

## Method of Dispensing Volatile Fluorides in Portable Greenhouses

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Equipment and procedures are described for producing nearly constant concentrations of fluosilicic or hydrofluoric acid in fumigating greenhouses ranging from less than one to several hundred parts per billion. The method makes use of diluted solutions (0.01 to 4%) of these acids which are atomized by an air pressure of 10 to 20 pounds per square inch through a platinum nozzle. The atomized droplets are then passed through an electrically heated tube (150° C.) where they are changed to the gaseous state before delivery to the air stream entering the fumigating greenhouses. Given concentrations of volatile fluorides can be maintained nearly constant in the greenhouses for as long as 5 weeks. The functioning of the apparatus is not affected by changes in temperature, and 3 liters of solution are sufficient for 12 days of uninterrupted fumigation.

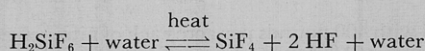
A STUDY of the effects of volatile fluorides on vegetation requires dispensing apparatus which delivers and controls a constant supply of volatile fluorides in the air stream. Several procedures were employed at Boyce Thompson Institute fulfilling, in part, these requirements. A method was developed whereby the concentration of hydrofluoric acid or fluosilicic acid was satisfactorily controlled (2). The adaptation of this method to field use together with several improvements and the results obtained in fumigating experiments using portable greenhouses is presented. Frequent sampling of air in the portable greenhouses, by means of an automatic air-sampling apparatus attached to each volatile fluoride generator, aided in controlling the fluorine concentration.

### Fumigating and Air-Sampling Equipment

The gas volume necessary for fumigation is obtained from a solution of hydrofluoric acid or fluosilicic acid diluted according to the desired fluoride content in the air. A pneumatic atomizer transforms the solution into fine droplets (mean diameter approximately 10 microns) which are then forced into a low-temperature oven where the acid passes from liquid to a gaseous state and is introduced into the air stream leading to the fumigation chambers.

When a hydrofluoric acid solution is used in all-polyethylene equipment, the volatile fluorides delivered to the treatment greenhouse are in the form of hydrofluoric acid, provided no silica-containing material is present. When fluosilicic acid solution is used in all-glass equipment, the following reactions may be expected to occur, the atomized

acid solution being evaporated in the hot tube and decomposed:



At the exit of the hot tube, the reaction is assumed to proceed from right to left, the plants thus being treated with fluosilicic acid. However, silicon tetrafluoride and hydrofluoric acid may occur in the atmosphere of the greenhouse if suitable conditions of temperature and moisture exist.

The approximately equivalent effects of atomized solutions of hydrofluoric acid and fluosilicic acid by the above described method on various species of plants were described in a recent report (4). Solutions of fluosilicic acid were used in the present tests involving portable greenhouses because of the greater convenience in using glass equipment.

The equipment used for dispensing the volatile fluorides is shown in Figure 1, A to E. The automatic air-sampling setup is shown in Figure 1, F to I. Both units are enclosed in the same wooden box, N (Figures 1 and 2), provided with louvers on four sides for ventilation, the front side functioning as a door. This box is 26 inches wide, 18 inches deep, and 37 inches high and is painted white and coated inside with paraffin.

**Volatile Fluoride-Dispensing Equipment.** The most important part of this equipment is the atomizer, E, made of a nozzle derived from the No. 15 DeVilbiss atomizer. In this case, the two removable side tubes for air and liquid supply are replaced by two tubes permanently welded at the base of the nozzle. In order to prevent corrosion, both the nozzle and the two tubes are made of platinum containing 10% rhodium. (The atomizers used in this work were

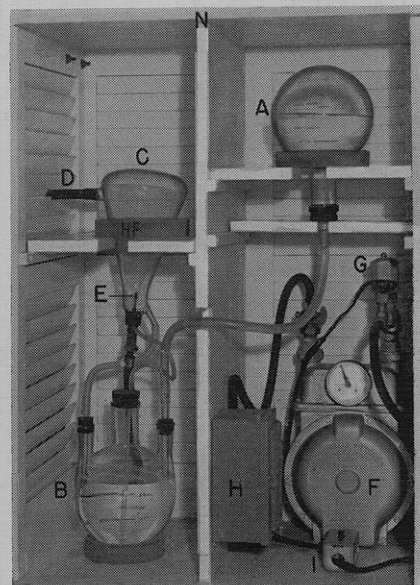


Figure 1. Volatile fluoride dispensing apparatus and automatic air-sampling equipment

