AN AMBIENT SAMPLING TECHNIQUE FOR PARTICULATE AND GASEOUS FLUORIDES

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Air Pollution Control Directorate

March, 1978

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1. RATIONALE

Several methods, both manual and automated, have been used to sample ambient air for fluorides. Most automated instruments (i.e. those providing collection, analysis and readout) are limited to sampling only the gaseous fluorides present in the air. Manual sampling systems can be very efficient, are convenient and amenable to field use, and can collect both a particulate and gaseous fluoride sample. A good review of manual sampling techniques was made by Farrah[1]. He reviews systems which can collect a total fluoride sample or provide separate collection of particulate and gaseous fluorides. In terms of gaseous fluorides, both wet (impingers, bubblers) and dry (impregnated filters or coated tubes) collection systems are reviewed. Obviously, many sampling systems could be designed, but from the standpoint of efficiency and ease of use (especially in field conditions), a dry collection filter system would be a good choice. Indeed, many investigators have employed this strategy. Elfers and Decker[2] used a membrane filter impregnated with sodium formate to collect a total fluoride sample. Huygens [3] used Whatman filters impregnated with a potassium hydroxide-glycerol solution to sample hydrogen fluoride. Mandl et al [4]

describe the use of a dual paper tape system for the separate collection of gaseous and particulate fluorides. Thompson et al [5] reviewed the use of Hi-volume glass-fibre filters analyzed for total fluorides.

In view of the efficiency and convenience associated with the dry collection technique, it was decided that such a system would be most amenable to field use. A dual membrane-filter system incorporating separate collection of particulate and gaseous fluoride fractions would form the basis of the sampler. This basic design had to be sufficiently flexible to accommodate the following considerations:

(a) What type of fluorides are to be measured?

(b) What is the minimum ambient concentration expected in the field?

(c) What is the detectability limit of the ananytical technique?

A distinction between the particulate and gaseous fluorides present in the air was an important requirement of the sampling system. Gaseous fluorides are the most phytotoxic so a separate indication of gaseous levels is necessary. However, water soluble particulate fluorides may also affect vegetation by being dissolved in the water

used by plants. Further, some agencies have fluoride standards for total fluorides as well as gaseous fluorides.

Having decided to collect both a particulate and gaseous sample, it then became necessary to consider the environment to be tested so that instrument parameters such as flowrates and sampling times could be optimized. A major problem in sampling for fluoride is that it is usually present in very low concentrations in the ambient air. Thus, the sampling system must be capable of collecting sufficient sample to be detected by the analytical technique. The design of the sampling instrument was based on;

(1) An expected minimum ambient air fluoride concentration of 0.05 μg F^{Θ}/m^3.

(2) An analytical detectability limit of 0.5 μg F^{Θ} per filter sample.

Thus the sampling instrument has to be capable of collecting at least 0.5 μg of fluoride from an ambient concentration of 0.05 μg F^{Θ}/m^3. Only two sampling parameters, the flowrate and time, could be adjusted to ensure that sufficient fluorides were collected. Therefore the instrument was designed to allow maximum control of these two parameters. Table 1 shows the relationship between

TABLE 1: RELATIONSHIP BETWEEN FLUORIDE LOADING AND VARIOUS COMBINATIONS OF SAMPLING FLOWRATES AND TIMES

SAMPLING FLOWRATE (C.F.M.)	*FLUORIDE LOADING (µg F^{Θ}) FOR SPECIFIED SAMPLING TIMES			
	3-HR.	6-HR.	12-HR.	24-HR.
1	0.26	0.51	1.01	2.02
2	0.51	1.02	2.04	4.08
3	0.77	1.53	3.06	6.12
4	1.02	2.04	4.08	8.15
5	1.28	2.55	5.10	10.19

*Assuming an ambient air concentration of 0.05 µg F^{Θ}/m^3

fluoride loadings on the filter with various combinations of sampling flowrates and times assuming an ambient concentration of 0.05 μg $F^{\ominus}/m^3$. This information was used as a guideline in designing the fluoride sampling unit to ensure optimum fluoride collection.

2. SAMPLER DESIGN

The fluoride sampler is basically a sequential air sampler. The innovative feature of this unit is that it is designed to allow sampling over a wide range of accurately measured sample volumes. This is accomplished through precise and variable control of the sampling flowrate and sampling time. Figure 1 is a schematic of the sampler showing its six basic components;

