stability

4.1. The mean relative standard deviation, a good measure of the precision, was $\pm 5.07\%$ in the range from 0.1 to 387 ppm exposure.

4.2. The overall accuracy of this method, defined as $\pm$ [absolute mean bias + 2 (mean relative standard deviation)] was $\pm 10.42\%$ in the range from 0.1 to 387 ppm exposure.

4.3. Exposed collection elements are stable for at least one month if kept from heat and light.

4.4. The fluoride ion in desorbed samples is stable (at least 1 year) if the solution is kept in polypropylene or polyethylene containers.

4.5. Unopened collection elements are stable for at least 1 year.

V. Apparatus

5.1. Orion model 701 digital pH-mV meter or equivalent.

5.2. Orion model 94-09A fluoride ion specific electrode or equivalent.

5.3. Calomel or equivalent references electrode.

5.4. Class A volumetric pipets, 1 ml, 10 ml, 20 ml for standard preparation.

5.5. Class A volumetric flasks for standard level prep. 1000 ml, 100 ml. Standard fluoride solutions should not be stored in glass containers for more than a few hours. Nalgene or other plastic volumetric labware may be used if precision and accuracy are sufficient. Likewise, automatic pipetting and dispensing systems may be employed.

5.6. 50 ml Polypropylene beakers with covers.

5.7. Forceps.

5.8. One liter beaker.

5.9. 100 ml graduated cylinder

5.10. Magnetic stirrer and stir bars for 50 ml beakers.

VI. Reagents - ACS reagent grade or equivalent.

6.1. Distilled water.

6.2. Glacial Acetic acid.

6.3. Sodium Hydroxide solution 5 M. Dissolve 20 gm NaOH in sufficient distilled water to give 100 ml solution. Caution: highly exothermic (prepare using water bath for cooling).

6.4. Sodium Chloride.

6.5. Sodium Citrate.

6.6. TISAB - (1/2 NIOSH strength) Place 500 ml distilled water in a 1 liter beaker. Add 57 ml glacial acetic acid, 58 gms sodium chloride, and 0.3 gms sodium citrate. Slowly add 5 N sodium hydroxide until pH is between 5 and 5.5. (A water bath may be employed to control temperature.) When solution cools to room temperature, transfer to a 2 liter volumetric flask and dilute to the mark with distilled water.²

6.7. Sodium Fluoride.

6.8.1. Sodium Fluoride stock solution. Dissolve 0.42 gm NaF in distilled water and dilute to 1 liter.

6.8.2. 10^{-3} Standard Solution. Dilute 1.0 ml of 10^{-2} M stock solution to 100 ml with TISAB solution. This solution contains 10^{-6} moles F^{-} /ml.

VII. Procedure for Analysis

7.1. The element is transferred to a 50 ml polypropylene beaker.

7.2. 20.0 ml TISAB solution is pipetted into the beaker and beaker is capped.

7.3. The element is allowed to desorb for 30 minutes with occasional shaking.

7.4. The sample is stirred and analyzed for fluoride with the fluoride electrode.

7.5. A blank (or blanks) is analyzed in the same manner as the samples.

VIII. Calibration and Standards

8.1 Because the HF concentrations normally encountered at TLV levels correspond to fluoride levels often below linear response range, the best procedure is to plot a standard curve that covers the range of interest. This method describes preparation of 4 standards at 1/10X, 1/2X, 1X and 2X the fluoride ion that would be collected for a 4 hour sample at TLV (3 ppm) levels for HF.

8.2. A 4 hour, 3 ppm exposure would yield 1.59 μ moles collected in 20.0 ml desorption solution (a concentration of 7.94×10^{-5} M). The 10^{-3} M standard contains 1 μ mole/ml.

Prepare a set of standards in 20.0 ml volumetric flasks as follows, by adding the appropriate amount of stock and diluting to 20.0 ml with TISAB.

<u>Amount Stock</u>	<u>Corresponding 4 hr TLV</u>
0.2 ml	0.38 ppm
1.0 ml	1.88 ppm
2.0 ml	3.75 ppm
4.0 ml	7.50 ppm

8.3. Analyze the standards in the same manner as the unknowns. Plot the standards on semilog graph paper, with the concentrations on the log axis expressed as $\mu\text{moles}/20\text{ ml}$. Draw the best-fit line through the plotted curve.

8.4. For levels below 0.4 ppm for 4 hours, the response is not linear. A similar standardization procedure is followed, but the best fit smooth curve is drawn through the experimental points rather than a straight line.