made according to specifications by American Platinum Works, Newark, N. J.) A hard-rubber cylinder, provided with a central vertical bore for the compressed-air supply and with a second right-angle bore extending through a side tube for the liquid supply, connects the atomizer to the atomization flask, C. The atomizer nozzle is mounted in the hard-rubber cylinder by means of High-Pyseal cement (Fisher Scientific Co. Catalog No. 4-759) applied with an electric soldering gun. A rubber tube is used to make the hard-rubber cylinder fit tightly into the neck of flask C. An air pressure of 15 to 20 pounds per square inch is used for the atomization, and the pressure is maintained constant by means of a pressure regulator (Air Reduction

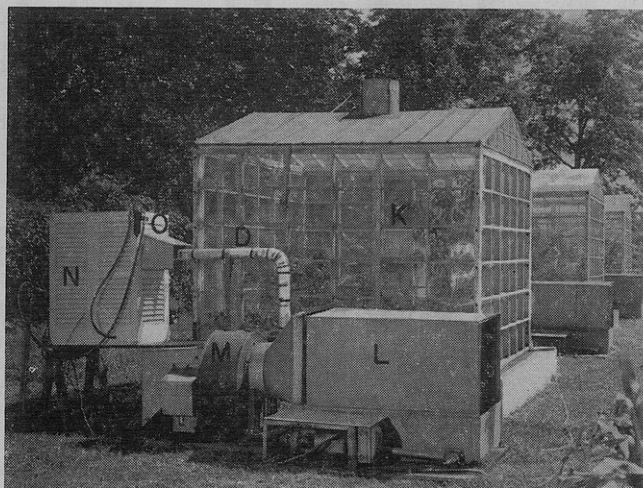


Figure 2. Equipment used for fumigating plants with volatile fluorides

Co., New York, Catalog No. 806, Style 8952). A central air filter is placed on the compressed-air line ahead of the regulator (Poro-Stone-Filter, R. A. Adams Co., Buffalo, N. Y., Type T. R. No. 2068048), each atomizer being protected by smaller individual Taylor air filters (Figure 2, O). Individual valves are provided for each atomizer.

The 3-liter, three-necked-borosilicate glass flask, B (Figure 1), contains the fluosilicic acid solution and is connected to the atomizer through the central tube. As a result of the Venturi effect in the atomizer, the solution flows from B into the nozzle and is atomized. The fine droplets are sent into the hot tube, D. The coarse droplets are condensed on the wall of the 2-liter Erlenmeyer flask, C, and returned through the side tube in flask, B; the liquid is thus recirculated. As a result of the atomization, part of the solution is used and part evaporated. The 3-liter borosilicate glass flask, A, functions as a leveling container to maintain a constant solution level in flask B, to which it is connected with Tygon tubing (inside diameter, 15 mm.; outside diameter, 25 mm.) to the glass tube passing through the rubber stopper in the right hand neck of flask B (Fig-

ure 1). As a result of the evaporation, the solution in B becomes progressively more concentrated, and in order to compensate for this change, the leveling solution in A is more dilute than the one in B. In the present tests, a solution three times more dilute was needed to compensate for the loss of water by evaporation. The 3 liters of solution contained in flask B were sufficient for a continuous atomization of 12 days.

The hot tube, D, is made of copper (inside diameter, 10 mm.; outside diameter, 14 mm.) with a length of 79 inches and is bent at an angle of 90 degrees. Electric heating is accomplished by means of a Nichrome wire, 244 inches long with a resistance of 2.120 ohms per foot, coiled around the tube previously covered with asbestos and cement (Insa-lute cement, Fisher Scientific Co., Catalog No. 4-760). The wire is covered with a layer of the same cement and is thermally insulated with asbestos tubes. In order to protect the hot tube from rain, three layers of roofing tar are applied, followed by two layers of thin aluminum foil and two layers of polyethylene film. The terminals are electrically insulated with glass beads