(1) Filter assembly

(2) Sequential solenoid valve

(3) Flowrate measurement and recording

(4) Elapsed sample time indicators

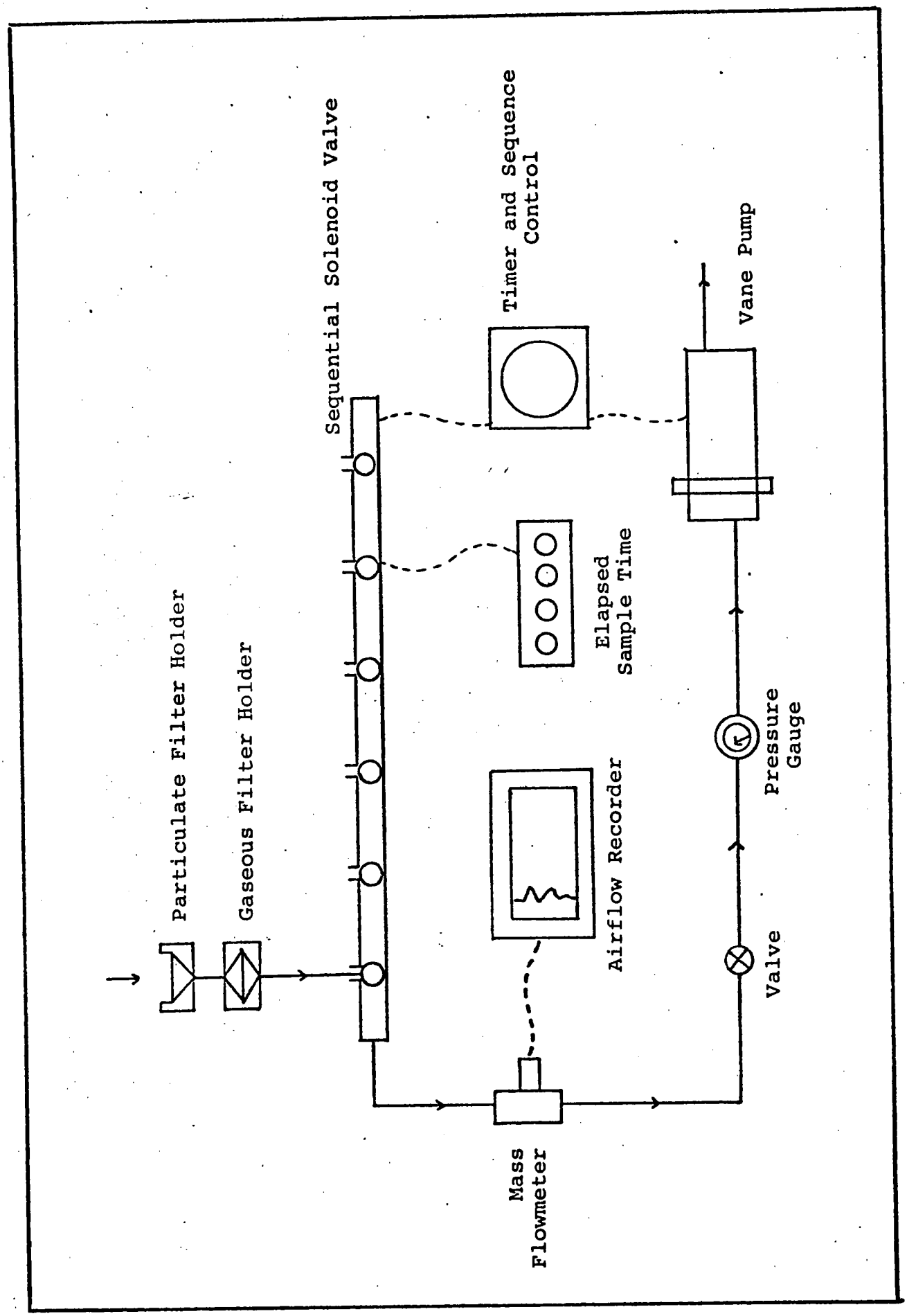
(5) Timer and sequence control

(6) Air pump

2.1 Filter Assembly

The filter assembly component is the external unit which operates in the ambient air environment being sampled. It consists of a specially designed shelter, the filter holders, the sample filters, and, tubing and