IX. Calculations

9.1. Read the number of μmoles collected directly off the standard curve. Because the curve is based on $\mu\text{moles}/20.0\text{ ml}$ volume, and the sample volume is identical to the standard volume, no volume correction is necessary.

9.2. Subtract the number of μmoles found on the blank from the amount found on the samples.

9.3. Convert the corrected μmole values to corresponding ppm values with the following formula:

$$\text{ppm} = (\mu\text{m})(3358)(T/298)(760/P)[(D_0)(t)(0.836)]^{-1} \quad (14)$$

where μm = micromoles of HF collected.

$3358 = [(\text{path length})/(\text{cross-sectional area})] \times 24,450 \text{ cm}^3/\text{mole}.$

D_0 = HF diffusion coefficient at 298 K = $0.25 \text{ cm}^2/\text{sec}.$

0.836 = experimentally determined calibration factor.

t = exposure duration, seconds.

T = exposure temperature (K).

P = exposure pressure (mm Hg).

$D = D_0 [T/298]^{1.5}.$

(Note: moles F^- recovered = moles HF collected)

APPENDIX II - NIOSH METHOD S-176*

Hydrogen Fluoride

Analyte:	Hydrogen Fluoride	Method No.: S176
Matrix:	Air	Range: 1.33-4.50 mg/cu m
OSHA Standard:	3 ppm (2.45 mg/cu m)	Precision ($\overline{CV}_T$): 0.057
Procedure:	Bubbler collection in 0.1 N sodium hydroxide, ion specific electrode	Validation Date: 8/1/75

1. Principle of the Method (Reference 11.1)

- 1.1 A known volume of air is drawn through a midget bubbler containing 10 ml of 0.1 N sodium hydroxide to trap hydrogen fluoride.
- 1.2 The resulting solution is made up to 25 ml with 0.1 N sodium hydroxide and transferred to a 50-ml polyethylene beaker.
- 1.3 The sample is diluted with 25 ml total ionic strength activity buffer (TISAB).
- 1.4 The diluted samples are analyzed using a fluoride ion specific electrode.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 1.33-4.50 mg/cu m at an atmospheric temperature and pressure of 22°C and 761 mm Hg, using a 45-liter sample. The probable useful range of this method is 0.245-7.35 mg/cu m for 45-liter samples.
- 2.2 The upper limit of the range of the method is dependent on the collection efficiency of the midget bubbler. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The collection efficiency for hydrogen fluoride was determined to be 0.991 ± 0.004 when sampled for 30 minutes at 1.5 liters per minute from a test atmosphere containing 4.50 mg/cu m.

*Taken from Vol. 3, NIOSH Analytical Manual

Interference

- 3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 Hydroxide ion is the only significant electrode interference; however, addition of the TISAB eliminates this problem. Very large amounts of complexing metals such as aluminum may result in low readings even in the presence of TISAB.

Precision and Accuracy

- .1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 1.33-4.50 mg/cu m was 0.057. This value corresponds to a standard deviation of 0.14 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- .2 A collection efficiency of 0.991 ± 0.004 was determined for the collecting medium. On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 5.5% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result in paragraph 10.4.

Advantages and Disadvantages of the Method

- .1 The samples collected in bubblers are analyzed by means of a quick, instrumental method.
- .2 There are no known disadvantages to the method.

Apparatus

- .1 Sampling Equipment. The sampling unit for the bubbler collection method consists of the following components:
 - 6.1.1 A glass "midget bubbler" containing the collection medium (Section 7.3). Bubbler stem unit consists of a two-hole rubber stopper to fit 1/8-in C.D. Teflon tubing.
 - 6.1.2 A prefilter unit which consists of the filter media and a polystyrene 37-mm, 2-piece cassette filter holder. The filter is a 37-mm mixed cellulose ester membrane filter with a 0.8-micrometer pore size. A cellulose backup pad should not be used, but care must be taken to insure that the filter is sealed tightly to avoid air leaks during sampling.

- 6.1.3 A pump suitable for delivering at least 1.5 liters per minute for 30 minutes. The sampling pump is protected from splashover or solvent condensation by a 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.
- 6.1.4 An integrating volume meter such as a dry gas or wet test meter.
- 6.1.5 Thermometer.
- 6.1.6 Manometer.
- 6.1.7 Stopwatch.
- 6.2 Volumetric flasks: 25-ml or convenient sizes.
- 6.3 Pipets: 1, 2, 4, and 5 ml.
- 6.4 Orion Model 94-09 fluoride specific ion electrode, or equivalent.
- 6.5 Reference electrode, Orion 90-01 single junction, or equivalent calomel or silver/silver chloride electrode.
- 6.6 Expanded scale millivolt-pH meter, capable of measuring to within 0.5 millivolt.
- 6.7 Polyethylene beakers, 50-ml capacity.
- 6.8 Magnetic stirrer and stirring bars for 50-ml beakers.