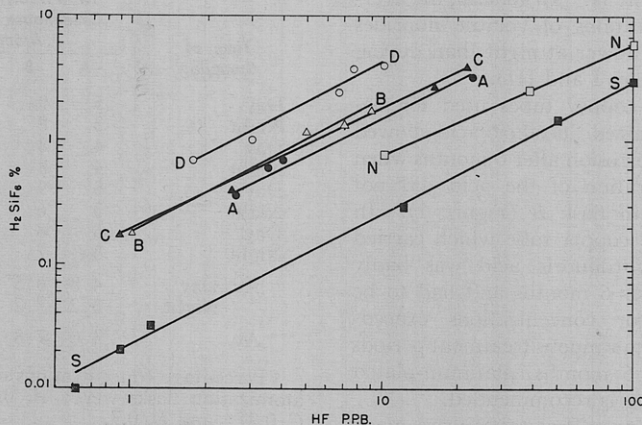


Figure 3. Calibration curves for six platinum atomizers

and provided with connectors (Fisher Scientific Co., Catalog No. 2-515A). This resistance is plugged directly in the 115-volt line and provides an air temperature of 150° C. at the exit of the hot tube for an intake of 2.5 amperes. One end of the hot tube is connected to the atomization flask, C (Figure 1), the other being introduced in the air duct (Figure 2). The air supply for the greenhouse is provided by the electric fan, M, with the adjustable gate set to deliver 1.5 air exchanges per minute. The air is previously humidified in the scrubber, L. The construction of the portable greenhouses shown in Figure 2 was described in a previous report (4).

#### Automatic Air-Sampling Device.

Each greenhouse was equipped with an automatic air-sampling device like the one previously described (3). It is shown in the right compartment of box N and includes an admission valve followed by a solenoid valve, G, controlled by an electric time clock, H, and a switch, I (Figure 1). The sampling time is preset on the time clock, which opens and closes the solenoid valve for the chosen length of time. This valve is connected with a vacuum source and through a dry meter, F, to a sampling absorber placed in the greenhouse, K.

These absorbers and the analytical procedures for the determination of fluoride have already been discussed in detail (3).

When interfering ions are known not to be present, an absorber [Figure 3, left, (7)] is used in sampling the air from the portable greenhouses. Its construction ensures an efficient recovery of the volatile fluorides passed through the absorber at rates up to 70 cubic feet per hour and using a volume of 50 to 70 ml. of absorbing solution. The absorber is easy to wash and has a blank of only 1  $\gamma$  of fluoride or less.

When interfering substances are known to be present, a steam distillation from a perchloric acid solution at 135° C. is necessary. For this purpose, apparatus [Figure 3, left, and Figure 4 (7)] was designed so that the absorption and steam distillation could be performed in the same container and thereby eliminate possible losses due to transfer of the sample.

In general, two air samples were taken for each 24 hours of fumigation—one from 9 A.M. to 1 P.M., and the second from 11 P.M. to 4 A.M. The rate of air flow through the absorber varied from 20 to 40 cubic feet per hour according to the concentration of fluorides in the greenhouses.

#### Results and Discussion

Data in Figure 3 show the relation between the concentration of fluosilicic acid in flask B (Figure 1) and the con-

**Table I. Atomization Characteristics Based on Average Concentrations of Volatile Fluoride Delivered to Portable Greenhouses**

No. Samples Taken per Test	Time of Sampling	Av. Concn. HF (P.P.B.) in Portable Greenhouse Supplied by 4 Different Atomizers <sup>a</sup>			
		A	B	C	D
6	Day	4.8	9.0	0.90	1.5
5	Night	4.0	6.5	0.72	1.2
3	Day	4.0	6.7	1.0	2.3
4	Night	4.5	7.0	0.65	1.5
4	Day	3.5	6.0	0.75	2.05
4	Night	3.5	5.2	0.6	1.5
5	Day	5.2	9.8	1.2	1.4
5	Night	4.6	7.0	1.04	1.4
4	Day	4.8	8.5	1.3	2.2
4	Night	3.2	7.2	0.7	2.0
Av.	Day	4.2	7.7	0.91	1.9
	Night	4.3	6.8	0.86	1.6
Av.		4.25	7.1	0.89	1.75

<sup>a</sup> Percentage concentrations of H<sub>2</sub>SiF<sub>6</sub> in the atomization flasks were: A, 0.7; B, 1.4; C, 0.21; and D, 0.7.

centration in volatile fluorides expressed as hydrofluoric acid in parts per billion by volume obtained in the portable greenhouses and fumigating cabinets for six different atomizers. The commercial, 30% fluosilicic acid used was considered as 100% in this work.

Atomizers *N* and *S* (Figure 3) were used with fumigating cabinets having a volume of approximately 200 cubic feet and one air exchange per minute. These cabinets were permanently located in a greenhouse.