FIGURE 1: FLUORIDE SEQUENTIAL AIR SAMPLER - SCHEMATIC



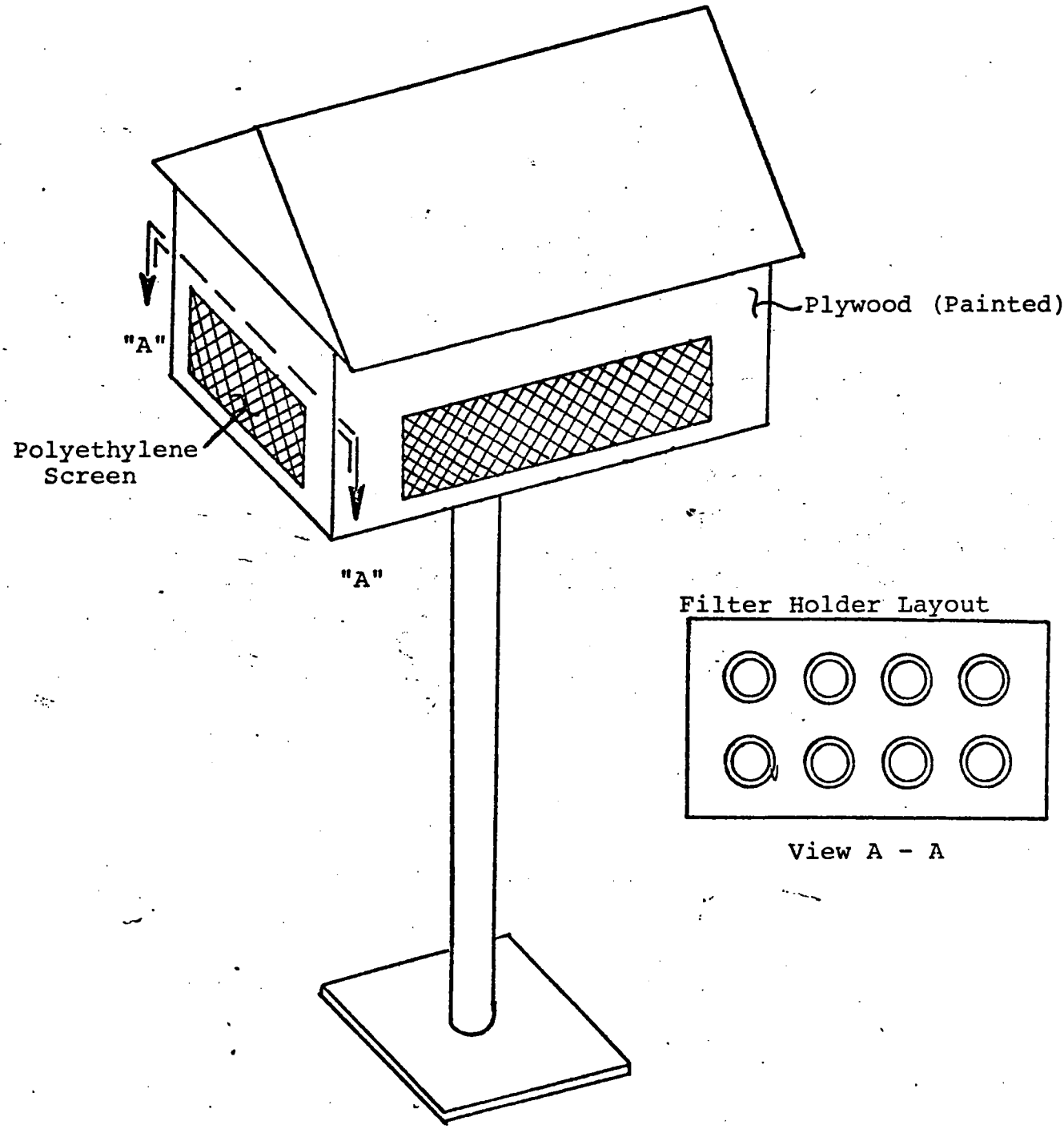
adapters which connect to the rest of the sampler located indoors. The filter assembly design could be varied to suit any particular sampling schedule used, but it was found that the most convenient assembly, in terms of size and flexibility, consists of a unit which contains eight separate sampling lines.

2.1.1 Filter Shelter

A sketch of the filter shelter appears in Figure 2. The filter shelter was designed to allow maximum exposure of the filters to the ambient environment while still protecting the exposed filter surface from direct contact of winds, rain and debris. The shelter box has overall dimensions of 56 cm x 36 cm x 20 cm. The peaked roof and eave openings were designed according to the same geometry as a standard Hi-volume sampler[6, 7]. Such Hi-volume samplers typically collect suspended particulate in the range of 0.1 to 100 μm (Stokes equivalent diameter). To further increase exposure of the filters to the ambient atmosphere, holes were cut into the sides of the shelter and covered with polyethylene screening. With such a design, the collection of the particulate sample should only be limited by the pore size of the filters used.

The shelter itself is constructed of plywood and aluminum which has been painted with several coats of exterior enamel paint. The shelter is supported about four feet above ground level on a steel post. The post is attached to a plywood base weighted with concrete blocks.

FIGURE 2: FILTER SHELTER



2.1.2 Types of Filters

Based on Farrah's review[1] it was determined that membrane filters would be best for this application. These filters have the advantages of retaining particles much smaller than their pore size, offering a longer residence time for gaseous molecules passing through the membrane, and having a relatively low adsorptive capacity for hydrogen fluoride.

It was necessary to use a filter of 5 μm porosity in order to limit the pressure drop across the dual filter system and thus reduce the load on the pump. Initial sampling was done using Gelman 5 μm GA Metricel (cellulose triacetate) filters but these were found to be too fragile for field use. They tended to crack and tear or stick to the sealing rings of the filter holders. Gelman 5 μm Acropor membrane filters were tested in an attempt to avoid these problems. These consist of an acrylonitrile polyvinyl-chloride copolymer membrane reinforced with nylon. They are quite strong and flexible and were found to be ideally suited to this application.