7. Reagents

All chemicals must be ACS reagent grade or equivalent. Polyethylene beakers and bottles should be used for holding and storing all fluoride-containing solution.

- 7.1 Doubly distilled water.
- 7.2 Glacial acetic acid.
- 7.3 Collection Medium: 0.1 N sodium hydroxide solution. Dissolve 4 g of sodium hydroxide in 1 liter distilled water.
- 7.4 Sodium hydroxide, 5 N solution. Dissolve 20 g of sodium hydroxide in sufficient distilled water to give 100 ml of solution.
- 7.5 Sodium chloride.
- 7.6 Sodium citrate.

7.7 Total Ionic Strength Activity Buffer (TISAB). Place 500 ml of doubly distilled water in a 1-liter beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride, and 0.30 g of sodium citrate. Stir to dissolve. Place beaker in water bath (for cooling) and slowly add 5 N sodium hydroxide until the pH is between 5.0 and 5.5. Cool to room temperature and pour into a 1-liter volumetric flask and add doubly distilled water to the mark.

7.8 Sodium fluoride, for preparation of standards.

7.9 Standard Fluoride Solution.

7.9.1 Dissolve 12.06 mg sodium fluoride in 0.1 N sodium hydroxide (prepared from doubly distilled water) and dilute to 100 ml with 0.1 N sodium hydroxide. This solution is equivalent to 0.0546 mg/ml F^- . One ml of this solution contains the amount collected at the 0.5X OSHA level, when sampling at 1.5 liters per minute for 30 minutes. The 0.5X level standard is made by spiking 10 ml of 0.1 N sodium hydroxide with 1 ml of the standard stock solution. Likewise, the 1X level standard is prepared with 2 ml, and the 2X level is prepared with 4 ml of the standard stock solution. The standards are diluted to 25 ml with 0.1 N sodium hydroxide and 25 ml TISAB is added prior to analysis with the fluoride ion specific electrode.

8. Procedure

8.1 Cleaning of Equipment. All glassware and plastic ware are washed in detergent solution, rinsed in tap water, and then rinsed with doubly distilled water.

8.2 Calibration of Personal Sampling Pumps. Each pump should be calibrated by using an integrating volume meter (Section 6.1.3) or other means.

8.3 Collection and Shipping of Samples

8.3.1 Pour 10 ml of the collection medium (Section 7.3) into the midjet bubbler, using a graduated cylinder to measure the volume.

8.3.2 Assemble the prefilter unit in the 2-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. A backup pad should not be used.

8.3.3 Connect the bubbler (via the adsorption tube) to the prefilter assembly and the vacuum pump with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and bubbler should be used. The air being sampled should not pass through any other tubing or other equipment before entering the bubbler.

- 8.3.4 Bubbler stem unit consists of a -hole rubber stopper to fit 1/8-in O.D. Teflon tubing. One piece of tubing conducts the analyte vapor below the level of the collection medium where the analyte is trapped. The short outlet tube is connected to the sampling pump.
- 8.3.5 Turn the pump on to begin sample collection. Care should be taken to measure the flow rate, time and/or the volume as accurately as possible. Record the atmospheric pressure and the temperature. If the pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1.5 liters per minute for 30 minutes. The flow rate should be known with an accuracy of $\pm 5\%$.
- 8.3.6 The pump rotameter should be observed frequently, and sampling should be terminated at any evidence of a problem.
- 8.3.7 Terminate sampling at the predetermined time and note sample flow rate and collection time.
- 8.3.8 After sampling, the bubbler stem may be removed and cleaned. Tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Wash the stem with 1-2 ml of the collection medium, adding wash to the bubbler. Transfer the contents of the bubbler to a 50-ml polyethylene bottle. Rinse the bubbler with 2-3 ml of the collection medium and seal the bottle tightly for shipment.
- 8.3.9 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.
- 8.3.10 Whenever possible, hand delivery of the samples is recommended. Otherwise, special bubbler shipping cases designed by NIOSH should be used to ship the samples.
- 8.3.11 A "blank" bubbler should be handled in the same manner as the bubblers containing samples (fill, seal, and transport) except that no air is sampled through this bubbler.
- 8.3.12 The filter may be discarded since the method is designed to measure gaseous hydrogen fluoride only.