Atomizers *A*, *B*, *C*, and *D* (Figure 3) were used for injecting volatile fluorides into the portable greenhouses having a capacity of 500 cubic feet and 1.5 air exchanges per minute. An air pressure of 15 pounds per square inch was used to operate atomizers *N* and *S*, and a pressure of 20 pounds per square inch was used to operate atomizers *A*, *B*, *C*, and *D*. Each atomizer has a given efficiency, determined by its construction. Atomizer *D* is less efficient than atomizers *A*,

*B*, and *C* under comparable conditions. Likewise, atomizer *S* is more efficient than atomizer *N* under the same working conditions.

The relative constancy of the concentration of volatile fluoride resulting from the atomization of a given concentration of fluoride solution is illustrated by the results in Table I. Although the four platinum nozzles had different atomization characteristics (see also Figure 3), each nozzle delivered a relatively constant concentration of volatile fluoride when supplied with a given concentration of fluoride solution. As the same concentration of the acid solution was supplied to a given nozzle throughout five successive tests of 7 days' duration each, the same constancy of delivery would probably hold for considerably longer periods.

The performance of the atomizer can be affected by changes in the air pressure, total or partial clogging of the nozzle, and by temperature changes. Changes in temperature from 60° to 106° F. had only a slight influence on the atomization setup. The results for a typical test are shown in Table II. In general, the average concentrations of volatile fluorides were slightly lower at night than during the day (Tables I and III).

The four copper tubes used for delivering atomized fluosilicic acid showed only slight corrosion after 6 months when the concentration of the acid did not exceed 4% in flask *B* (Figure 1). In contrast, the copper tube which carried atomized hydrofluoric acid was badly corroded after 6 months and had to be replaced. For concentrations exceeding 4% and continuous treatment periods longer than 6 months, platinum-plated copper tubing is recommended.

Corrosion-proof hot tubes were made by inserting Teflon tubes (straight tube,

40 inches long; inside diameter, 1/2 inch outside diameter, 3/4 inch) inside the copper tubes. Such hot tubes have been successfully used for 1 year of continuous operation with HF and H<sub>2</sub>SiF<sub>6</sub> solutions without corrosion.

Special equipment is necessary to dispense hydrofluoric acid gas. The glass equipment shown in Figure 1 was replaced with polyethylene thick-walled containers (American Agile Corp., Cleveland 3, Ohio), as follows: container *A*, a 1-gallon bottle in the neck of which a Tygon tube is forced (inside diameter, 15 mm.; outside diameter, 23 mm.); container *B*, a 1-gallon jar with a flat cover; and the atomization container, *C*, a 0.5-gallon bottle. The necessary tubing was soldered to these containers using polyethylene tubes and an electric soldering gun. Polyethylene rods were used as soldering material. The apparatus thus constructed has been used for over a year with satisfactory results.

It is believed that the volatile fluoride-dispensing apparatus may be used also for injecting other volatile substances, such as hydrochloric and hydrobromic acids. Particulate matter, such as sodium fluoride and sodium chloride, can be delivered if solutions of these salts are used.

#### Literature Cited

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**Table II. Influence of Temperature on Concentration of Volatile Fluorides in a Portable Greenhouse**

Temperature, ° F.	HF (P.P.B.) in Portable Greenhouse Supplied by Atomizer <sup>a</sup>	
	C	D
90-106	22	7
56-60	19	7
94-102	18	6
82	20	7
76-60	26	7
80	28	8
68	19	6
74-100	24	6
Av.	22	6.8

<sup>a</sup> Percentage concentrations of H<sub>2</sub>SiF<sub>6</sub> in the atomization flasks were: C, 3 and D, 2.5.

**Table III. Results of Analyzing Air for Volatile Fluorides during One Test**

Time of Sampling	HF (P.P.B.) in Portable Greenhouse Supplied by Atomizer <sup>a</sup>			
	A	B	C	D
Day	5	9	2	2
Night	3	8	1	2
Day	4	8	1	2
Night	4	8	1	2
Day	5	9	1	2
Night	3	6	0.4	2
Day	5	8	...	3
Night	3	7	0.4	2
Av. Day	4.8	8.5	1.3	2.2
Night	3.2	7.2	0.7	2.0
Av.	4.0	7.8	1.0	2.1

<sup>a</sup> Percentage concentrations of H<sub>2</sub>SiF<sub>6</sub> in atomization flasks were: A, 0.7; B, 1.4; C, 0.21; and D, 0.7.