To collect the particulate fluorides in the air sample both plain Acropor filters and Acropor filters impregnated with a 0.1 M citric acid solution have been evaluated. The gaseous fluoride-collecting filter consists of an Acropor filter impregnated with a solution of 10% NaOH-5% glycerol in water. All filters are transported to and from the field in Millipore Petrislide™ containers. These have an inner rim which secures the filter in the container thus preventing movement.

2.1.3 Filter Holders

The filter shelter is designed to hold eight sets of filters which allows unattended operation for one week on a 24 hour sample cycle. Each set consists of an open-faced holder for the particulate collecting filter, combined in series with an in-line holder for the gaseous collecting filter. These holders accept 47 mm diameter filter discs. The open-faced holder is of aluminum construction with a stainless steel filter support pad. This holder is sprayed with a thin coating of methyl methacrylate to avoid the possible sorption of reactive fluorine compounds on its surfaces. (An all stainless steel open-faced holder would be preferred to this aluminum one but no such commercially available product could be found). The in line holder is constructed of stainless steel.

2.1.4 Umbilical

The umbilical line connects the filter assembly unit, which is located outside, with the rest of the sampling unit located indoors. The umbilical consists of eight lengths of 13 mm (½ in.) i.d. polyethylene tubing. Each set of filter holders is connected to one of the solenoids on the sequential valve by means of a separate length of the tubing.

2.2 Sequential Solenoid Valve

The choice of a suitable valving system depended on factors such as size, cost and flow restrictions. To allow the required high flowrates of up to 1 dm^3/s (∿2 c.f.m.) it was necessary to choose a solenoid with as large an orifice as possible. To keep the sampler to a reasonable size, the internal plumbing was limited to a maximum pipe size of 6 mm (¼ in.). Thus, the largest solenoid which could be adapted to this system was one having an orifice of 7 mm. (9/32 in.). This was found to be suitable for this application. The sequential valve consists of 12 such solenoids assembled with brass pipe fittings. The solenoids are electrically operated and controlled by the timer and sequence system to open sequentially after a certain sampling time.

2.3 Timer and Sequence Control

This unit consists of an adjustable timing device (time range adjustable up to 30 hours) coupled with an

electrical reset stepper switch. It controls the length of the sample period and automatically steps to the next solenoid valve after the preset sampling time has expired. To allow for 24-hour sampling for a period of one week, the control is set to cycle sequentially through valves one to eight and then reset to valve one and repeat the cycle.

2.4 Elapsed Sample Time Indicators

The precise sample time for each individual sample is determined by recording the amount of time that each solenoid valve is in operation. This is accomplished by means of electrically activated resettable elapsed time indicators. There is one indicator for each solenoid which records the total number of minutes that the solenoid was operating.

2.5 Flowrate Measurement and Recording

The flowrate through the system is accurately determined by means of a linear mass flowmeter. This unit operates on a thermal principle which depends on the mass flow of the gas and its heat capacity to change the temperature along a heated conduit. It operates independent of changes in the temperature or pressure of the ambient air being sampled and reports the air flowrate corrected to a standard temperature of 20^{o}C and standard pressure of 760 mm Hg. The model used has a range of 0-50,000 standard cubic centimeters per minute (sccm). The voltage output of

the flowmeter is recorded on a strip chart recorder giving a permanent record of the flowrate conditions over the entire sampling period. The flowrate is adjusted by means of a valve located between the solenoids and the flowmeter.

2.6 Air Pump

The air pump has to be of sufficient capacity to maintain a high flowrate over the sampling period. The pump used is a 175 watt (¼ H.P.) carbon vane vacuum pump which is capable of drawing a sample over the range of flowrates required. In field conditions, the pump operates in the system at about 20 in. Hg. vacuum.

2.7 Cost

Table 2 is a cost breakdown for one sampler. The cost of individual major components and source of supply are indicated. This sampler is considered to be a cost-effective unit for the following reasons;

1) It allows collection of both a particulate and gaseous fluoride sample.
2) It allows accurate determination of sample volumes by precise control of flowrates and sample time.
3) Being a sequential air sampler its use is not restricted to collecting fluorides. Any pollutant requiring manual sampling techniques could be sampled with this instrument.