8.4 Analysis of Samples

- 8.4.1 The sample in each bubbler is analyzed separately.
- 8.4.2 Quantitatively transfer the contents of the polyethylene bottle to a 25-ml volumetric flask. Make up to volume with 0.1 N sodium hydroxide.
- 8.4.3 Transfer the sample to a 50-ml polyethylene beaker. Add 25 ml of TISAB and stir with a magnetic stirrer.
- 8.4.4 Lower the fluoride ion specific electrode and reference electrode into the stirred solution and record the resulting millivolt reading (to the nearest 0.5 mv) after it has stabilized (drift less than 0.5 mv/min).

9. Calibration and Standards

- 9.1 Prepare three fluoride standard solutions as described in Section 7.9 at each of three levels (0.5X, 1X, and 2X the standard).
- 9.2 Insert the fluoride ion specific electrode and the reference electrode into one of the standards at the 0.5X level, and stir the solution with the magnetic stirrer.
- 9.3 Record the resulting millivolt reading to the nearest 0.5 millivolt.
- 9.4 Repeat steps 9.2 and 9.3 for the remaining standard solutions.
- 9.5 Calibration standards at each level should be repeated twice daily.
- 9.6 Average the six millivolt readings at each level.
- 9.7 Prepare the standard curve by plotting the three averaged millivolt readings vs mg F^- on semilog paper. Plot the mg F^- on the log axis.

10. Calculations

- 10.1 Read the weight in mg corresponding to each millivolt reading from the standard curve. No volume corrections are needed, because the standard curve is based on mg/50 ml volume, and the volume of the samples is identical to the volume of the standards.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample bubbler

mg blank = mg found in blank bubbler

10.3 Calculate the mg of hydrogen fluoride by multiplying the mg fluoride ion found (Section 10.2) by 1.05, which is a conversion factor to convert mg F⁻ to mg HF.

10.4 The concentration of the analyte in air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.3)} \times 1000 \text{ liter/cu m}}{\text{Air volume sampled (liter)}}$$

10.5 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 Elfers, L.A. and C.E. Decker, "Determination of Fluoride in Air and Stack Gas Samples by Use of an Ion Specific Electrode, Anal. Chem., 40 (11), p. 1658 (1968).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

APPENDIX III

PREPARATION OF STOCK SOLUTIONS FOR POST-EXPOSURE STABILITY TESTS

Solution A. Dilute 1.0 ml of HF solution (49%) to 100 ml.
Resulting solution contains 5.635 μg HF per μl of solution.
Thus:

<u>Amount of Solution A</u> <u>(μl)</u>	<u>Amount of HF Contained Therein</u> <u>(μg)</u>
2.0	11.27
4.0	22.54
8.0	45.08

Solution B. Dilute 2.0 ml of HF solution (49%) to 50 ml.
Resulting solution contains 22.54 μg HF per μl of solution.
Thus 5.0 μl of solution B contains 112.7 μg of HF.

APPENDIX IV - CALIBRATIONS FOR FIELD STUDY

1. Personal Sampling Pumps.

Flow meter readings on each pump were checked at the beginning and end (as well as at the middle, in some cases) of each test run. Each pump was independently calibrated vs. an SKC 1.0 liter soap bubble meter (see Figures 9, 10, and 11). The actual flow rate was subsequently read from the curves. On 8 August 1980, pump 2 malfunctioned. Subsequently, the calibration policy was reviewed with the following changes: At the beginning and end of each run, the pump flow rate was checked with a Kurz Model 540S hot-wire calibrated flow-meter. The Kurz meter itself was calibrated vs. the SKC bubble tower (see Figure 12). Corrected flow rates were then read off this curve.

2. F⁻ Selective Ion Electrode/pH Meter Calibration.

Samples of standard F⁻ concentration were analyzed with the Orion Model 701A digital pH meter and 96-09 combination fluoride electrode. Results are presented below and in Figure 13:

<u>F⁻ Standard Concentration, M</u>	<u>pH Meter Reading, mV</u>
Low level Standard Curve (non-linear) {	
5.0 x 10 ⁻⁷	+5.4
1.0 x 10 ⁻⁶	-7.0
2.0 x 10 ⁻⁶	-17.7
5.0 x 10 ⁻⁶	-34.3
Linear portion of curve {	
1.0 x 10 ⁻⁵	-49.1
1.0 x 10 ⁻⁴	-106.2
1.0 x 10 ⁻³	-165.3

The curve of Figure 13 was used in all subsequent sample analyses. The 10⁻⁵ M standard was checked daily.