TABLE 2: COST BREAKDOWN - FLUORIDE SEQUENTIAL AIR SAMPLER

ITEM*	SUPPLIER	COST**
Mass Flowmeter (0-50,000 sccm)	Matheson	$1020.00
Strip Chart Recorder	Watanabe	$1038.00
Filter Holders (8 in-line, 8 open-face)	Gelman	$1805.00
Solenoids, Counters, Cabinets and Hardware	Electrosonic	$1099.00
Carbon Vane Pump (¼ H.P.)	Wainbee	$ 248.00
Swagelok Fittings	Ottawa Valve	$ 273.00
Automatic Timer	Landis & Gyr	$ 65.00
Tubing, Clamps, Misc.	Fisher Scientific	$ 87.00
Filter shelter (Lumber & Supplies)	-	$ 100.00
	TOTAL	$5735.00

EXPENDABLES	SUPPLIER	COST**
Acropor Filter (16)	Gelman	$ 5.12
Petri Dishes (16)	Millipore	$ 2.88
Culture Tubes (16)	Canlab	$ 0.80
TISAB Solution (250 mℓ)	Fisher	$ 0.80
Recorder Chart Paper (¼ roll)	Watanabe	$ 2.50
	TOTAL	$12.10

* The assembled unit has overall dimensions of 90 cm x 53 cm x 42 cm

** The prices quoted were effective March, 1978

4) The more expensive components of the instrument such as flowmeter, recorder, and filter holders, can be directly used in any environmental laboratory in a variety of other applications.

The cost of expendable materials (sampling and analytical) required to operate the samplers for a period of one week on a 24-hour sampling schedule has also been indicated in Table 2.

3. SAMPLER PERFORMANCE CHARACTERISTICS

Probably the major difficulty in attempting to obtain discrete gaseous and particulate fluoride samples is the possibility of sorption of the reactive gaseous fluorides on the particulate filter. This would cause a bias in the results as the sorbed fluorides, which were present as gaseous fluorides in the ambient air, would be reported as particulate fluorides. If this gaseous sorption is large, such a bias could be serious because gaseous fluorides are the more phytotoxic. Thus, reported levels might not account for observed effects on plant receptors. On the other hand, if the reported results indicated that a standard or criteria based on gaseous fluorides has been exceeded, then the bias acts as a built in assurance that

the levels of gaseous fluoride in the air sampled were indeed in excess of the limit. Any such sorption effects should therefore be quantified and attempts made to reduce this error as much as possible.

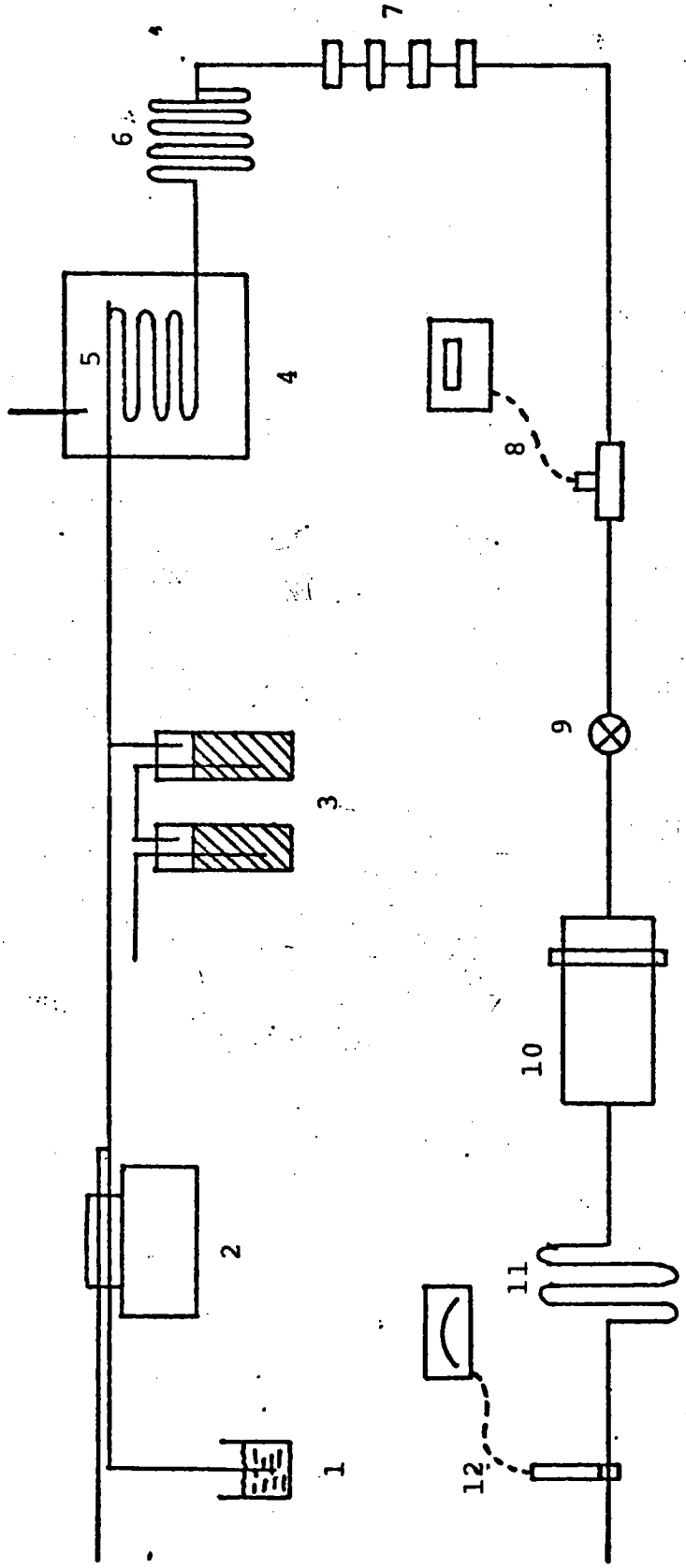
A second potential source of error inherent in the sampler design is the collection efficiency of the system. Once the gaseous fluorides in the air sampled have passed through the first (particulate) filter, they must be quantitatively trapped on the second impregnated filter. This is especially critical in high flowrate sampling because of the shorter residence time of the air sample through the gaseous filter. This means that two parameters of the gaseous filter must be maximized. Firstly, the filter medium should be chosen to maximize the residence time of the gas passing through the filter. Secondly, the absorbing medium used to impregnate the filter should be as efficient as possible in combining with the gaseous fluoride in the sample.

Most investigators who use manual fluoride sampling systems have acknowledged these sorption and efficiency problems, and many have evaluated them extensively for their particular sampler. To quantify these problems in this sampler, an apparatus to generate atmospheres of known fluoride concentrations was required.

3.1 Hydrogen Fluoride Generator

The HF generator used was based on a principle recently reported by Jacobson and Heller of the Boyce Thompson Institute [8]. A known amount of a standard hydrogen fluoride solution, mixed with a metered amount of make up air, is volatilized yielding a hydrogen fluoride gas stream of known concentration. A schematic of the apparatus used in the laboratory is given in Figure 3. A solution of dilute hydrofluoric acid, is pumped into the system at a known rate by means of a Technicon proportioning pump. Dry laboratory air is introduced to make up the desired concentration. The mixture enters an oven maintained at a temperature of 160°C. Hydrogen fluoride gas is volatilized from the solution as it passes through a 5 metre coil of Teflon tubing in the oven. After the heated gas stream leaves the oven it is cooled down to about room temperature by passing through a 3 metre coil of Teflon tubing, prior to reaching the test filters. A mass flowmeter (0-50,000 sccm), located downstream of the filters, monitors and displays the air flowrate. This flowrate is controlled by means of a valve located between the pump (½ h.p.) and flowmeter. After passing through the pump the air is again cooled to about room temperature before passing over a relative humidity sensor which displays the humidity of the gas sample. All tubing from the proportioning pump to the test filters was Teflon to lessen sorption of the reactive fluorides in the system. The proportioning pump tubing was calibrated regularly to ensure accurate liquid flowrates.

FIGURE 3: HYDROGEN FLUORIDE GENERATOR - SCHEMATIC



1 Dilute hydrofluoric acid
2 Proportioning pump with liquid splitter
3 Greenburg-Smith impingers with silica gel
4 Thermostatically controlled oven with temp. indicator
5 HF volatilization coil
6 Cooling coil
7 Test filters
8 Mass flowmeter with readout
9 Flow control valve
10 Carbon vane vacuum pump
11 Cooling coil
12 Relative humidity sensor with readout.

3.2 Sorption and Collection Effeciency Tests

Other investigators [1, 9] have reported that membrane filters are relatively unreactive to gaseous fluorides. Pack and Hill [9] report that sorption of gaseous fluorides on membrane filters amounted to about 7% compared to about 23% for paper filters in parallel tests. Mandl et al [4] suggest treating the particulate filter (a paper filter in their case) with a nonvolatile organic acid (0.1 M citric acid) to ensure quantitative passage of gaseous fluoride through the filter. Based on their information, both untreated and treated particulate filters were evaluated.

Tests to evaluate the sorption of gaseous fluoride on the particulate filter and the efficiency of collection of the gaseous filter were performed concurrently by using four test filters in the HF generator. The first of these filters is a typical particulate filter and the remaining three are gaseous filters. Known concentrations of HF gas are metered through the filters so sorption of any of the gas on the first (particulate) filter can be determined. The collection efficiency of the second (gaseous) filter can be determined by noting if any of the gas passes through to the last two filters used as back-ups. To determine such effects, the HF concentrations were varied to produce a heavy loading of fluorides (200-400 μg F^{Θ}), and, a lighter loading which was more typical of levels encountered in the field (10-20 μg F^{Θ}). Due to the large pressure drop across

the four filters, the pump was capable of maintaining a nominal flowrate of about 280 cm^3/s which is about 60% of nominal flowrates used in the field. The relative humidity of the gas stream was about 10%.