FIGURE 10: DATA FOR PUMP #2 CALIBRATION

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FIGURE 12: KURZ METER CALIBRATION

2 of 2

FIGURE 13: SELECTIVE ION ELECTRODE/pH METER CALIBRATION

APPENDIX V - DIFFUSION COEFFICIENT CALCULATIONS

Diffusion coefficients referred to in this report are calculated from the formula of Fuller, Shettler, and Giddings (equation 16) [9]:

$$D_{AB} = \frac{1.00 \times 10^{-3} T^{1.75} (1/M_A + 1/M_B)^{1/2}}{P[(\sum_A V_i)^{1/3} + (\sum_B V_i)^{1/3}]^2} \quad (16)$$

where:

T	= temperature, (K)
D_{AB}	= diffusion coefficient, (cm ² /sec).
M_A, M_B	= molecular weight, vapor A, B (gms/mole)
V_i	= atomic diffusion volume for atom i (cm ³ /mole)
$\sum_A V_i, \sum_B V_i$	= molecular diffusion volume for molecule A, B (cm ³ /mole) (equals sum of all atomic V_i in molecule A, B)
P	= pressure (atmospheres) - assumed to be 1.0 for present purposes.

Molecular or atomic diffusion volumes are given for many atoms and molecules, but no data is given for HF or for F. The atomic diffusion volumes are of dimensions chosen to roughly correspond to the LeBas values for structural contributions to the molar volume. In other formulas such as the Gilliland Approximation [16], the LeBas volumes are summed in a similar fashion to the summing of diffusion volumes in the Giddings formula. Therefore, for lack of better data the LeBas volume for F, 8.7 cm³/mole, is used as an estimate of the atomic diffusion volume for F [17].

A. Calculation for HF/Air

Parameters for Fuller, Shettler, Giddings Formula:

T	= 298K
M_A	= M_{AIR} = 29.0 gms/mole.
M_B	= M_{HF} = 20.01 gms/mole
V_H	= $1/2 V_{H_2}$ = 3.54 cm ³ /mole [9]
V_F	= 8.7 cm ³ /mole (LeBas value)
$\sum_{HF} V_i$	= $V_H + V_F$ = 12.24 cm ³ /mole

$$\sum_{\text{AIR}} V_i = 20.1 \text{ cm}^3/\text{mole} [9]$$

Applying equation 1 to these data yields:

$$D_{AB} = 0.246 \text{ cm}^2/\text{sec.}$$

B. Calculation for H₂O·HF Complex/Air

(Note: this complex may be present under some conditions of gasbadge exposure; see Section VII - A).

Parameters for Fuller, Shettler, Giddings formula:

$$\begin{aligned} T &= 298\text{K} \\ M_A &= M_{\text{AIR}} = 29.0 \text{ gms/mole} \\ M_B &= M_{\text{complex}} = 38.03 \text{ gms/mole} \\ V_{\text{HF}} &= 12.24 \text{ cm}^3/\text{mole} \text{ (calculated as on previous page)} \\ V_{\text{H}_2\text{O}} &= 12.7 \text{ cm}^3/\text{mole} [9] \\ \sum_{\text{complex}} V_i &= V_{\text{H}_2\text{O}} + V_{\text{HF}} = 24.94 \text{ cm}^3/\text{mole.} \\ \sum_{\text{air}} V_i &= 20.1 \text{ cm}^3/\text{mole} [9]. \end{aligned}$$

Applying equation 1 yields:

$$D_{AB} = 0.166 \text{ cm}^2/\text{sec.}$$

C. Calculation for SO₂/Air

Parameters for Fuller, Shettler, Giddings formula:

$$\begin{aligned} T &= 298\text{K} \\ M_A &= M_{\text{AIR}} = 29.0 \text{ gms/mole} \\ M_B &= M_{\text{SO}_2} = 64.07 \text{ gms/mole} \\ \sum_{\text{SO}_2} V_i &= 41.1 \text{ cm}^3/\text{mole} [9] \\ \sum_{\text{AIR}} V_i &= 20.1 \text{ cm}^3/\text{mole} [9] \end{aligned}$$

Applying equation 1 yields:

$$D_{AB} = 0.126 \text{ cm}^2/\text{sec.}$$

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