Five separate tests runs were performed for each fluoride level and combination of filters examined. The results are summarized in Tables 3 & 4. It is obvious from these results that the particulate filters treated with citric acid very effectively reduce the amount of gaseous sorption on this filter. For unusually heavy fluoride loadings there was a 3% reduction in sorption of HF. With typical ambient loadings a more pronounced reduction of 13% was noted. Thus it is recommended that treated particulate filters be used in ambient air sampling by this technique. The collection efficiency of the gaseous filter is acceptable. For heavy fluoride loadings a maximum of about 7% of the gaseous fluoride passed through the gaseous filter. However, for the typical loadings, only 0 to 2% of the gaseous fluorides passed through.

4. FIELD PERFORMANCE OF THE SAMPLER

The primary design requirement of this fluoride sampler was to allow precise and variable control of sampling flowrates and sampling times so that sufficient sample could

TABLE 3: SORPTION AND EFFICIENCY RESULTS USING UNTREATED PARTICULATE FILTERS

		Particulate Filter	1st Gaseous Filter	2nd Gaseous Filter	3rd Gaseous Filter	Total
Heavy Loading	Average F^{θ} Collected (µg)	13.5	225.6	13.0	0.3	252.4
	Average % of Total	5.3	89.4	5.2	0.1	
	Range (%)	4.4-6.6	837-940	0.5-11.8	0.0-0.5	
Typical Loading	Average F^{θ} Collected (µg)	1.9	10.1	0.0	0.0	12.0
	Average % of Total	15.8	84.2	0.0	0.0	
	Range (%)	12.0-18.1	81.9-88.0	0.0	0.0	

NOTES:
1. Particulate filters were 5 µm Acropor membranes
2. Gaseous filters were 5 µm Acropor membranes impregnated with a 10% NaOH - 5% glycerol fixative to trap gaseous fluoride.
3. The average values reported for each loading range are the results of five separate test runs.

TABLE 4: SORPTION AND EFFICIENCY RESULTS USING TREATED PARTICULATE FILTERS

		Particulate Filter	1st Gaseous Filter	2nd Gaseous Filter	3rd Gaseous Filter	Total
Heavy Loading	Average F^{θ} Collected (µg)	7.3	337.0	22.9	0.2	367.4
	Average % of Total	2.0	91.7	6.2	0.1	
	Range (%)	1.8-2.2	85.8-99.0	1.1-12.0	0.0-0.3	
Typical Loading	Average F^{θ} Collected (µg)	0.5	16.8	0.4	0.0	17.7
	Average % of Total	2.8	94.9	2.3	0.0	
	Range (%)	0.0-4.1	90.4-100.0	0.0-6.0	0.0	

NOTES:
1. Particulate filters were 5 µm Acropor membranes impregnated with 0.1 m citric acid to allow passage of gaseous fluorides.
2. Gaseous filters were 5 µm Acropor membranes impregnated with a 10% NaOH - 5% glycerol fixative to trap gaseous fluorides.
3. The average values reported for each loading range are the results of five separate test runs.

be collected to detect the generally low levels of fluorides present in the ambient air. We have used the instrument in the field with various combinations of flowrate and sampling times. Sampling flowrates have ranged from about 0.25 to 1.00 dm^3/s (0.5 to 2.0 c.f.m.). Sampling times of six, twelve, and twenty-four hours have been used. The shorter sampling times require greater inputs in terms of man-hours to service the station, expendable supplies required (e.g. filters, analytical supplies), and analytical support. A sampling scheme involving the collection of 24 hour samples at a nominal flowrate of 0.5 dm^3/s (1 c.f.m.) has been found to be the most practical and convenient in field use. Collecting 24 hour samples has the following advantages:

1) This is the most commonly used short term averaging period in any standards, regulations or criteria.

2) It allows for unattended operation of the sampler for a period of one week.

3) The amount of expendable supplies and analytical support is reduced.

A flowrate of 0.5 dm^3/s (1 c.f.m.) insures that very low ambient fluoride levels can be determined with good analytical accuracy. For example, if the ambient air concentration averages 0.05 $\mu g\ F^{\ominus}/m^3$, a total of about 2 $\mu g\ F^{\ominus}$ would be collected, which is about four times the analytical limit. An example of the type of data collected

during an actual field survey is given in Table 5.

The various components of the sampler have proven to be very reliable in field use. The only major instrument component to fail after continuous field service for six months was a pump (worn vanes). Other failed components, which were easily repaired at the sampling site, included jammed solenoids and malfunctioning elapased time meters. Such failures were very infrequent and, in the case of the elapsed time meters, no data was lost since the sample time could be obtained from the flowrate recording and chart speed.

Most invalidated field data has been caused by external sources such as power failures, operator oversights in maintenance procedures, and tampering with equipment by unauthorized persons. Severe snowstorms have caused samples to be invalidated due to deposition of snow on the particulate filter heads. This problem was reduced by covering the side openings of the filter shelter during winter sampling.

5. ANALYSIS OF COLLECTED SAMPLES

The collected particulate and gaseous filters are analyzed for fluoride ion content using the fluoride specific ion electrode technique. This technique detects

TABLE 5: EXAMPLE OF DATA FROM ACTUAL FIELD SURVEY

FIELD DATA: 24 HOUR AVERAGE FLUORIDES AND WIND

Station : A
Sample Period: beginning 1200

DATE d/ m	WIND Dir. (8pt)	% Time	FLUORIDE CONCENTRATION (ug/m3 as HF) P.F.	G.F.	T.F.	RATIO OF P.F./G.F. (24hr)
11/ 7	S	42	0.22	0.17	0.38	1.3
12/ 7	SW	33				
13/ 7	NW	46				
14/ 7	SW	58	0.69	0.22	0.91	3.1
15/ 7	SW	33	0.29	0.35	0.64	0.8
16/ 7	SW	54	0.26	0.43	0.69	0.6
17/ 7	W	33	0.33	0.33	0.66	1.0
18/ 7	SW	46	0.26	0.27	0.53	1.0
19/ 7	SW	75				
20/ 7	SW	63				
21/ 7	N	54	0.18	0.11	0.29	1.6
22/ 7	NW	42	0.44	0.11	0.54	4.1
23/ 7	SW	83	1.39	0.36	1.76	3.8
24/ 7	SW	75	3.22	2.04*	5.25	1.6
25/ 7	NW	83	0.35	0.07	0.42	5.0
26/ 7	NW	54	0.31	0.09	0.40	3.4
27/ 7	SW	58	1.13	0.24	1.37	4.6
28/ 7	S	54	0.54	0.21	0.76	2.5
29/ 7	SW	67	0.37	0.49	0.86	0.7
30/ 7	NW	50	0.71	0.17	0.88	4.2
31/ 7	SW	58	1.61	0.77	2.38	2.1
1/ 8	W	50	0.37	0.44	0.81	0.8
2/ 8	W	33	0.90			
3/ 8	SW	63	1.14	0.68	1.82	1.7
4/ 8	SW	75	2.44	1.64*	4.08	1.5
5/ 8	SW	46	1.94	0.80	2.74	2.4
6/ 8	C	45	0.66	0.27	0.93	2.4
7/ 8	C	45	0.48	0.35	0.83	1.4
8/ 8	W	75	0.52	0.36	0.88	1.5
9/ 8	W	29	0.59	0.15	0.74	3.9
10/ 8	NE	67	0.17	0.20	0.37	0.9
11/ 8	SW	54	0.58	0.75	1.33	0.8
12/ 8	SW	63	2.28	0.46	2.75	4.9
13/ 8	SW	71	0.69	0.84	1.53	0.8
14/ 8	W	29	0.46	0.49	0.96	0.9
15/ 8	SW	63	1.13	0.24	1.37	4.8
16/ 8	NE	46	0.30	0.55	0.85	0.5
17/ 8	SW	46	0.14	0.16	0.29	0.9
18/ 8	SW	58	0.56	0.29	0.85	1.9
19/ 8	SW	58	0.34	0.19	0.53	1.8
20/ 8	SW	50	1.68	0.32	2.00	5.2
21/ 8	S	29	0.31	0.69	0.99	0.4
22/ 8	SW	71	1.89	0.50	2.39	3.8
23/ 8	SW	67	0.71	0.34	1.05	2.1

* indicates N.A.Q.O. max. acc. limit of 0.85ug/m3 exceeded

only the water soluble fluorides present in the sample. Water soluble fluorides are the phytotoxic forms and, in any case, tests [5] have shown that nearly all fluorides collected on filters, whether glass fibre or membrane, is water soluble. This analytical technique cannot identify specific fluoride compounds which may have been present in the particulate or gaseous sample. Results are generally reported as equivalent HF concentration corrected to standard conditions of 25°C and 760 mm Hg.

In the laboratory, field samples are transferred from the Petrislides to plastic culture tubes. A known volume of a 1:1 solution of distilled water and TISAB (Total Ionic Strength Adjustment Buffer) are added to dissolve the soluble fluorides from the filters. The culture tube is capped and placed on a rotary mixer for one hour at moderate speed. After agitation, the sample solution is transferred to a plastic beaker and a further rinse of the filter is added. The beaker is numbered and capped to await analysis.

The fluoride specific ion electrode consists of a single crystal of lanthanum fluoride (LaF_3) doped with a rare earth element, europium II, and cemented to a plastic tube containing an internal solution of 0.1 M NaCℓ and 0.1 M NaF. This electrode is used with a single junction reference electrode. Sample solutions are analyzed by immersing the electrodes in them and recording the electrode potential reading which is displayed on a pH/ion meter. The

concentration of fluoride ion in the solution is determined by comparing the output of the meter with previously prepared standard curves.

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